

ABSTRACT

Title of Dissertation: SELF-ASSEMBLY OF PRECISION
POLYOLEFIN BLOCK COPOLYMERS AND
SUGAR-POLYOLEFIN CONJUGATES

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Self-assembling materials have become ubiquitous in modern society. Thus, a great challenge exists in developing nonpolar building blocks for self-assembling materials in a simple, efficient, and scalable manner. It is also important to find new ways in which to utilize such building blocks in a versatile manner. In this work, precision polyolefins and end-group functionalized poly(α -olefinates) (x-PAOs) were successfully used as simple, easily accessible nonpolar building blocks for the development of new nanostructured materials. Specifically, living coordination polymerization (LCP) was employed to generate well-defined crystalline-amorphous BCPs. Although the low degree of incompatibility between the two hydrophobic blocks would typically prevent microphase separation, the high degree of conformational asymmetry between the blocks was sufficient to induce the formation of nanostructures. Additionally, x-PAOs were used as macroinitiators for ring-opening

polymerization to produce self-assembling amphiphilic polyolefin-*b*-polyester diblock copolymers.

The development of nanostructured ‘smart’ materials that can respond to external stimuli on practical time scales and moderate conditions also remains a challenge and is a topic of great academic and industrial interest. For thermoresponsive systems in the solid-state, the goal of establishing extremely low kinetic barriers for order-to-order nanostructural transitions has not yet been reached. Notably, the synthesis and characterization of a new class of low molecular weight atactic sugar-polyolefin hybrid conjugates was carried out, and the study demonstrated that these new materials can meet this challenge. These amphiphilic hybrid conjugates consist of hydrophobic x-PAO “tails” chemically tethered to hydrophilic saccharide “head” groups and display organized nanostructures in the bulk and within ultra-thin films with sub-10 nm features. The conjugates studied displayed a rich and dynamic self-assembly behavior in the form of multiple ‘order-to-order’ phase transitions within the bulk and ultrathin-films (< 100 nm), which were investigated by SAXS/GISAXS with a synchrotron x-ray source as a function of temperature. These results demonstrate the utility of sugar-polyolefin conjugates as nanostructured smart materials for nanotechnological applications and show that precision polyolefins and x-PAOs are excellent nonpolar building blocks for self-assembling materials.

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AND SUGAR-POLYOLEFIN CONJUGATES

by

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Table of Contents

Acknowledgements.....	ii
Table of Contents.....	iii
List of Tables	vi
List of Figures	vii
List of Schemes.....	x
List of Abbreviations	xi

Chapter 1: Introduction.....	1
1.1 Development of Coordination Polymerization Techniques.....	1
1.1.1 The Zeigler-Natta Process.....	1
1.1.2 Homogeneous Metallocene Catalysts.....	3
1.1.3 Development of Coordinative Chain Transfer Polymerization Techniques.....	5
1.2 Living Polymerizations.....	7
1.2.1 Key Characteristics	7
1.2.2 Living Coordination Polymerization	9
1.3 Living Coordination Polymerization with CpAM Systems.....	11
1.3.1 Living Degenerative Group-Transfer Coordination Polymerization.....	13
1.4 Living Coordinative Chain Transfer Polymerizations with CpAM System.....	15
1.4.1 LCCTP of Olefins	15
1.4.2 End-group Functionalized Poly(α -olefinates).....	16
1.5 Self-assembly.....	18
1.5.1 Classical Surfactant Self-assembly.....	20
1.5.2 Block Copolymer Self-assembly	22
1.5.3 Self-assembly in Systems Utilizing Nonpolar Building Blocks.....	27
1.6 References.....	30

Chapter 2: Expanding the Range of x-PAO Building Blocks via LCCTP	39
2.1 Background	39
2.1.1 High Tg Amorphous Polymers and their Applications.....	39
2.1.2 Cyclopolymerization of 1,5-hexadiene and 1,6-heptadiene via LCP and LCCTP	41
2.2 Accessing High Tg or Semi-crystalline Low Molecular Weight x-PAOs.....	43
2.2.1 Synthesis of OH-PMCP and OH-aPMCH	43
2.2.2 Characterization of OH-PMCP	45
2.2.3 Characterization of OH-aPMCH.....	47
2.3 OH-PAOs as Versatile Nonpolar Building Blocks.....	48
2.4 PMCP- <i>b</i> -Polyester Diblock Copolymer	49
2.4.1 Synthesis and Characterization of PMCP- <i>b</i> -PCL	49
2.4.2 Self-assembly of PMCP- <i>b</i> -PCL.....	51
2.5 PAO- <i>b</i> -PPG- <i>b</i> -PAO Triblock Copolymers.....	53

2.5.1 Synthesis and Characterization	54
2.5.2 Self-assembly	56
2.6 Conclusions	59
2.7 Experimental Information	60
2.7.1 Materials	60
2.7.2 Instrumentation	60
2.7.3 Synthesis	62
2.8 References	65
 Chapter 3: Conformational Asymmetry in Polyolefin Copolymers	68
3.1 Background	68
3.1.1 Conformational Asymmetry in BCPs	68
3.1.2 Conformationally Asymmetric BCPs via LCP	69
3.2 PMCP- <i>co</i> -PMCH Random Copolymers	70
3.2.1 PMCP-PMCH Homopolymer Blend	71
3.2.2 Synthesis and Characterization	72
3.2.3 Tuning Physical Properties	73
3.3 Diblock Copolymers Containing Poly(4-methyl-1-pentene)	75
3.3.1 Design Considerations	75
3.3.2 Synthesis	76
3.3.3 Characterization and Self-assembly	78
3.4 PH- <i>b</i> -PMP- <i>b</i> -PH Triblock Copolymers	85
3.4.1 Synthesis and Characterization	86
3.4.2 Self-assembly	87
3.5 Poly(octadecene)- <i>b</i> -isotactic poly(propylene) Diblock Copolymers	89
3.4.1 Synthesis and Characterization	89
3.6 Conclusions	92
3.7 Experimental Information	93
3.7.1 Materials	93
3.7.2 Instrumentation	93
3.7.3 Synthesis	95
 Chapter 4: Synthesis and Preliminary Characterization of a Cellobiose-atactic Polypropylene Conjugate	101
4.1 Background	101
4.1.1 Thermoresponsive “Smart” Materials	101
4.1.2 Previous Work on Sugar-Polyolefin Conjugates	102
4.2 Design Considerations	103
4.2.1 Establishing a high χ Low N System	103
4.2.2 Selection of (D)-(+)-Cellobiose	104
4.2.3 Use of Low Molecular Weight Atactic Polypropylene	105
4.2.4 Click Chemistry	106
4.3 Synthesis and Characterization of CB-aPP Conjugate	108
4.3.1 Synthesis	108

4.3.2 Characterization	110
4.4 Bulk and Thin Film Self-assembly of CB-aPP Conjugate.....	111
4.4.1 Self-assembly in the Bulk State	112
4.4.2 Self-assembly in the Thin Film State.....	114
4.5 Conclusions.....	119
4.6 Experimental Information.....	120
4.6.1 Materials	120
4.6.2 Instrumentation	120
4.6.3 Synthesis	123
4.7 References.....	125
Chapter 5: Dynamic Phase-Behavior of Sugar-Polyolefin Conjugates: <i>In Situ</i>	
Synchrotron Studies	129
5.1 Background	129
5.1.1 Small Angle X-ray Scattering (SAXS)	129
5.1.2 Grazing-Incidence Small Angle X-ray Scattering (GISAXS).....	131
5.2 Sugar-Polyolefin Conjugates Investigated	132
5.3 Thermal Stability of CB-aPP Conjugates	133
5.4 Self-assembly of CB-aPP in the Bulk State.....	134
5.4.1 Lamellar Morphology	135
5.4.2 Lamellar to Hexagonally Perforated Lamellar Phase Transformation	135
5.4.3 Hexagonally Perforated Lamellar to Gyroid Phase Transformation	138
5.4.4 Gyroid to Cylinder Phase Transformation	141
5.5 Thin Film Preparation.....	143
5.6 GISAXS Linera Temperature Ramp Experiments	143
5.7 Factors Affecting Thin Film Self-assembly.....	145
5.7.1 Film Thickness and aPP Chain Length.....	145
5.7.2 Processing History	148
5.7.3 Changing Sugar Head-Group.....	151
5.8 Unprecedented Access to Gyroid Nanostructured Films.....	154
5.8.1 Current Examples in Literature.....	154
5.8.2 GYR Phase in Sugar-Polyolefin Conjugate Films.....	156
5.9 Conclusions.....	157
5.10 Experimental Information.....	159
5.10.1 Materials	159
5.10.2 Instrumentation	159
5.10.3 Synthesis	162
5.11 References.....	163
Chapter 6: Conclusions and Future Work	169
Appendix.....	172
References.....	236

List of Tables

Table 2.1: Summary of PMCP materials made from LCCTP.....	46
Table 2.2: Characterization of PAO- <i>b</i> -PPG- <i>b</i> -PAO materials.....	55
Table 3.1: Characterization of PMCP, PMCH, and PMCP- <i>co</i> -PMCH materials.....	74
Table 3.2: Diblock materials made from LCP.....	77
Table 3.3: Thermal properties of PO- <i>b</i> -PMP diblocks.....	80
Table 3.4: Thermal properties of PD- <i>b</i> -PMP diblocks.....	83
Table 3.5: Characterization of PH- <i>b</i> -PMP- <i>b</i> -PH materials.....	87
Table 3.6: Thermal properties of POD- <i>b</i> -PP diblocks.....	90
Table 4.1: Characterization of I-aPP used for CB-aPP.....	108
Table 5.1: Summary of OOTs observed during SAXS upon heating of 34 and 35	135
Table 5.2: Morphology and OOT temperature ranges for CB-aPP by GISAXS.....	146
Table 5.3: Characterization of I-aPP materials used for conjugates.....	163

List of Figures

Figure 1.1: Structures of some metallocene precatalysts for olefin polymerization...	3
Figure 1.2: Structures of some precatalysts for living polymerization of α -olefins....	10
Figure 1.3: General structure and structures of some CpAM preinitiators	11
Figure 1.4: Surfactant self-assemblies based upon a critical packing parameter	21
Figure 1.5: Schematics of two types of nonconventional surfactants.....	22
Figure 1.6: Schematic illustrations of common types of AB-type BCPs.....	23
Figure 1.7: Theoretical BCP phase diagram and illustrations of phases	24
Figure 1.8: Schematic illustration of the cone-column model	26
Figure 2.1: Molecular weight of PMCP as a function of reaction time	44
Figure 2.2: ^1H -NMR spectrum of OH-PMCP	45
Figure 2.3: DSC curve of OH-PMCH	48
Figure 2.4: Labelled ^1H -NMR spectrum of PMCP- <i>b</i> -PCL.....	50
Figure 2.5: SAXS data for a bulk sample of PMCP- <i>b</i> -PCL	51
Figure 2.6: ps-tm AFM analysis of thin films of PMCP- <i>b</i> -PCL	52
Figure 2.7: Thermal analysis of OH-PAOs	53
Figure 2.8: 1D SAXS analysis of PMCP- <i>b</i> -PPG- <i>b</i> -PMCP	56
Figure 2.9: ps-tm AFM phase images of PMCP- <i>b</i> -PPG- <i>b</i> -PMCP	57
Figure 2.10: ps-tm AFM phase images of PMCH- <i>b</i> -PPG- <i>b</i> -PMCH	58
Figure 3.1: Representative ^{13}C -NMR of PMCP- <i>co</i> -PMCH materials	73
Figure 3.2: T_g as a function of f_{PMCH} in PMCP- <i>co</i> -PMCH materials	75
Figure 3.3: ps-tm AFM analysis of thin films of PH- <i>b</i> -PMP	79
Figure 3.4: ps-tm AFM analysis of thin films of PO- <i>b</i> -PMP	81

Figure 3.5: ps-tm AFM analysis of thin films of PO- <i>b</i> -PMP	82
Figure 3.6: ps-tm AFM analysis of thin films of as-cast PD- <i>b</i> -PMP	84
Figure 3.7: ps-tm AFM analysis of thin films of annealed PO- <i>b</i> -PMP	85
Figure 3.8: ps-tm AFM analysis of thin films of isotactic PH- <i>b</i> -PMP- <i>b</i> -PH	87
Figure 3.9: ps-tm AFM analysis of thin films of atactic PH- <i>b</i> -PMP- <i>b</i> -PH	88
Figure 3.10: 1D SAXS plots for aPOD- <i>b</i> -PP materials	91
Figure 4.1: General structure of sugar-polyolefin conjugates.....	102
Figure 4.2: Structure of (D)-(+)-Cellobiose	104
Figure 4.3: Structure of propargyl terminated (D)-(+)-Cellobiose	107
Figure 4.4: ¹ H-NMR of CB-aPP (<i>N</i> =31) conjugate.....	110
Figure 4.5: DSC curve of CB-aPP (<i>N</i> =31) conjugate.....	111
Figure 4.6: 1D and 2D SAXS of unannealed CB-aPP (<i>N</i> =31) conjugate.....	112
Figure 4.7: DLS of CB-aPP (<i>N</i> =31) conjugate.....	113
Figure 4.8: AFM and GISAXS of unannealed CB-aPP (<i>N</i> =31) conjugate	115
Figure 4.9: Time-dependent AFM series of annealed CB-aPP (<i>N</i> =31) conjugate	116
Figure 4.10: GISAXS of CB-aPP (<i>N</i> =31) conjugate at various temperatures.....	118
Figure 4.11: GISAXS and AFM of CB-aPP (<i>N</i> =31) conjugate at 38 °C	119
Figure 5.1: TGA profiles of CB-aPP conjugates	134
Figure 5.2: 1D SAXS plots of unannealed CB-aPP conjugates 34 and 35	136
Figure 5.3: Stacked 1D SAXS plots of 34 during the LAM → HPL transition and characterization of HPL phase	138
Figure 5.4: Stacked 1D SAXS plots of 34 and 35 during HPL → GYR transition....	141
Figure 5.5: 1D SAXS plot of 34 in the GYR phase at 160 °C	142

Figure 5.6: Stacked 1D SAXS plots of 34 during the GYR→HEX transition; 1D SAXS plots of 34 in the HEX phase and 35 in the GYR phase	143
Figure 5.7: GISAXS patterns of 35 during linear temperature ramp	145
Figure 5.8: Phases and their respective transition temperatures during GISAXS of CB-aPP conjugates	148
Figure 5.9: GISAXS patterns of 35 after quenching from 145 °C	149
Figure 5.10: GISAXS patterns of 35 during different temperature jump sequences	150
Figure 5.11: GISAXS patterns of 34 held isothermal at 60 °C; temperature ranges for phases coexisting; GISAXS pattern of 34 during rapid temperature jump	152
Figure 5.12: Schematic illustration of anomeric group orientation in CB and MB ...	153
Figure 5.13: GISAXS patterns of 37 during linear temperature ramp	154
Figure 5.14: Indexed GISAXS patterns of 35 in the GYR phase and schematic illustrations of the GYR unit cell	157

List of Schemes

Scheme 1.1: General mechanism of CCTP	5
Scheme 1.2: General mechanism of CSP	6
Scheme 1.3: Activation of III and olefin insertion	12
Scheme 1.4: Mechanism of LCCTP	15
Scheme 1.5: Synthetic route to x-PAOs	18
Scheme 2.1: Synthetic route to OH-PMCP and OH-PMCH.....	43
Scheme 2.2: Synthetic route to PMCP- <i>b</i> -PCL	49
Scheme 2.3: General Synthetic route to PAO- <i>b</i> -PPG- <i>b</i> -PAO	54
Scheme 3.1: General synthetic route to PMCP- <i>co</i> -PMCH random	72
Scheme 3.2: General synthetic route to PH/PO/PD- <i>b</i> -PMP	76
Scheme 3.3: Synthetic route to PH- <i>b</i> -PMP- <i>b</i> -PH via LCP	86
Scheme 3.4: Synthetic route to aPOD- <i>b</i> -iPP and iPOD- <i>b</i> -iPP	89
Scheme 4.1: General scheme for a CuAAC click reaction	106
Scheme 4.2: General synthetic route to N ₃ -aPP	108
Scheme 4.3: Synthetic route to <i>N</i> -acetylated propargyl cellobiose	109
Scheme 4.4: Synthetic route to 34 via click chemistry	109
Scheme 5.1: Structure and characteristics of sugar-polyolefin conjugates	132

List of Abbreviations

ZN	Ziegler-Natta
HDPE	High density polyethylene
MAO	Methylaluminumoxide
CCTP	Coordinative chain transfer polymerization
CTA	Chain transfer agent
CSP	Chain shuttling polymerization
CSA	Chain shuttling agent
M_n	Number average molecular weight
PDI	Polydispersity index
BCP	Block copolymer
X_n	Average degree of polymerization
LCP	Living coordination polymerization
CpAM	Cyclopentadienyl amidinate
MeDet	Living degenerative methyl-group transfer polymerization
LCCTP	Living coordinative chain transfer polymerization
NMR	Nuclear magnetic resonance
x-PAOs	End-group functionalized poly(α -olefins)

C_{PP}	Critical Packing Parameter
CAC	Critical aggregation concentration
S	Spheres
HEX	Hexagonally Packed Cylinders
GYR	Gyroid
LAM	Lamellae
HPL	Hexagonally perforated layers
f_A	Fraction of block A
χ	Flory-Huggins interaction parameter
N	Total degree of polymerization
T_g	Glass transition temperature
$ZnEt_2$	Diethyl zinc
ROP	Ring opening polymerization
CL	ϵ -caprolactone
PCL	Poly(caprolactone)
PMCP	Poly(1,3-methylene cyclopentane)
aPMCH	Atactic Poly(1,3-methylene cyclohexane)
GPC	Gel permeation chromatography
DSC	Differential scanning calorimetry
aPMP	Atactic Poly(4-methyl-1-pentene)
SAXS	Small angle x-ray scattering
GISAXS	Grazing-incidence small angle x-ray scattering
Ps-tm AFM	Phase-sensitive tapping mode atomic force microscopy

PPG	Poly(propylene glycol)
aPP	Atactic Polypropylene
PH	Poly(1-hexene)
PO	Poly(1-octene)
PD	Poly(1-decene)
POD	Poly(1-octadecene)
iPP	Isotactic Polypropylene
T_m	Melting temperature
T_c	Crystallization temperature
d	Domain spacing
CB	(D)-(+)-Cellobiose
Gal	Galactose
MB	Melibiose
DLS	Dynamic light scattering
HOPG	Highly ordered pyrolytic graphite
C-Si	Carbon-coated silicon
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
OOT	Order-to-order transition
ODT	Order-to-disorder transition
T_{ODT}	Order-to-disorder transition temperature

Chapter 1: Introduction

1.1 Development of Coordination Polymerization Techniques

Polyolefins, or polymers produced from simple olefin monomers, have become ubiquitous in the modern world. Polyolefins are used in a wide variety of applications, ranging from consumer goods like grocery bags and containers, to adhesives, automotive parts, and medical applications. The global demand for polypropylene and polyethylene alone is expected to reach approximately 200 million metric tons per year by the year 2020.¹ Despite the simplicity of the hydrocarbon monomers, the versatility of polyolefins lies in the diversity of the molecular architectures, which can give rise to vastly different physical properties. Unfortunately, there is a limited toolset available for the production of polyolefins with precisely controlled structures, requiring expensive transition metal catalysts that limit the efficiency of the polymerization, as well as the scalability and reproducibility. Previous work in the Sita Group has focused on overcoming these obstacles to design and synthesize polyolefins with precisely controlled molecular weights and narrow polydispersities, called “precision polyolefins,” in order to expand the range of polyolefin materials. However, over the last several decades there have been significant advances in the field of living polymerization techniques.

1.1.1 The Ziegler-Natta Process

Among the most important discoveries in chemistry were the Ziegler-Natta catalysts for the coordination polymerization of olefins, which reduced the activation

energy for polymerization and allowed the polymerization of olefins to occur even under mild conditions.² In the early 1950s, the commercialization of the Zeigler-Natta (ZN) process revolutionized the development of commodity plastics.³ In 1953, Ziegler discovered the use of a heterogeneous transition metal catalyst based on titanium tetrachloride (TiCl_4) with diethylaluminum chloride $[(\text{C}_2\text{H}_5)_2\text{AlCl}]$ as a cocatalyst to form high molecular weight high density polyethylene (HDPE) via coordination polymerization at room temperature.^{4, 5} Shortly after, this catalyst was used by Giulio Natta for the formation of crystalline polypropylene.^{6, 7} In the 1970s, magnesium chloride was added as a support during polymerization, which significantly increased the activity of the catalysts. Ziegler and Natta jointly won the 1963 Nobel Prize in Chemistry for their contributions to the field of polymer chemistry. The discovery of the ZN process rejuvenated the polymer field and paved the way for a multitude of discoveries that ushered in the Plastics Era.⁸ Today, the ZN catalysts are still among the most utilized within the polymerization industry on a global scale, especially for the production of polypropylene.⁹

Though revolutionary, the original ZN process is not without its limitations. The most widely accepted mechanism for the ZN process, which was first proposed by Arlman and Cossee in 1964,¹⁰ begins with the formation of an olefin adduct at the open coordination site on the metal center of the heterogeneous catalyst. However, since heterogeneous catalysts can have different active sites, there is very little stereocontrol in the polymerization process. To improve the stereocontrol, Lewis bases have been added to the polymerization, but this only provides a minor improvement to the

stereoregularity of the final polymer structure.² The presence of multiple active sites also causes the polymers produced to have broad molar mass distributions.

1.1.2 Homogeneous Metallocene Catalysts

A new generation of ZN catalysts based upon homogeneous metallocene complexes were developed that allowed for the fine-tuning of polyolefin properties. The development of homogeneous metallocene ZN catalysts offered more versatile methods for the polymerization of olefins because the electronics and sterics of the cyclopentadienyl-type ligands can be modified such that tailoring polyolefins could

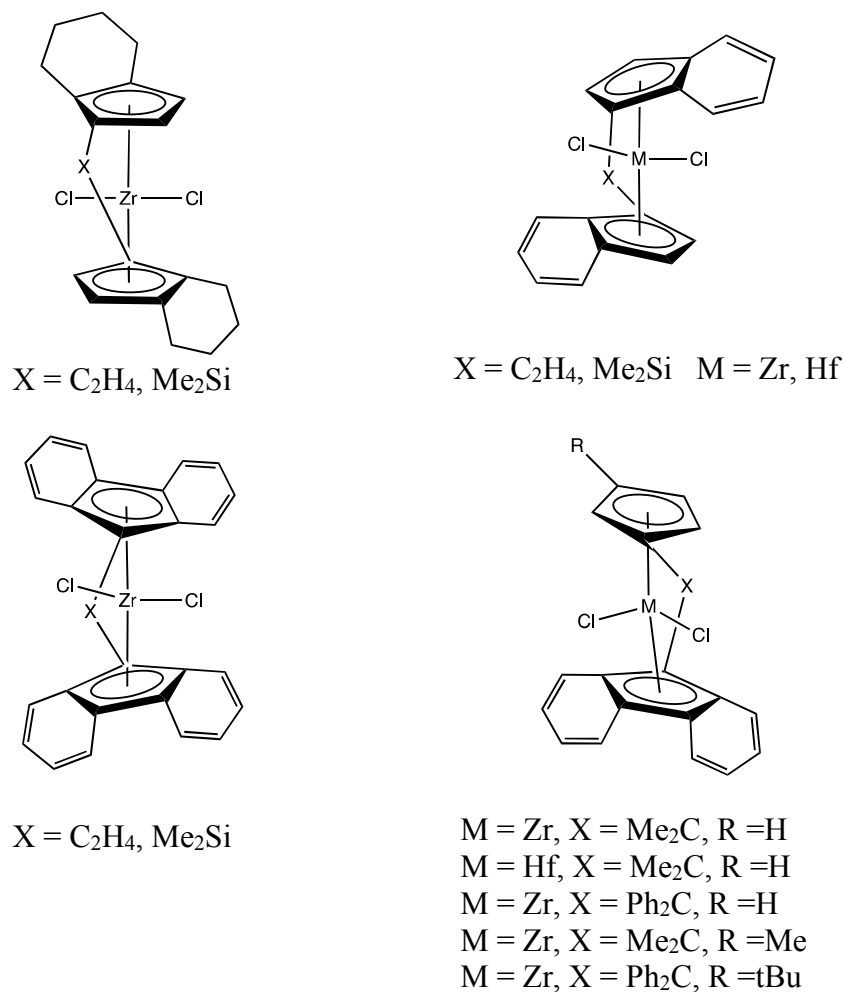


Figure 1.1: Structures of some metallocene pre-catalysts for olefin polymerization. Figure adapted from reference 11.

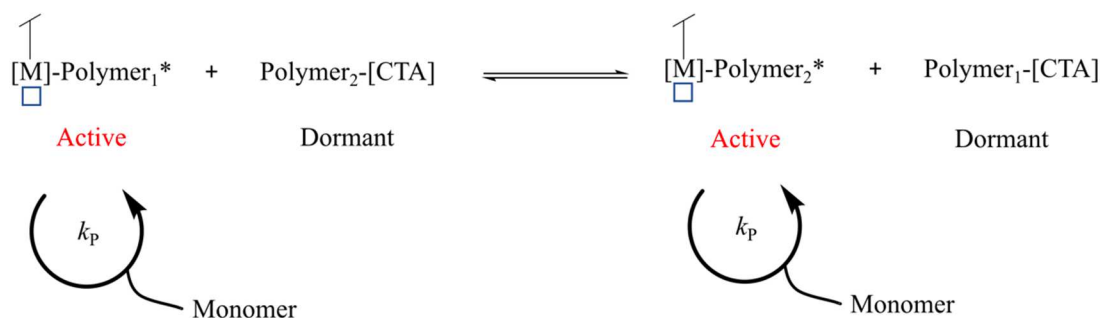
become a reality.¹¹ The structures of several common metallocene precatalysts used in the polymerization of olefins are shown in Figure 1.1. The metallocene precatalysts are of the general formula Cp_2MX_2 , where Cp=cyclopentadienyl, M=metal, and X=CH₃ or halide and must be used in conjunction with a cocatalyst, such as triethylaluminum or diethylaluminum chloride. A great deal of research was done on metallocene systems with various alkyl groups and a diethylaluminum chloride cocatalyst, but it was found that the polymerizations were plagued with fast aging processes after a short induction time.¹²⁻¹⁵ A significant improvement in activity was observed with the discovery of methylaluminumoxane (MAO) from the combination of trimethylaluminum and water and its use as a cocatalyst, which made metallocene catalysts significantly more active than original ZN catalysts.¹¹

Although the exact structure and role of MAO is to this day not fully understood, the mechanism of the polymerization of olefins by heterogeneous metallocene catalysts with MAO was more straightforward than that with first generation ZN catalysts. The MAO is utilized in two ways: first, the MAO serves to alkylate the metallocene precatalyst in the dichloride form, and second, the MAO activates the alkylated precatalyst by methyl abstraction to provide a cationic species with a vacant site for olefin coordination. Additionally, by altering the ligand environment of the precatalysts, isotactic, syndiotactic, atactic, and elastomeric polyolefins could now be synthesized. The increase in activity from the use of MAO coupled with the versatility of metallocene complexes enabled a new era of control over polyolefin microstructures.¹⁶

1.1.3 Development of Coordinative Chain Transfer Polymerization Techniques

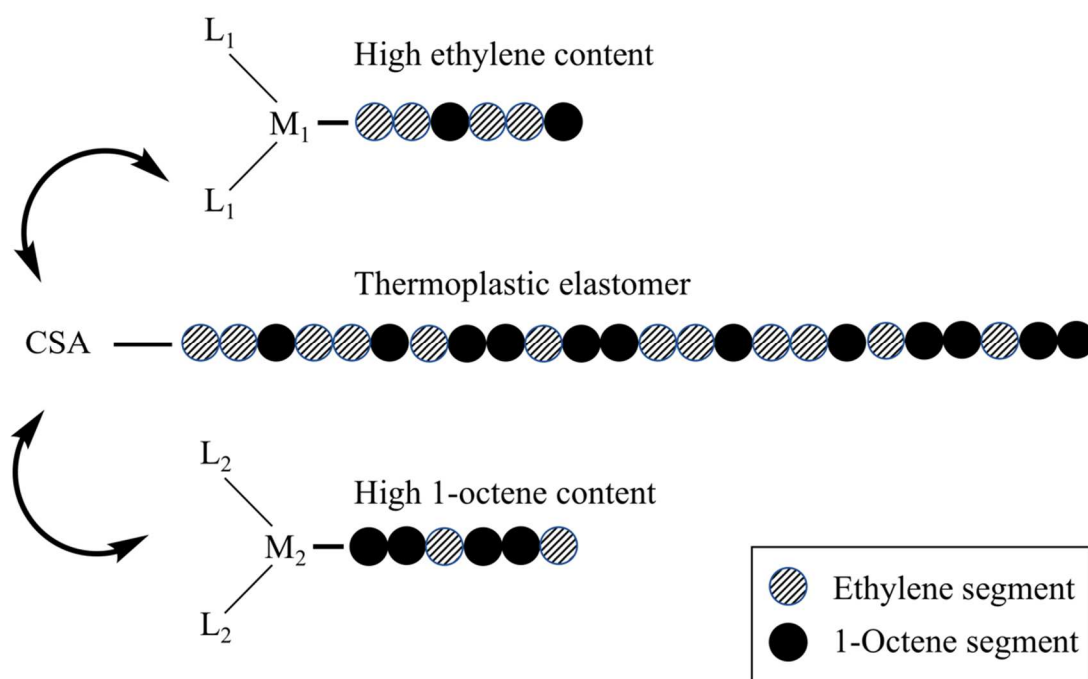
Although single-site metallocene catalysts for olefin polymerization led to great improvements in developing polyolefin materials with controlled molecular weights and microstructures, a significant limitation existed. The use of ZN catalysts relies upon expensive transition metals for polymerization, in which only one polymer chain can grow per molecule of catalyst. To overcome this limitation, coordinative chain transfer polymerization (CCTP) was explored by many groups (Scheme 1.1).¹⁷⁻²² CCTP uses a chain transfer agent (CTA) in the form of a main group metal alkyl species in addition to a transition metal catalyst to enable the growth of more than one polymer chain per expensive transition metal catalyst in a controlled manner. The growing polymer chain can transfer from the active catalyst species to the dormant CTA during the polymerization via transalkylation, enabling large quantities of polymers to be synthesized. Additionally, end-group functionalization of the polymer chains is possible due to the polymer-CTA bonds at the end of polymerization. However, the use of a CTA does not inherently prevent unwanted termination pathways (other than transalkylation to CTA), such as β -hydride elimination.²³⁻²⁵

Scheme 1.1: Coordinative chain transfer polymerization (CCTP). [M] represents the transition metal propagating species. Figure adapted from reference 26.



Chain shuttling polymerization (CSP) is another useful technique reported by Arriola and coworkers in 2006, which the authors used for the straightforward synthesis of multiblock polyethylene-*co*-poly(1-octene) statistical copolymers that acted as thermoplastic elastomers.²⁰ The microstructure resulted from polymer chains growing on two different catalysts in addition to a CTA (or chain shutting agent, CSA). Because the comonomer reactivity ratios varied for the two catalysts, ethylene-rich (crystallizable) and 1-octene-rich (noncrystallizable) segments could be produced sequentially from the two catalysts via transalkylation to the CSA.

Scheme 1.2: Chain shuttling polymerization (CSP). M_1 and M_2 represent the transition metals from catalysts 1 and 2 respectively. L_1 and L_2 represent their respective ligand sets. Figure adapted from reference 26.



1.2 Living Polymerizations

1.2.1 Key Characteristics

The idea of living polymerization, or polymerization that proceeds in the absence of undesirable, irreversible chain-termination pathways, has become pivotal to modern polymer chemistry and materials science.^{27, 28} Although extremely useful, polymerizations by heterogeneous ZN catalysts or homogeneous metallocene catalysts have polydispersities greater than 2.0. There was evidence of living polymerizations as early as the 1930s,²⁹⁻³¹ but the term “living” was coined by Michael Szwarc in 1956 in a landmark paper in *Nature* to describe the polymerization of styrene under anionic conditions.³² Living polymerization affords excellent control over the polymer product’s molecular weight and architecture and leads to extremely narrow, Poisson-like distributions of molecular weights.³³ Since then, significant effort has been made to perfect and expand this technique, and it can now be found in cationic, radical, coordination, and ring-opening polymerization systems as well.³⁴⁻⁴⁰ This work has enabled the synthesis of polymers with well-defined complex structures, such as gradient, block, graft, star, cyclic, and end-group functionalized polymers with controlled molecular weights and narrow polydispersities (<1.2) that are scientifically and industrially invaluable.

Chain-growth polymerizations (e.g. free-radical polymerizations) contain four main steps: initiation, propagation, chain transfer, and termination. Through elimination of the latter two processes, more control over the polymerization can be obtained. However, while “living” polymerizations completely eliminate undesirable

termination pathways, “controlled” polymerizations suppress them but do not eliminate them. There are several main criteria which must be true in order for a polymerization to be deemed living: 1) the concentration of the active propagating species is constant throughout the polymerization and there is first-order kinetic behavior. 2) The number average molecular weight (M_n) of the polymer increases linearly with monomer conversion and can be predetermined as a result of maintaining a constant number of chains throughout the polymerization. This is true when the rate of initiation is faster than the rate of propagation and there is an absence of irreversible chain transfer/termination reactions. The average degree of polymerization, X_n , is dependent upon the initial ratio of monomer to initiator, according to

Equation 1.1:
$$X_n = \frac{[M]_0}{[I]_0}$$

where $[M]_0$ and $[I]_0$ are the initial concentrations of monomer and initiator respectively.

3) The polymers should possess a Poisson distribution of molecular weights and contain a very narrow molecular weight distribution (e.g. polydispersity index (PDI)). Finally, in the absence of irreversible chain transfer and termination processes, 4) all chains remain “living” after full consumption of monomer and addition of more monomer resumes propagation, enabling the formation of well-defined block copolymers (BCPs) and other complex architectures as well as end-group functionalized polymers. The polymerization remains living until a termination step is purposefully performed.

1.2.2 Living Coordination Polymerization

A significant relationship exists between the potential applications of a polymer and its physical and mechanical properties, which are largely defined by the polymer's composition and architecture. In today's society, polyolefins comprise some of the most important and valuable materials. Therefore, the development of synthetic techniques for the living polymerization of α -olefins with versatile architectures, controlled molecular weights, and narrow polydispersities is a challenge that must be met. Despite major progress in living polymerization techniques starting in the 1950s, living coordination polymerization (LCP) was not reported until several decades later in 1979. Several challenges exist in living coordination polymerizations. With metallocene catalysts, for example, insertion of the double bond occurs until β -hydride and/or β -alkyl elimination reactions take place.^{41, 42} This is further complicated by the use of alkyl aluminum cocatalysts, which provide an additional transfer reaction pathway via the aluminum center.⁴² Previously, efforts were made to diminish the frequency of chain transfer and elimination reactions that terminate propagation, such as lowering the reaction temperature to reduce the occurrence of these termination pathways. Unfortunately, lowering the temperature can also cause precipitation of polymers from solution during the polymerization, thereby decreasing the controlled nature.³³

Consequently, it was determined that a promising route towards the development of LCP was by designing catalysts that could not undergo undesirable termination pathways and did not need to be activated by alkyl aluminum species. Significant advances have been made in the last two decades to make the LCP of α -

olefins, α,ω -nonconjugated dienes, and cyclic olefins a reality. The first example of the LCP of olefins was reported by Doi et al. using a soluble vanadium-based Ziegler catalyst of the formula $[\text{V}(\text{acetylacetonate})_3]$ activated by Et_2AlCl to produce partially syndiotactic polypropylene with extremely narrow molecular weight distributions.^{43, 44} However, there were several drawbacks to this catalyst system, including that the living characteristics were only observed at very low reaction temperatures, the percentage of active vanadium sites was very low, and the catalyst system was limited to only certain monomers. However, it was found that subtle changes to the ligands of the vanadium complexes had large effects on the catalytic behavior.⁴⁵ Since then, several notable catalysts have been developed for the LCP of olefins that are capable of controlling the composition, microstructure, and architecture of polyolefin materials (Figure 1.2).⁴⁶⁻⁵²

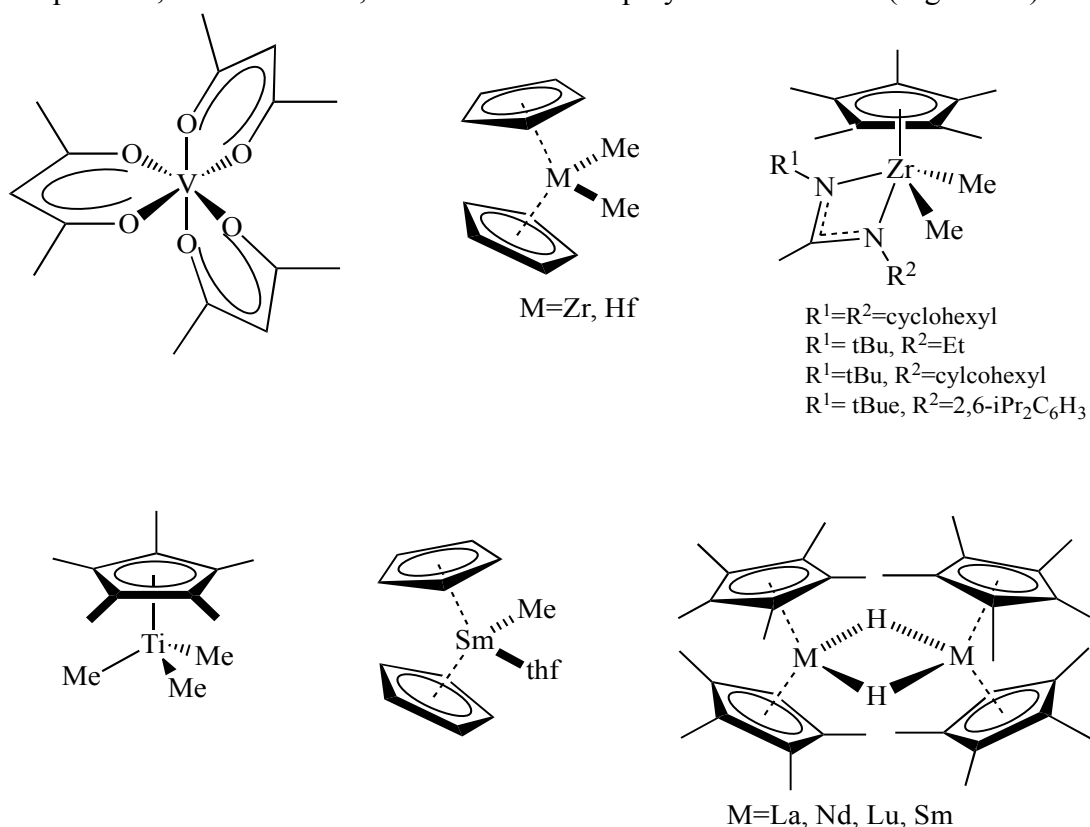


Figure 1.2: Several selected precatalysts for the living polymerization of α -olefins

1.3 Living Coordination Polymerizations with CpAM System

The physical properties of polymers, and thus potential applications, are highly dependent upon the structure of the polymer. For example, by increasing the percentage of stereoirregularities in predominantly isotactic polypropylene materials, the materials can range from stiff plastics to flexible plastics and thermoplastic elastomers.⁵³ As polyolefins became increasingly high in global demand at the start of the 21st century, the demand to develop a polymerization technique for α -olefins that had both living character and good stereo control increased as well. To this end, the Sita Group has developed group 4 cyclopentadienyl amidinate (CpAM) complexes (Figure 1.3) for the living, stereospecific coordination polymerization of α -olefins. The initiators are easily synthesized in high yields from a one-pot synthesis and completely inhibit chain termination pathways (e.g. β -hydride elimination and irreversible chain-transfer to metal alkyls).^{50, 54-57} The CpAM system has enabled a new class of precision polyolefins to be synthesized with excellent control over the molecular weight and microstructure of the polymer and with extremely narrow PDI (e.g. <1.1) through reversible group transfers.

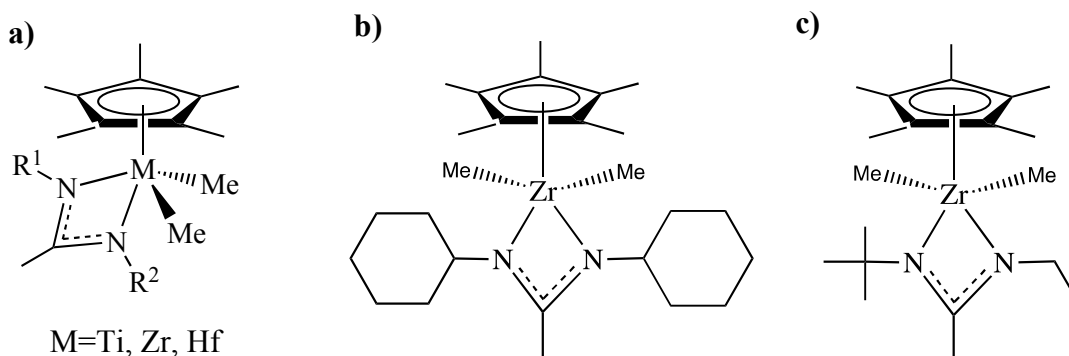
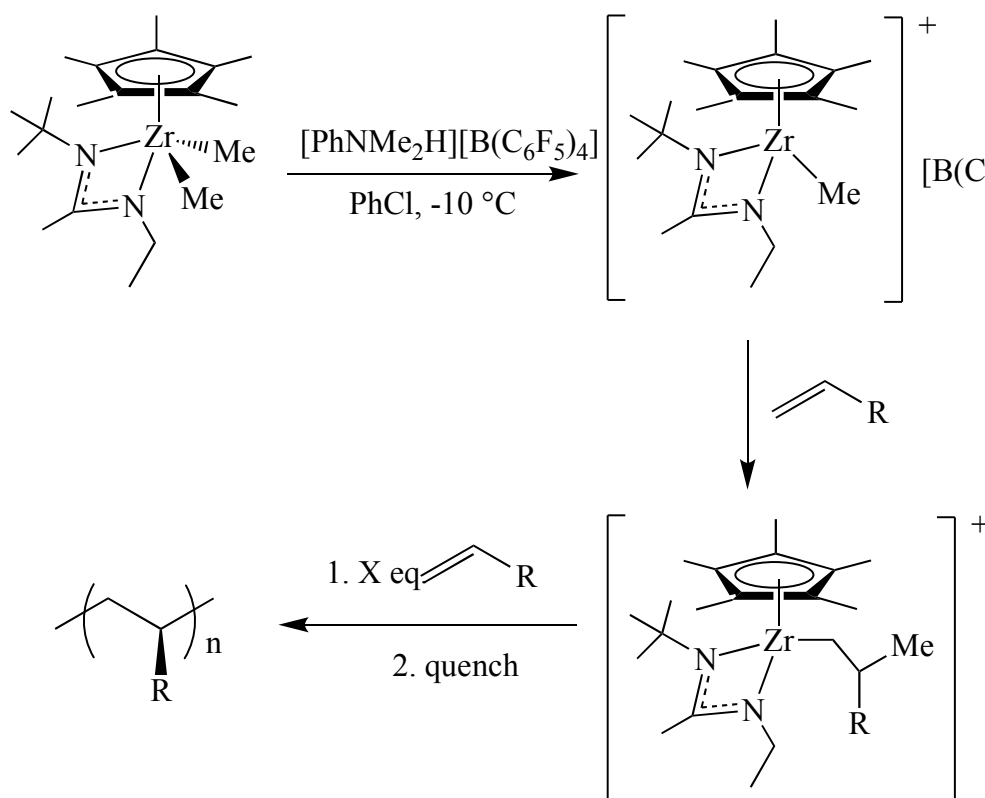


Figure 1.3: a) general structure of CpAM preinitiators; b) and c) show CpAM preinitiators that provide stereoirregular and stereoregular polyolefins, respectively.

The preinitiators shown in Figure 1.3 have been shown to be capable of the living polymerization of α -olefins and α,ω -nonconjugated dienes after activation with a borate of the formula $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ at ambient or sub-ambient temperatures in chlorobenzene. However, ^{13}C -NMR analysis of poly(1-hexenes) made from the cyclohexyl preinitiator in Figure 1.3b showed a lack of stereocontrol of the polymer microstructure during the polymerization due to the C_s symmetry of the preinitiator. Given the success of chiral C_1 symmetric *ansa*-bridged metallocenes to produce highly isotactic polypropylene,⁵⁸ C_1 symmetric CpAM preinitiators were synthesized (Figure 1.3c). Gratifyingly, when activated by the borate, this initiator was successful in

Scheme 1.3: Activation of C_1 symmetric preinitiator and subsequent stereoselective living polymerization of α -olefins. Figure adapted from reference 22.



performing the living, highly stereospecific polymerization of 1-hexene to produce high molecular weight, highly isotactic poly(1-hexene). When the reaction temperature was cooled to -10 °C, the PDI of the polymers were as low as 1.03.⁵⁹ Therefore, Sita et al. presented the first catalyst system for the living *and* stereospecific coordination polymerization of an α -olefin.

1.3.1 Living Degenerative Group-Transfer Coordination Polymerization

After the success of the CpAM catalyst system, Sita and coworkers also reported a method for the programmable incorporation of stereoerrors in polyolefins through living degenerative methyl group-transfer coordination polymerization (MeDet). In this technique, two populations of transition metal species exist: one containing active, propagating sites and the other containing dormant, nonpropagating sites. With substoichiometric activation of the C_1 symmetric preinitiator in Figure 1.3b by the borate, the two species can undergo reversible exchange through rapid methyl group transfer. In this case, the configurationally unstable dormant species will undergo metal-centered epimerization while the active species simultaneously propagates. However, after a methyl group exchange, the active species becomes dormant and undergoes the epimerization process. Because the methyl exchange process is rapid and reversible, the active and dormant species appear to effectively propagate at the same rate. The amount of stereoerrors incorporated is proportional to the concentration of dormant metal centers, and thus can be easily controlled by changing the amount of the borate coininitiator used at the beginning of the polymerization. As long as the rates of epimerization and exchange are much greater

than the rate of polymerization, the polydispersity remains close to 1. Additionally, X_n is simply inversely proportional to the initial concentration of preinitiator regardless of the initial concentration of borate coinitiator.²²

The MeDet method has been utilized to produce a large range of polypropylene materials with narrow polydispersities with varying stereochemical structures, ranging from stiff plastics to fully amorphous materials.⁵⁴ Theoretically, polypropylene materials with an entire spectrum of microstructures could be easily synthesized in this manner. Sita and coworkers further demonstrated that this method could also be used to form the first example of an atactic-isotactic stereogradient polypropylene material, as well as discrete isotactic-atactic stereoblock polyolefins through switching MeDet “on” and “off” as a function of time during the polymerization through partial methylation of the cationic active sites and full demethylation of the dormant sites. In this manner, a family of atactic-isotactic stereoblock polypropylene with elastomeric properties were prepared.⁵⁵

1.4 Living Coordinative Chain Transfer Polymerizations with CpAM System

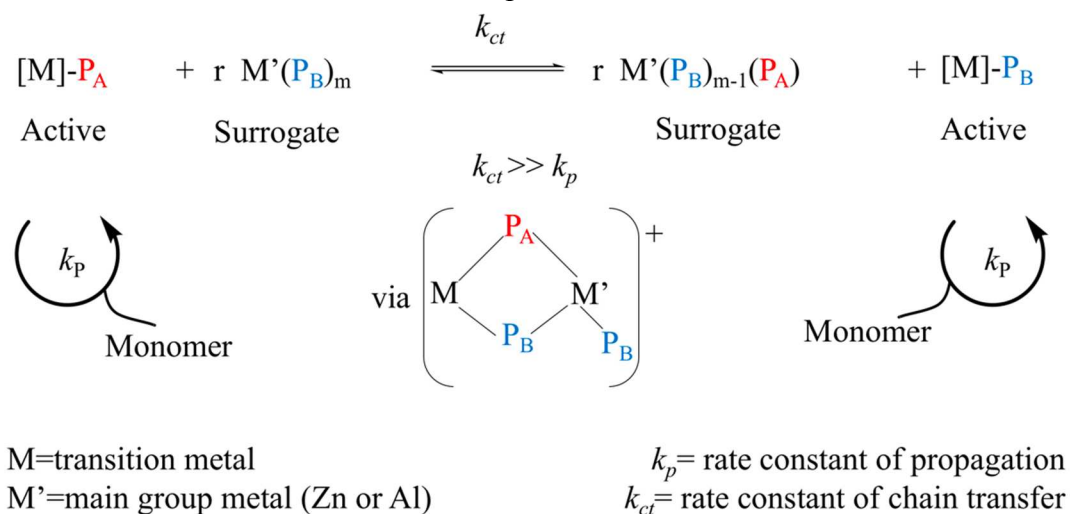
Despite progress in the field of LCP of olefins, there are still significant drawbacks to the technique. For example, because the final polymer depends on the initial concentration of initiator, and only one chain can grow per active site, an issue arises regarding scalability; larger scale polymerizations require greater amounts of transition metal catalysts, which can be prohibitively expensive. A solution to this “one chain per active site” limitation is to utilize a chain transfer agent, such as diethyl zinc, in the polymerization. Although coordinative chain transfer polymerizations of α -

olefins were reported in the 1990s, they were limited to the controlled oligomerization of ethylene.^{20, 60} It was not until 2008 that the Sita Group reported the first definitive example of the living coordinative chain transfer polymerization (LCCTP) of propylene and higher α -olefins.^{61, 62} Sita et al. reported a large molecular weight range of atactic polypropylene materials possessing extremely narrow polydispersities that could be produced in the presence of varying amounts of diethyl zinc as the chain transfer agent. LCCTP of olefins provides the opportunity to design, produce, and investigate the physical properties of a broad range of new classes of precision polyolefins, and establishes a viable solution to the “one chain per active site” limitation on the yield imposed by traditional living coordination polymerization.

1.4.1 LCCTP of Olefins

LCCTP is based on the rapid and reversible polymeryl group transfer between active transition metal propagating species and excess equivalents of inactive main group metal alkyl species serving as “surrogate” chain growth sites (Scheme 1.4).

Scheme 1.4: Mechanism of LCCTP. Adapted from reference 22.



Under LCCTP conditions, the rate of chain transfer is much greater than the rate of propagation ($v_{ct} \gg v_p$) and thus the active and surrogate species appear to effectively propagate at the same rate and the final polymer yield is now a function of the amount of the relatively inexpensive main group metal alkyl species rather than the expensive transition metal active species. The value of X_n is now inversely proportion to the concentration of the surrogate species for a given amount of monomer according to

Equation 1.2:
$$X_n = \frac{[M]_0}{([Active]_0 + [Surrogate]_0)}$$

and in the absence of termination pathways, the PDI of the final material will be extremely narrow (e.g. <1.1).

Sita et al. demonstrated that LCCTP could be performed with a C_s symmetric hafnium preinitiator of the formula $Cp^*HfMe_2[N(Et)C(Me)N(Et)]$ activated by the $[PhNHMe_2][B(C_6F_5)_4]$ coinitiator in the presence of various amounts of diethyl zinc ($ZnEt_2$) as the CTA. Under these conditions, the desirable characteristics of a living coordination polymerization were maintained. Atactic polypropylene materials of a large range of precisely controlled molecular weights and extremely narrow polydispersities were prepared simply by varying the equivalents of the CTA. They demonstrated that LCCTP is efficient with as few as five equivalents of CTA relative to the transition metal species, and as many as several hundred equivalents.

1.4.2 End-group Functionalized Poly(α -olefinates)

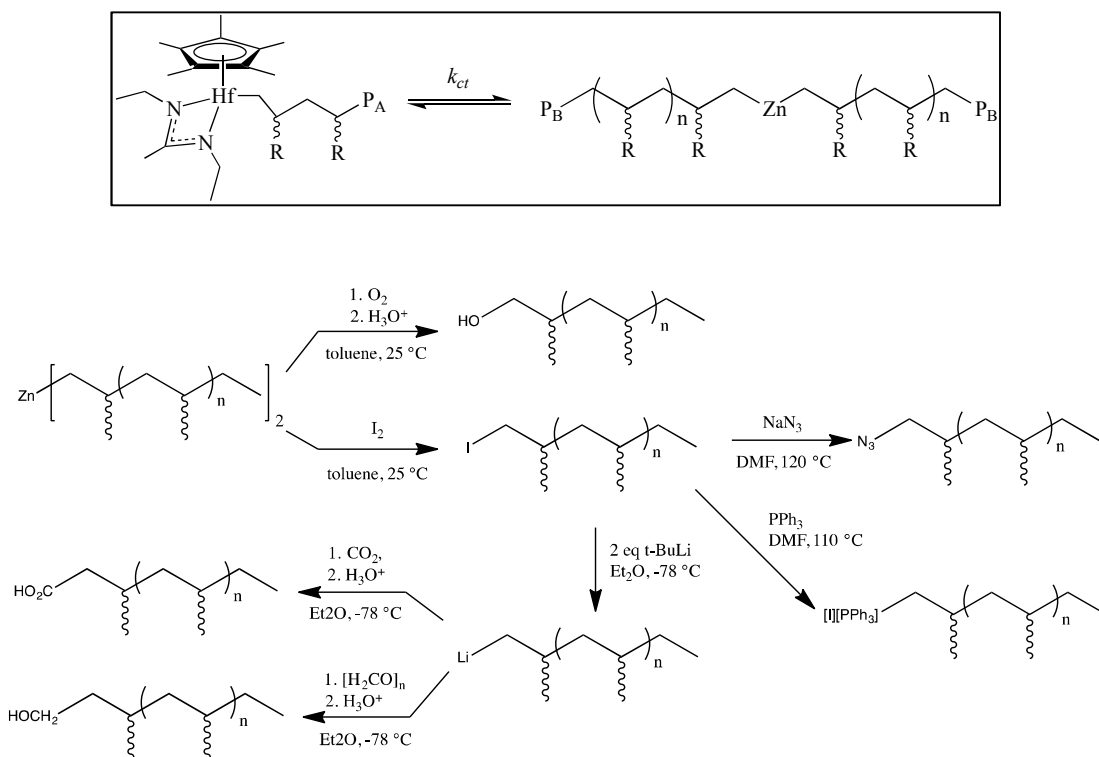
Before the discovery of LCCTP, non-living CCTP was the most efficient method with which to incorporate functionality into polyolefin chains. The concept of end-group functionalization is an extremely important part of polymer chemistry and

applications of polymers because it can incorporate functional groups that are otherwise incompatible with the polymerization techniques. For example, end-group functionality can assist in the characterization of polymers through nuclear magnetic resonance (NMR) by the end-group resonances, and they have been used to assist in the ionization process of polymers during mass spectrometry.⁶³ Functionalities can also be useful for a wide variety of applications, such as post-polymerization transformations, formation of complex polymer architectures (e.g. graft polymers), macroinitiation of ring opening polymerization, and synthesis of functional monomers for use in step-growth polymerizations.⁶⁴⁻⁶⁷

In 2016, Sita and coworkers demonstrated the utility of LCCTP for obtaining a versatile new class of non-polar building blocks for amphiphilic materials represented by end-group functionalized poly(α -olefinates) (x-PAOs).⁶⁸ The potential for facile and quantitative end-group functionalize the polyolefins stems from the weak metal-carbon bond produced by the CTA at the end of the polymerization. At the end of LCCTP with ZnEt_2 as the CTA and prior to workup, virtually all of the polymer chains are in the form of a $\text{Zn}(\text{polymeryl})_2$ product. As a result, x-PAOs can be prepared through the addition of appropriate quenching agents and subsequent post-polymerization chemical transformations (Scheme 1.5). For example, with the addition of oxygen or excess iodine, hydroxy- or iodo- terminated polyolefins are produced respectively, which can be further functionalized to provide azido-, carboxy-, and triphenyl phosphonium- terminated polyolefins.⁶⁹ This wide variety of end group functionalities, along with the control over molecular weight as described previously, are what make LCCTP precision polyolefins so valuable. Herein, the utilization of x-

PAOs as nonpolar building blocks for the self-assembly of amphiphilic materials is described.

Scheme 1.5: Synthetic route to various x-PAOs via LCCTP



1.5 Self-assembly

Molecular self-assembly, in which molecules are directed to assemble through noncovalent interactions without external directive, has become a key concept in supramolecular chemistry and is used in a multitude of applications including materials technology, catalysis, medicine, biomedical engineering, and nanopatterning for increased data storage and processing.⁷⁰⁻⁷⁵ As the overall understanding of self-assembly and molecular design increases, chemists are now able to synthesize self-assembling materials with greater diversity and control. Notably, the self-assembly of

amphiphiles (materials comprised of chemically linked polar and non-polar segments) provides important scientific and industrial materials with extensive applications in fields such as drug delivery and nanotechnology. Consequently, an ever-growing area of research focuses on the development of new classes of building blocks for amphiphiles and other self-assembling polymeric materials that are designed to afford control over self-assembly, and hence, the final nanostructure that is formed. To this end, precision polyolefins synthesized via LCP or LCCT as non-polar building blocks have the potential to greatly impact this field. The work presented in this thesis served to explore new ways with which to utilize these precision polyolefin building blocks.

In order to intelligently design new self-assembling materials, it is important to understand what governs self-assembly processes and to develop models for the self-assembly of various amphiphilic and hydrophobic systems (e.g. surfactants, block copolymers, hybrid materials, etc.). Molecular self-assembly is driven by noncovalent interactions (e.g. hydrogen bonding, hydrophobic interactions, electrostatic interactions, van der Waals forces, π - π interactions, etc.). Overall, the fundamental thermodynamic principle of self-assembly is the presence of a favorable enthalpic driving force that is strong enough to overcome an unfavorable entropic contribution from an increase in organization, leading to the self-assembled structure existing at a thermodynamic minimum at equilibrium.⁷⁶ In the work presented here, the design of several novel self-assembling polymeric materials is described; these materials were influenced by surfactant self-assembly, the microphase separation of block copolymers, and the self-assembly of other types of amphiphilic systems.

1.5.1 Classical Surfactant Self-assembly

One of the most classic examples of self-assembly comes from small molecule surfactants in aqueous media, which are generally organic amphiphiles composed of a small polar head-group and a small to moderately-sized nonpolar (e.g. saturated or unsaturated hydrocarbon) tail. The polar head-group can be neutral, ionic, or zwitterionic. Above a critical aggregation concentration (CAC), surfactants can reversibly and dynamically form various phases in polar or nonpolar media in order to minimize unfavorable interactions with the solvent, such as micelles, cylinders, and bilayers. For example, in polar solvents the polar head-groups will orient towards the solvent and the nonpolar tails will migrate above the interface (either liquid/air or liquid/liquid); this disrupts the cohesive energy at the interface and favors the formation of surfactant aggregation. Because these self-assemblies are based entirely on noncovalent interactions, the structures are dynamic and can be changed in response to various external stimuli (e.g. temperature, pH, etc.), making them useful in a variety of applications such as detergents, emulsifiers, wetting agents, etc.⁷⁷

The theory of self-assembly for surfactants has been expertly explained in two pioneering studies by Tanford⁷⁸ and Israelachvili⁷⁹. Tanford proposed that the formation of aggregates at equilibrium is a result of balancing the interfacial free energy at the water/structure interface with the repulsion between surfactant head-groups. Israelachvili and coworkers presented a critical packing parameter for predicting the size and shape of surfactant aggregation depending on the molecular geometry of the surfactant head-group and tail. The critical packing parameter, C_{pp} , is determined by

Equation 1.3:
$$C_{PP} = \frac{V}{al}$$

where V is the volume of the tail, a is the area of the head-group, and l is the relative length of the tail. The ratio of these three variables determine the morphology of the aggregates. For example, when $p < 1/3$ spheres are formed, when $1/3 < p < 1/2$ cylinders are formed, when $1/2 < p < 1$ vesicles are formed, and when $p=1$ lamellae (bilayers) are formed (Figure 1.4). Accordingly, the hydrophobic tail of the surfactant plays a significant role in determining the geometry of the self-assembly.

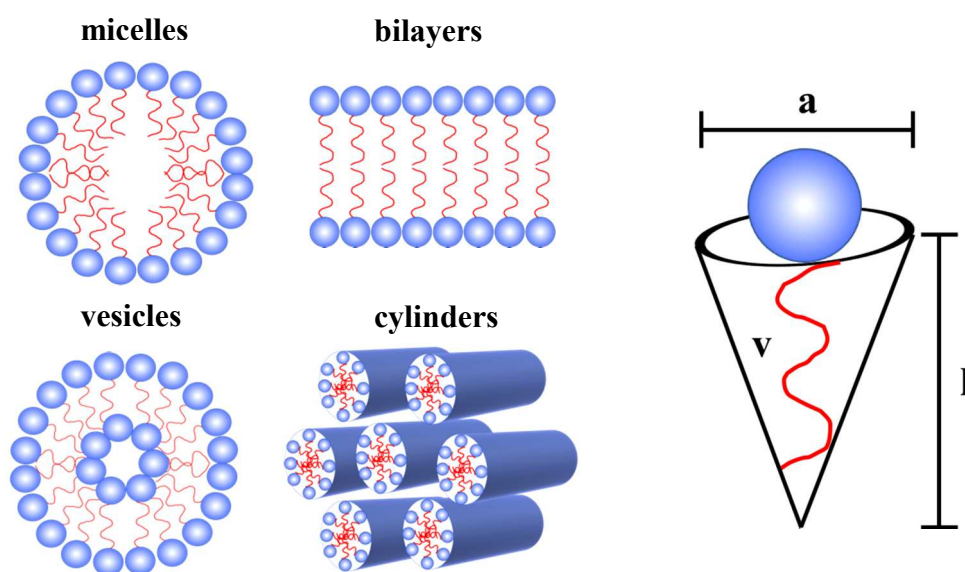


Figure 1.4: Surfactant self-assemblies based upon a critical packing parameter

Beyond the conventional types of surfactants, the discovery and synthesis of more complex systems has made predicting the self-assembly structure more challenging. For example, Gemini and Bola surfactants (Figure 1.5) are nonconventional surfactants that are used in a wide range of applications, such as drug and gene delivery, dispersants, and solubilizers.⁷⁷ Gemini surfactants contain two hydrophilic head-groups that are linked by a spacer, with each head-group possessing a hydrophobic tail. The two hydrophobic tails are in close proximity and cause a shift

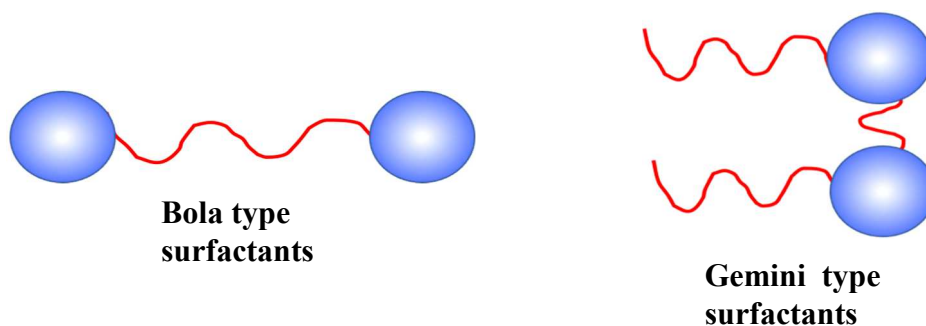


Figure 1.5: Schematics of two types of nonconventional surfactants

in self-assembly behavior by lowering the CAC and forming thread-like micelles below the CAC.⁸⁰ Bola surfactants contain two hydrophilic head-groups linked together by a single hydrophobic tail. Along with the classical self-assembly phases shown in Figure 1.4, Bola surfactants have been shown to form helical structures and microtubular assemblies.⁸¹

Although surfactants are abundant in industrial, cosmetic, and pharmaceutical products, their small molecule structure inherently limits the diversity and stability of surfactants. Additionally, it is often assumed that surfactant solutions are in instantaneous equilibrium with respect to structure formation; however, several days are often required for the formation of, or disruption to, an equilibrium phase structure.⁸²

1.5.2 Block Copolymer Self-assembly

During the last few decades, the self-assembly of amphiphilic BCPs have also been widely studied. Their unique properties, increase in stability relative to small molecule aggregates, and diverse applications have been the focus of extensive

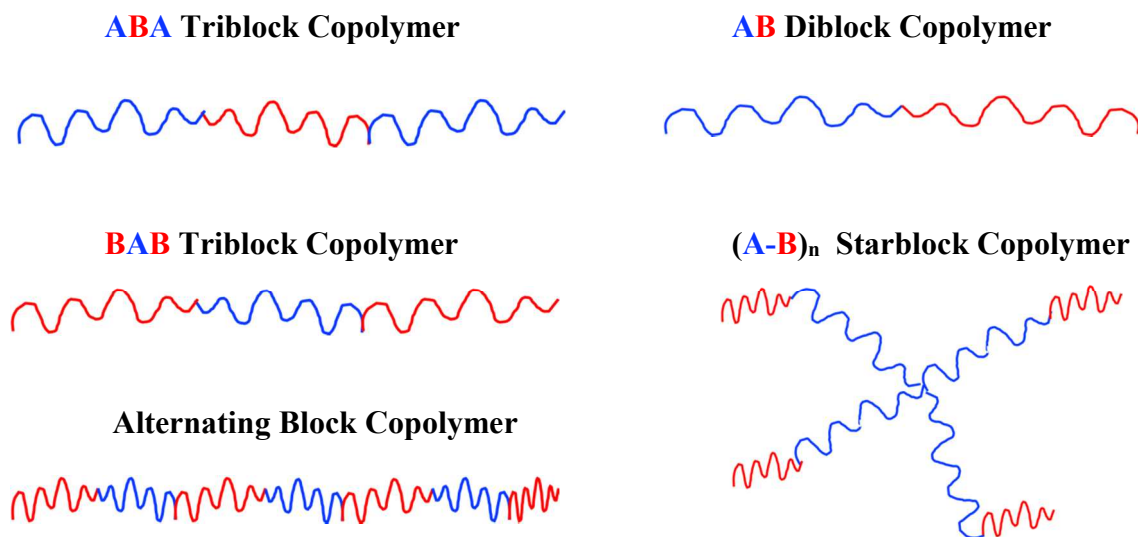


Figure 1.6: Schematic illustrations of common types of AB-type amphiphilic BCPs

scientific and industrial interest in fields such as medicine and drug delivery, photoelectric materials, nanotechnology, catalysis, and others.⁸³ BCPs are defined as two or more homopolymer subunits linked together by covalent bonds. With the recent development of more sophisticated polymerization techniques, especially living polymerizations, block copolymers can be prepared with well-defined molecular weights and complicated architectures. Although polymers of various architectures (e.g. graft copolymers, starblock copolymers, dendritic polymers, etc.) have been found to self-assemble into a variety of different structures⁸⁴, the most comprehensively studied systems for self-assembly are AB-type linear amphiphilic block copolymers (Figure 1.6). As a function of composition, BCPs can microphase separate into a variety of classic morphologies, such as spheres (S), hexagonally packed cylinders (HEX), a three-dimensional bicontinuous gyroid (GYR), and lamellae (LAM) in addition to more complex phases, such as hexagonally perforated layers (HPL) (Figure 1.7).

In the case of amphiphilic BCPs, both hydrophobic block(s) and hydrophilic block(s) are incorporated but are immiscible, and will, by nature, repel each other. Consequently, the like segments tend to aggregate and self-assembly is driven by an

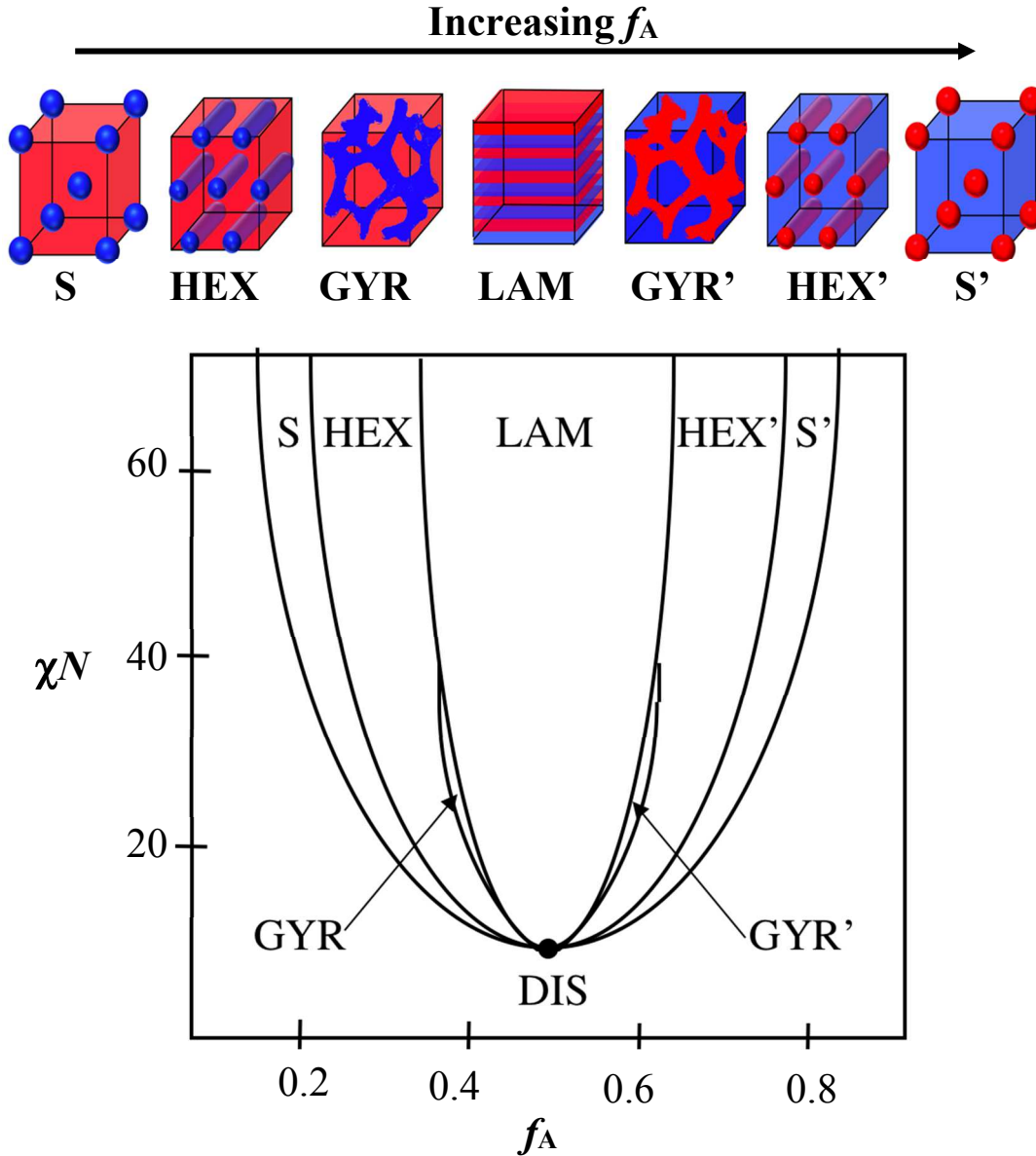


Figure 1.7: top) schematic illustrations of the classical morphologies formed by BCPs during microphase separation; bottom) theoretical BCP phase diagram. Figure adapted from reference 85.

unfavorable mixing enthalpy as well as a small mixing entropy. Such segregation cannot lead to macroscopic phase separation because the blocks are covalently linked; instead, microphase separation occurs on the molecular level and ordered structures are formed.⁸⁵

A great deal of effort has gone into understanding the thermodynamic principles behind block copolymer self-assembly; though the original Flory-Huggins theory can sufficiently describe the phase behavior of polymer blends⁸⁶, it is unsuitable to accurately describe the microphase separation of a covalently linked block copolymer.⁸⁷ In 1980, Leibler used the product χN and the composition f_A to calculate a theoretical phase diagram from which a qualitative prediction of morphology can be made for a fixed χN (Figure 1.7).⁸⁸ He found that diblock copolymer self-assembly is essentially controlled by three main factors: the volume fractions of the A and B blocks (f_A and f_B , where $f_A + f_B = 1$), the overall degree of polymerization (N , where $N = N_A + N_B$), and the A-B segment-segment Flory-Huggins interaction parameter (χ), which specifies the degree of incompatibility between blocks. The χ -parameter has also been found to vary inversely with temperature^{85, 89, 90} according to

Equation 1.4:
$$\chi_{AB} = \left(\frac{z}{k_B T} \right) \left[\epsilon_{AB} - \frac{1}{2} (\epsilon_{AA} + \epsilon_{BB}) \right]$$

Where z is the number of nearest neighbors per polymer repeat unit, k_B is the Boltzmann constant, T is the absolute temperature, and ϵ_{AB} , ϵ_{AA} , and ϵ_{BB} are the interaction energies of A-B, A-A, and B-B segments, respectively.

The formation of the various phases can be attributed to a competition between enthalpic (interfacial energy between the two blocks) and entropic (chain stretching)

factors. The immiscible blocks will microphase separate away from each other in a manner that will minimize interfacial area and thus lower the total interfacial energy. As a result, stretching of the polymer chains occurs in a manner that deviates from the preferred coil conformation. According to a well-studied cone-column model for morphologies (Figure 1.8)⁹¹, highly asymmetric BCPs will favor the more curved morphologies as this gives the system the lowest interfacial area relative to other morphologies. Morphological transitions from S to HEX to LAM occur as a result of polymer chains adopting new arrangements in an effort to reduce chain-stretching.⁸⁵

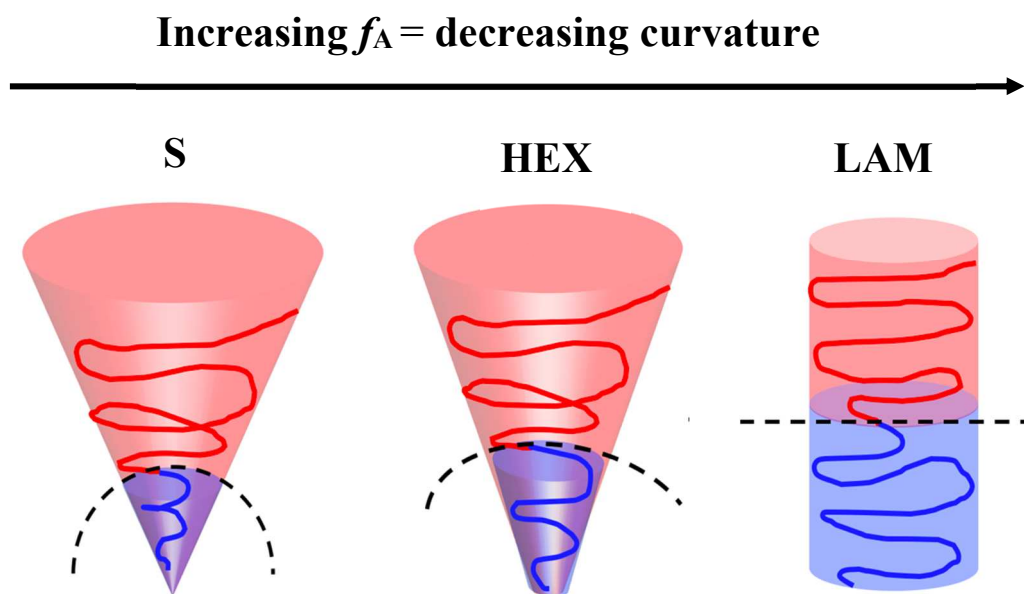


Figure 1.8: Schematic illustration of the cone-column model for morphological transitions in AB diblock copolymers. As f_A increases, the energetically favorable morphology shifts from more curved to less curved. The dashed lines represent the interface between the A and B domains. Figure adapted from references 85 and 91.

Leibler also established that the minimum value of χN needed for microphase separation to occur in symmetric BCPs is 10.495. For polyolefins, which lack strong specific interactions (e.g hydrogen bonding, dipole interactions, etc.), χ is generally small and positive. Thus, as temperature increases and/or the product of χN decreases, the incompatibility between the two blocks becomes too small for microphase separation and structured BCPs will undergo an order-to-disorder transition (ODT) at a given temperature (T_{ODT}) and become disordered. Hence, despite the versatility of BCPs, it can be difficult to achieve microphase separation because the product of χN must be high. It is particularly difficult for BCPs with a low overall degree of polymerization; as N decreases, the χ -parameter must become exceptionally high. Research in high χ , low N systems has been increasing significantly recently due to their potential applications in nanotechnology.⁹²

1.5.3 Self-assembly in Systems Utilizing Nonpolar Building Blocks

Research interests have recently been shifting towards amphiphilic “hybrid” materials, which utilize the principles and advantages of both small molecule surfactants and block copolymers. As new polymerization techniques and versatile coupling chemistries are developed, new types of macromolecules can be synthesized, and previously undiscovered self-assembly behavior can be observed. For example, Cheng and coworkers reported a class of self-assembling macromolecules called “giant surfactants” containing functional derivatives of large molecular nanoparticles as “head” groups, like [60]fullerenes (C_{60}) or polyhedral oligomeric silsesquioxanes (POSS), covalently linked to nonpolar polystyrene “tails.”⁹³⁻⁹⁵ Cheng et al. reported

remarkable sensitivity of self-assembled structures on the chemical composition and topology of the giant surfactants, and have shown that these materials can provide access to a wide variety of classic and complex morphologies upon thermal or solvent vapor annealing.⁹⁶ Additionally, Borsali and coworkers reported the formation of a high χ , low N hybrid system of natural-*b*-synthetic polymers composed of oligosaccharide/silicon-containing block copolymers.⁹⁷ These materials self-assembled into well-defined nanostructures with sub-10 nm domain spacings as a result of the strong incompatibility between the hydrophilic and hydrophobic blocks. This imbalance was further enhanced by the difference in chain-stiffness between the rod-like oligosaccharide block and the flexible coil conformation of the polymer block. They also reported the self-assembly of maltoheptaose-*b*-polystyrene BCPs into micellar nanoparticles in a THF/water mixture. The micelles were able to encapsulate gold nanoparticles. Despite the ability of these systems to form self-assembled nanostructures, they are not without limitations. For example, the versatility of the molecular nanoparticle head group of “giant surfactants” is limited by the ability to functionalize it (e.g. cost, scalability, etc.), and both “giant surfactants” and natural-*b*-synthetic hybrid block copolymers utilize high glass-transition temperature (T_g) polymer tails, such as polystyrene, making them relatively rigid and limiting the versatility of the systems.

The development of nanostructured materials that can respond to external stimuli on practical time scales and moderate conditions remains a challenge and is a topic of great academic and industrial interest. To this end, the work presented in this document describes the progress made in utilizing seemingly simple precision

polyolefins made from LCP and LCCTP as nonpolar building blocks for the self-assembly of a variety of new, more complex materials. Specifically, x-PAOs provided access to polyolefin materials with tunable molecular weights, narrow polydispersities, and programmable physical properties. With inspiration from the classical models of self-assembling materials (e.g. surfactants, BCPs, etc.), these x-PAOs were used to both expand the range of self-assembling polyolefin materials and develop an entirely new class of self-assembling materials represented by sugar-polyolefin conjugates.

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Chapter 2: Expanding the Range of x-PAO Building Blocks via LCCTP

2.1 Background

Although polyolefins have become ubiquitous in modern society, a challenge still remains in designing methods to expand the currently available library of ‘precision polyolefins’ with controlled degrees of polymerization and narrow polydispersities. Living coordinative chain-transfer polymerization (LCCTP), introduced by the Sita Group, is based on the rapid and reversible polymeryl group transfer between an active transition-metal propagating species and an inactive main-group metal alkyl “surrogate” species. It has the advantage of maintaining all of the desired characteristics of traditional living polymerizations while using less of an expensive transition-metal initiator. Additionally, with LCCTP, facile and quantitative end-group-functionalization is possible due to the reactive zinc-carbon bond of the polymer chains in the form of $\text{Zn}(\text{polymeryl})_2$ at the end of LCCTP, including $-\text{OH}$, $-\text{I}$, $-\text{N}_3$, and $-\text{COOH}$ chemical moieties.¹⁻⁸ However, to date, reports using LCCTP have been limited to amorphous polyolefins with low glass transition temperatures (T_g). This study served to expand the LCCTP system to provide x-PAOs with a high T_g , amorphous nature or a semi-crystalline nature.

2.1.1 High T_g Amorphous Polymers and their Applications

The glass transition temperature, or T_g , is a property of amorphous polymers that plays an extremely important role in determining the physical properties of a

material. When a polymer is cooled below the T_g it becomes hard and brittle and exists in its “glassy” state; when it is heated above the T_g it exists in a more flexible “rubber” state. The nature of the glass transition has historically been supported by theories from both a kinetic component^{9, 10} and a thermodynamic component.^{11, 12} Kinetic theories describe the transition as a dynamic process caused by “freezing” the movement of polymer chain segments, while thermodynamic theories describe the transition as a true second-order thermodynamic transition in which conformational entropy increases as temperature increases.¹³

The temperature range at which this transition occurs is a significant factor in determining the applications of a material. For example, items made out of hard plastics utilize polymers while in their glassy state (below the T_g), thus requiring materials with relatively high T_g (e.g. well above room temperature), while items requiring softer, rubbery polymers, such as car tires, utilize polymers while in their rubbery state (above the T_g).

The value of T_g is highly dependent upon the mobility of the polymer chain; as chains become more mobile, the T_g decreases. As a result, polyolefins typically display very low values of T_g (well below room temperature), which causes diminished physical properties (e.g. poor strength in areas such as compression, tension, shear, etc.) at elevated temperatures and limits their use in various applications. To overcome this limitation, efforts have been made to introduce hard segments (high T_g) into the polyolefin to increase the utility temperature. However, this remains a challenge due to the selectivity of coordination polymerization techniques and a lack of functionality for post-polymerization modifications.¹⁴⁻¹⁶ Recently, Ying et al. reported the formation of

multifunctionalized polyolefin-based elastomers from styrene moieties via graft-from anionic living polymerization.¹⁷ However, a challenge still remains in developing simple and efficient living coordination polymerization techniques capable of providing access to high-utility polyolefin-based materials.

2.1.2 Cyclopolymerization of 1,5-hexadiene and 1,6-heptadiene via LCP and LCCTP

The Sita Group has previously reported the living coordination polymerization (LCP) of ethene, propene, and higher α -olefins, as well as the living cyclopolymerization of 1,5-hexadiene and 1,6-heptadiene, using a group 4 metal dimethyl, cyclopentadienyl, amidinate (CpAM) complex of the formula $[\text{Cp}^*\text{M}[\text{N}(\text{R}^1)\text{C}(\text{R}^2)\text{N}(\text{R}^3)](\text{Me})_2]$ ($\text{M} = \text{Zr}$ and Hf , $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) as an initiator activated by a stoichiometric amount of borate, $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**II**) to produce polyolefins with tunable degrees of polymerization and extremely narrow polydispersities, $\bar{D}$, where $\bar{D} = \text{M}_w/\text{M}_n$. More recently, we have also reported the living coordinative chain transfer polymerization (LCCTP) of ethene, propene, longer-chain α -olefins, and α,ω -non-conjugated dienes to produce scalable quantities (e.g. kilograms) of end-group-functionalized poly(α -olefinates) (x-PAOs) with tunable degrees of polymerization and extremely narrow molecular weight distributions (e.g. < 1.1) using the initiator $[\text{Cp}^*\text{Hf}(\text{Me})\{\text{N}(\text{Et})\text{C}(\text{Me})\text{N}(\text{Et})\}][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (**I**) activated by **II** and in the presence of excess equivalents of a main-group-metal alkyl species, such as diethylzinc (ZnEt_2), which acts as the chain-transfer agent.¹⁻⁸

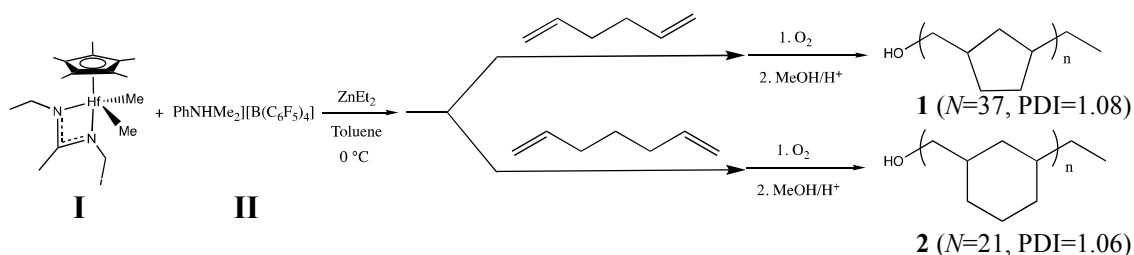
LCCTP enables the facile end-group functionalization of polyolefins. Of particular interest is the hydroxyl group (-OH), which could incorporate a polar functionality into the polyolefin chains that is otherwise incompatible with the polymerization method. Though the coordination cyclopolymerization of 1,5-hexadiene to produce poly(1,3-methylene cyclopentane) (PMCP) is well established in literature, current examples of OH-PMCP are limited.¹⁸⁻²² For example, Waymouth and coworkers have reported the formation of OH-PMCP via the cyclopolymerization of 1,5-hexadiene using methylaluminumoxane (MAO) as a chain transfer agent.²³ The OH-PMCP was then used as a macroinitiator for the ring-opening polymerization (ROP) of ϵ -caprolactone (CL) to form PMCP-*b*-PCL. However, a broad molecular weight distribution was observed for the diblock copolymers ($\mathcal{D}$ = 2.3-4.7) due to a lack of control in the 1,5-hexadiene cyclopolymerization.

In 2013, Crawford and Sita reported the stereoengineering of 1,6-heptadiene via living coordination polymerization (LCP) to produce poly(1,3-methylene cyclohexane) (PMCH). This was done through the sub-stoichiometric activation of neutral dimethyl preinitiators of the general formula $(\eta^5\text{-C}_5\text{R}_5)\text{Zr}[\text{N}(\text{R}^1)\text{C}(\text{R}^2)\text{N}(\text{R}^3)](\text{Me})_2$ using less than 1 equivalent of the $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ coininitiator **II** to produce an initial concentration of dormant species.²⁴ It was found that increasing the concentration of dormant species through a decrease in equivalents of **II** caused a steady change from highly stereoregular PMCH to stereoirregular, but still highly 1,3-*c-iso*-selective, PMCH. Few examples of PMCH are represented in literature, and to the best of our knowledge, the present work is the first example of OH-PMCH.²⁵

2.2 Accessing High T_g or Semi-crystalline Low Molecular Weight x-PAOs

2.2.1 Synthesis of OH-PMCP and OH-aPMCH

Scheme 2.1: General synthetic route to OH-PMCP and OH-PMCH



As previously discussed, at the end of LCCTP and before workup, virtually all polymer chains are in the form of a Zn(polymeryl)₂ with a reactive zinc-carbon bond. Consequently, LCCTP enables the facile and quantitative end-group functionalization of polymer chains through various chemical transformations to form x-PAOs.^{26, 27} Scheme 2.1 presents the synthetic route used to obtain hydroxy-terminated poly(1,3-methylene cyclopentane) (OH-PMCP **1**) and hydroxy-terminated atactic poly(1,3-methylene cyclohexane) (OH-aPMCH **2**) from 1,5-hexadiene and 1,6-heptadiene, respectively. The OH-PAOs were obtained under LCCTP conditions and quenched overnight at room temperature using purified oxygen gas at 5 psi. They were subsequently exposed to acidic methanol and purified via passage through a silica gel plug to produce large quantities of the final OH-PAO products. The successful OH-termination was confirmed by ¹H-NMR through the appearance of resonances (c.a. 3.45 ppm) representing the diastereotopic protons on the carbon adjacent to the OH end-group (see Supplemental Results). Additionally, the living character of these polymerizations was supported by gel permeation chromatography (GPC), which

yielded monomodal traces with very narrow polydispersities (< 1.1), and $^1\text{H-NMR}$ through an absence of vinylic end-group resonances, which would arise from termination via β -hydride elimination during the polymerization. Another indication that the cyclopolymerization occurred in a living fashion is that the number average molecular weight (M_n) measured by GPC increased linearly with respect to reaction time during the cyclopolymerization (Figure 2.1).

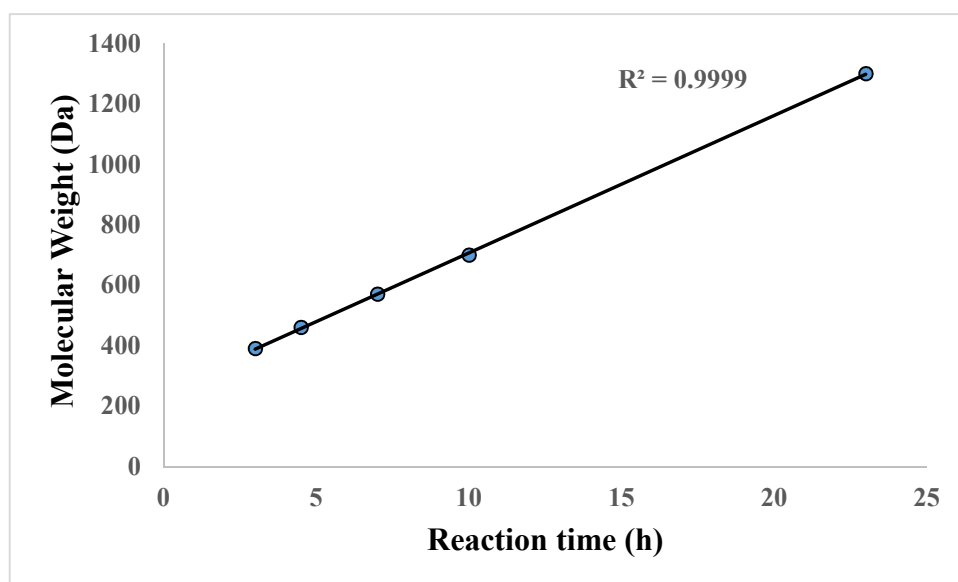


Figure 2.1: Linear increase in molecular weight of PMCP as a function of reaction time during the cyclopolymerization of 1,5-hexadiene

2.2.2 Characterization of OH-PMCP

In addition to the end-group resonance in the ^1H -NMR of OH-PMCP, two additional resonances can be observed at 4.9 ppm and 5.5 ppm corresponding to pendant vinyl groups as a result of uncyclized monomer units (Figure 2.2).²³ Despite several attempts at optimization, between 1-2% pendant vinyl groups existed in OH-PMCP materials synthesized via LCCTP, which is consistent with previous reports from the Sita Group.^{1, 24} During the propagation step of LCCTP, these pendant vinyl groups are undesirable due to the potential for cross-linking after the 1,5-hexadiene

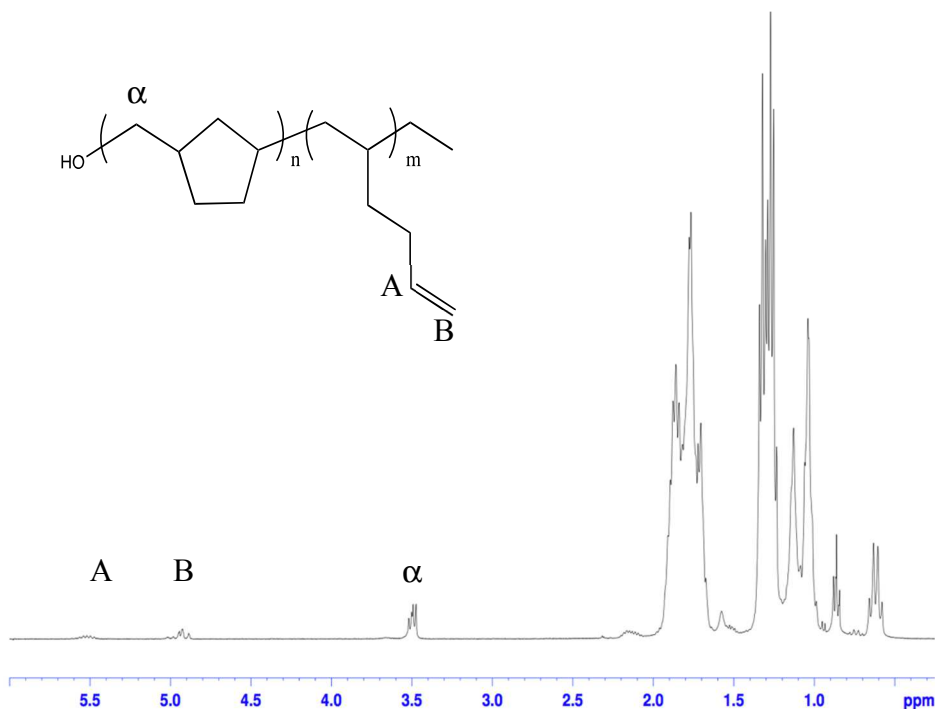


Figure 2.2: ^1H -NMR spectrum of **1** containing 1.87% uncyclized monomer units

monomer has been completely consumed. During this study, efforts were made in order to optimize the LCCTP of 1,5-hexadiene to increase regioselectivity and produce low weight OH-PMCP with minimal pendant vinyl groups and cross-linking. The

results of this optimization are summarized in Table 2.1. It was determined that the most important factor in obtaining the desirable product was the reaction temperature; while LCCTP is typically performed at temperatures approximately -5 °C to 0 °C,

Table 2.1: Summary of reaction conditions and characterization of several cyclopolymerizations of 1,5-hexadiene via LCCTP

Run	Temp. (°C)	Eq. ZnEt ₂	Eq. 1,5- HxD	[Initi- ator] (mM)	Mn ^a (kDa)	PDI ^a	% vinyl groups ^b	% cross- linking ^a	% yield
2.1	-6	2.7	200	1.0	2.5	1.21	2.00	34	84.1
2.2	-17	5.5	400	1.0	4.8	1.16	1.46	28	85.0
2.3	-15	2.7	200	1.0	2.3	1.06	1.87	15	87.5
2.4	-20	5.5	400	0.8	2.2	1.49	1.35	10	83.5
2.5	-20	5.5	400	0.6	1.7	1.19	1.28	0	88.9
2.6 (1)	-21	5.5	400	1.0	3.1	1.08	1.92	0	87.6

^aDetermined by GPC analysis at 40 °C using polystyrene standards and THF as the eluent. ^bDetermined by ¹H-NMR analysis.

significant cross-linking occurred at a temperature of -6 °C. The best results were obtained at temperatures less than or equal to -20 °C, producing OH-PMCP with less than 2 % pendant vinyl groups and 0 % cross-linking. It was also found that increasing the equivalents of the chain transfer agent and 1,5-hexadiene relative to initiator I

produced more desirable results. The OH-PMCP produced in Run 2.6 (**1**) was utilized for further studies. GPC analysis provided a M_n of 3.0 kDa with a PDI of 1.08.

1 was also analyzed by differential scanning calorimetry (DSC) to determine its thermal properties. Despite cyclopolymerization with the C_s symmetric **1** and $ZnEt_2$ as the chain transfer agent, which typically affords only atactic, amorphous x-PAOs, it was characterized by a melting temperature (T_m) of 62 °C and a crystallization temperature (T_c) at 55 °C in addition to a low T_g of -47 °C. This is consistent with the melting of a predominantly *trans* ring conformation.²⁸ The semi-crystalline nature of OH-PMCP coupled with its hydroxyl-group functionality prompted the further investigation of this material in various applications.

2.2.3 Characterization of OH-aPMCH

Similarly to OH-PMCP **1**, the successful end-group functionalization and living character of the cyclopolymerization of OH-aPMCH **2** were confirmed by 1H -NMR and GPC analyses (see Supplemental Results). Unlike OH-PMCP, however, a complete lack of resonances in the 1H -NMR spectrum corresponding to pendant vinyl groups indicated a more regioselective process with 100 % cyclopolymerization. By utilizing LCCTP which affords atactic polymers, the OH-aPMCH produced in this study was stereoirregular and thus completely amorphous, which eliminated complications associated with highly stereoregular PMCH, such as undesirable crystalline properties and poor solubility. However, despite the lack of an observable T_m or T_c in the DSC of **2** and its very low molecular weight (2.0 kDa), the OH-PMCH material is still characterized by a T_g of 53 °C, which is significantly higher than the T_g

values of any previously reported polymers made via LCCTP (Figure 2.3). GPC analysis provided a M_n of 2.0 kDa and a PDI of 1.06.

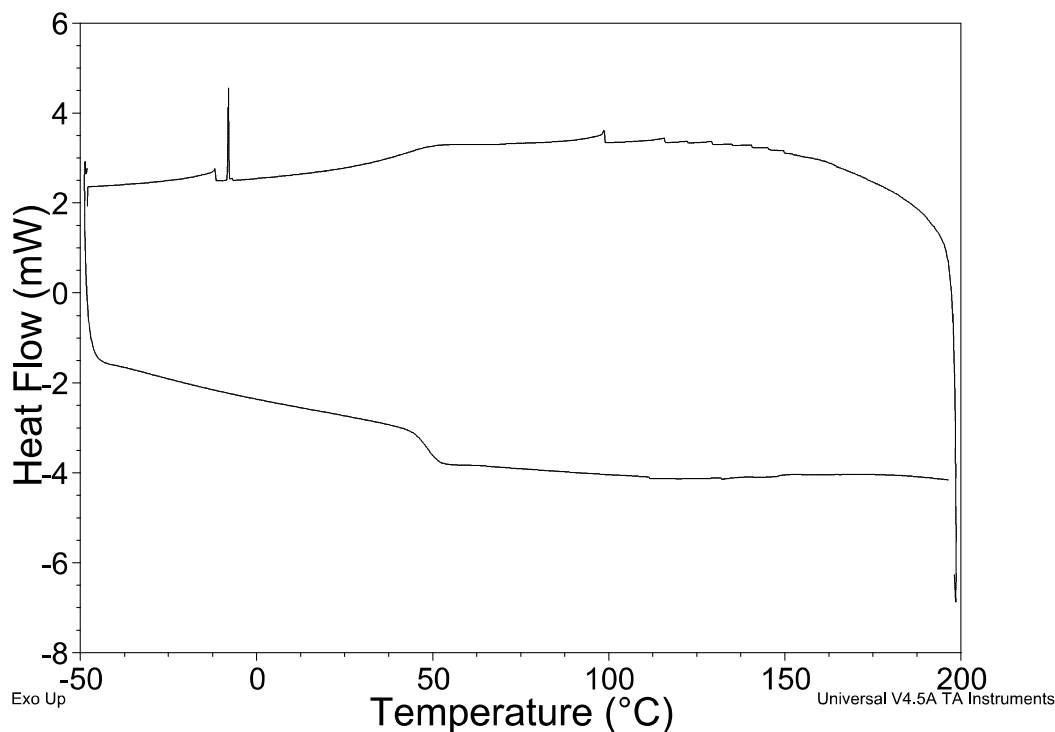


Figure 2.3: DSC curve of **2** (heat/cool/heat at 10 °C/min from -50 °C to 200 °C)

2.3 OH-PAOs as Versatile Nonpolar Building Blocks

Significantly, the formation of OH-PMCP and OH-aPMCH via LCCTP as described here greatly broadens the scope of end-group functionalized polyolefin materials currently available via living chain transfer polymerization techniques by providing access to materials with increased glass transition temperatures or rigid character. Coupled with the excellent control over molecular weight and extremely narrow polydispersities, these OH-PAOs provide a unique platform for the use of x-PAO materials as nonpolar building blocks for the development of self-assembling

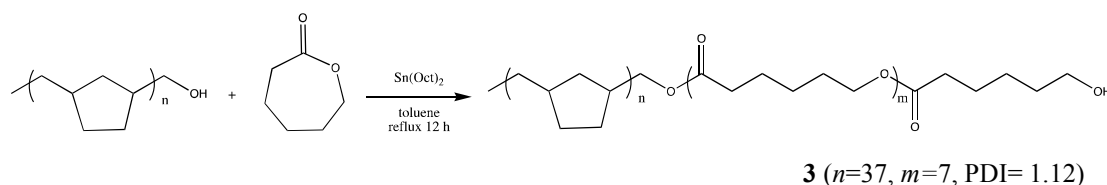
materials. Recently, a previous member of the Sita Group reported on the use of hydroxy-terminated atactic poly(4-methyl-1-pentene) (OH-aPMP) and hydroxy-terminated atactic polypropylene (OH-aPP) of varying chain lengths to systematically study the self-assembly of PAO-*b*-polyester diblock copolymers.²⁹ LCCTP provided a convenient method for OH-aPP and OH-aPMP that were used as macroinitiators in the ROP of lactones and lactides to provide self-assembling, biocompatible diblock copolymers. In this study, two applications for OH-PMCP and OH-aPMCH are presented; first as an extension of the previous work on the use of OH-PAOs as macroinitiators for ROP, and second as building blocks for the formation of “hard-soft-hard” elastomeric triblock copolymers.

2.4 PMCP-*b*-Polyester Diblock Copolymer

Because the previous study by Thomas included the use of only atactic, amorphous OH-PAOs²⁹, it was of interest to determine if a microphase-separated PAO-*b*-polyester diblock copolymer could be prepared from a more rigid, semi-crystalline PAO tail. To this end, OH-PMCP **1** was used as a macroinitiator for the ROP of ϵ -caprolactone (CL) to synthesize a PMCP-*b*-PCL diblock copolymer which was investigated for self-assembly.

2.4.1 Synthesis and Characterization of PMCP-*b*-PCL

Scheme 2.2: Synthetic route to PMCP-*b*-PCL



Scheme 2.2 presents the synthetic method used to synthesize PMCP-*b*-PCL **3** from the corresponding OH-PMCP **1** and ϵ -caprolactone. **1** was refluxed in the presence of Tin(II) 2-ethylhexanoate as a catalyst with the formula $[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2]_2\text{Sn}$ (also known as stannous octoate) and ϵ -caprolactone to acquire the diblock material.

The successful synthesis of **3** was confirmed by GPC and ^1H -NMR. GPC data indicated an increase in molecular weight (from 3.0 kDa to 3.7 kDa) and polydispersity (from 1.08 to 1.12) that would be expected from a “controlled” polymerization process. The ^1H -NMR spectrum also lacks the resonances associated with the protons adjacent to the OH end-group seen in the spectrum of **1** (Figure 2.4).

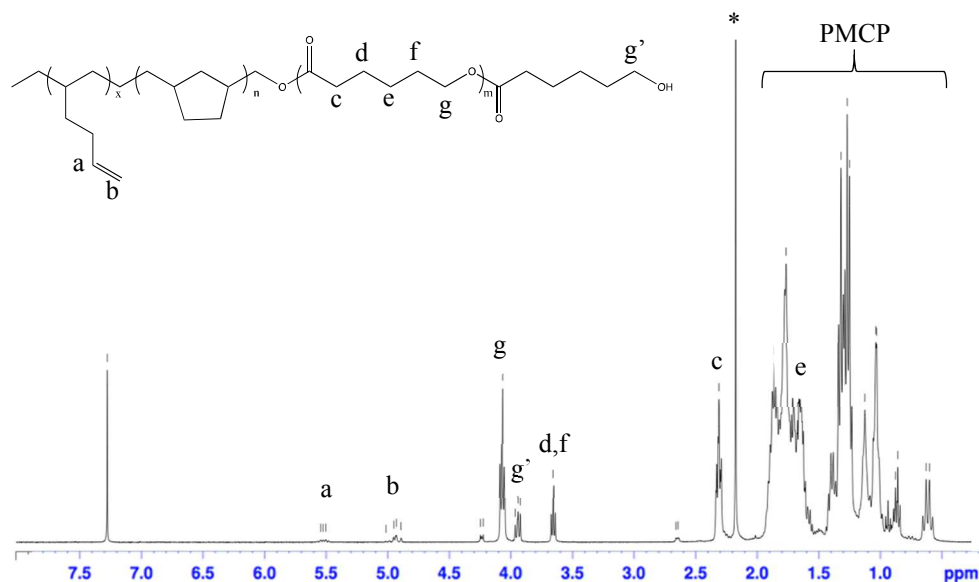


Figure 2.4: Labelled ^1H -NMR spectrum of **3** (500 MHz, CDCl_3 , 25 °C). Peak labelled with an asterisk represents acetone.

2.4.2 Self-assembly of PMCP-*b*-PCL

Thermal analysis of **3** by DSC provided two distinct glass transition temperatures at -19.6 °C and 10.3 °C, as well as a melting temperature of 86.7 °C and crystallization temperature of 77.7 °C. The presence of two distinct values for T_g implies that the two blocks of the PMCP-*b*-PCL diblock copolymer are immiscible. Thus, the self-assembly of this material was investigated in both the bulk and thin film states via Small angle x-ray scattering (SAXS) and atomic force microscopy (AFM), respectively. For the bulk material, SAXS was conducted on a lab-scale instrument at the University of Maryland (Figure 2.5). Indeed, well-defined microphase-separation between the PMCP and PCL domains did occur as evidenced by the peaks in the 1-dimensional SAXS plot. The ratio of the peaks (1:2:3) indicate a lamellar morphology with a domain spacing of 12.6 nm. However, crystalline regions were also observed.

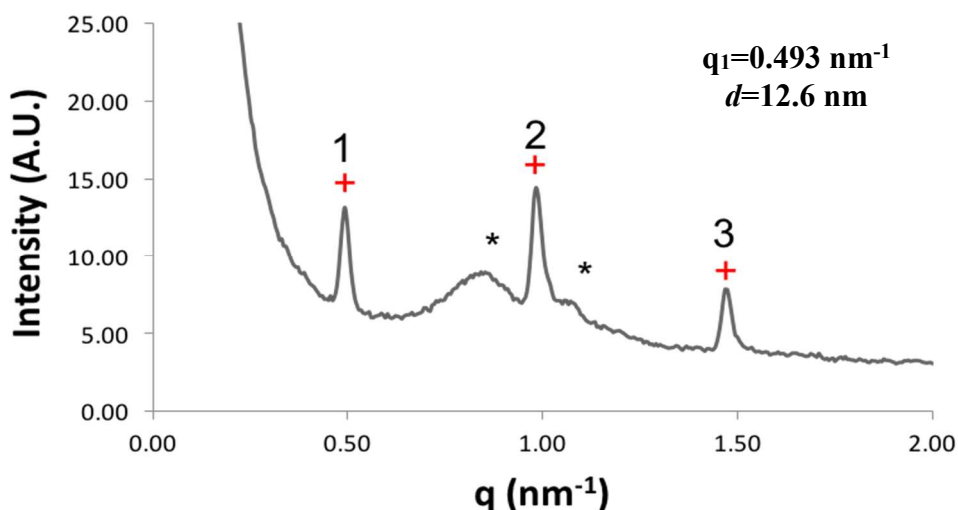


Figure 2.5: SAXS data for a bulk sample of **3** (unannealed) indicating presence of both crystalline domains (*) and microphase-separated lamellae with a 1:2:3 scattering ratio (+)

Given the self-assembly in the bulk, it was of interest to study the self-assembly within thin films as well. Thin films were prepared by spin-casting of a 0.5 % (w/v) solution of **3** in acetone onto the native SiO₂ layer of Si (100) substrates and were analyzed by phase-sensitive tapping mode AFM (ps-tm AFM) (Figure 2.6). In the as-cast film (Figure 2.6a), layered structures were observed, which are consistent with the formation of lamellae. Cross-sectional analysis of an “as-cast” film (Figure 2.6c) provides an average step-height of 11.8 ± 1.2 nm, consistent with the domain spacing of the lamellae formed by the bulk material as seen by SAXS. Thermal annealing at 90 °C overnight *in vacuo* served to increase overall order of the lamellae, but also caused an increase in dewetting from the surface of the substrate (Figure 2.6b).

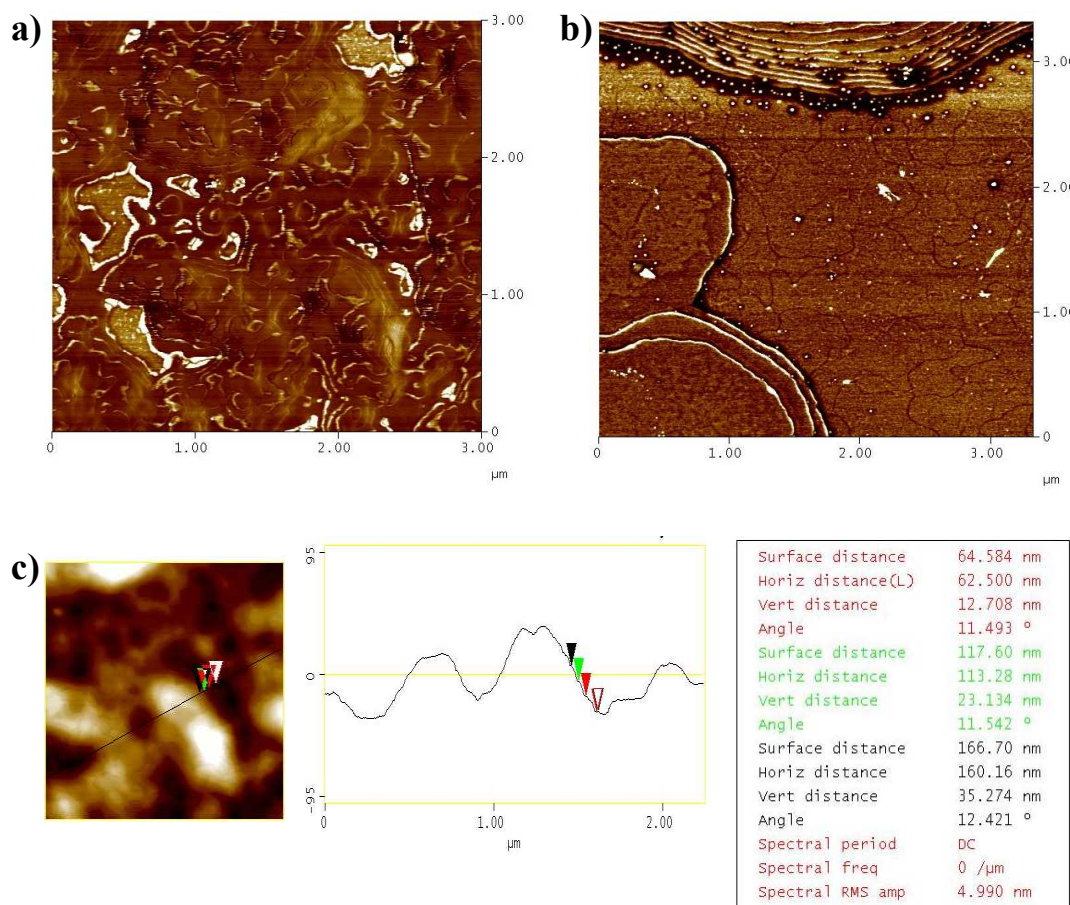


Figure 2.6: ps-tm AFM analysis of thin films of **3** a) before and b) after annealing at 90 °C for 14 h; c) cross-sectional analysis of as-cast film of **3**

2.5 PAO-b-PPG-b-PAO Triblock Copolymers

OH-PAOs were coupled to an α,ω -diisocyanato-terminated polymer to form triblock copolymers with thermoplastic elastomeric properties.^{30, 31} Specifically, diisocyanato-terminated poly(propylene glycol) (PPG) of about 2.0 kDa was used to form “hard-soft-hard” triblock copolymers with PAO end-blocks displaying narrow polydispersities. These types of BCPs are typically thermoplastic elastomers and may exhibit microphase separation between the incompatible hard and soft segments. For the triblock copolymers containing PMCP and PMCH, the crystallinity and relatively high T_g of the PMCP and PMCH end-blocks respectively should be sufficiently incompatible with the low T_g (~ -86 °C), amorphous PPG middle-block to display phase-segregation.¹³ LCCTP was also used to synthesize hydroxy-terminated atactic polypropylene (OH-aPP, 4) and poly(4-methyl-1-pentene) (OH-aPMP, 5), each

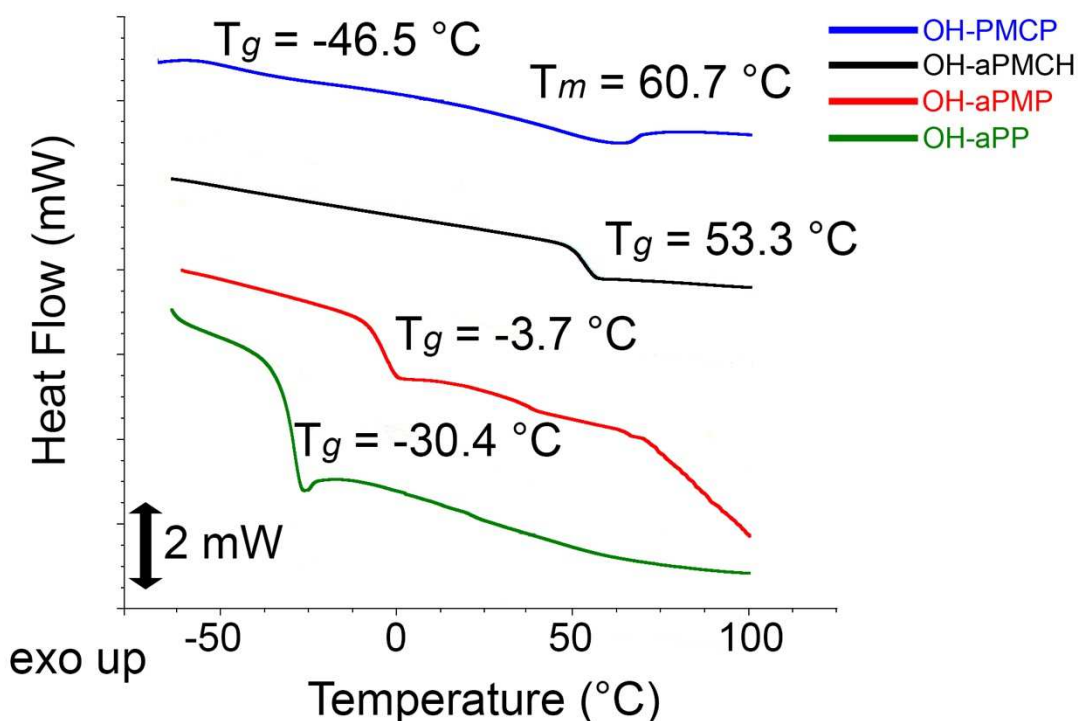
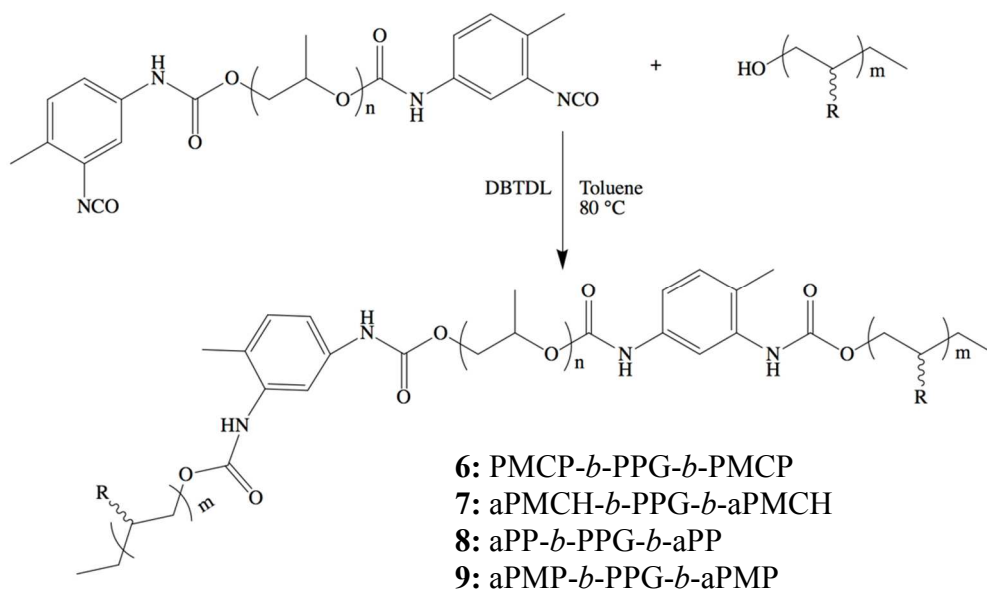


Figure 2.7: Thermal analysis of 1-5 using DSC.

with T_g values below room temperature, which were also used in this study as comparison (Figure 2.7). Although a full, systematic study of the self-assembly of these materials is still required, preliminary results indicate that this is a successful method for preparing potentially elastomeric hard-soft-hard triblock copolymers using OH-PAOs.

2.5.1 Synthesis and Characterization

Scheme 2.3: General synthetic route to PAO-*b*-PPG-*b*-PAO triblock copolymers



In this study, 2 equivalents of OH-PAOs **1-5** were coupled to the telechelic polymer tolylene 2,4-diisocyanato-poly(propylene glycol) (PPG) using dibutyltin dilaurate (DBTDL) as a catalyst to produce ABA type triblock copolymers with PPG sandwiched between PAO end-blocks (PAO-*b*-PPG-*b*-PAO products **6-9**) as shown in

Scheme 2.3.³¹ The successful synthesis was confirmed by ¹H-NMR and ¹³C-NMR (see Supplemental Results) and the materials were characterized by GPC and DSC. GPC (summarized in Table 2.2).

Table 2.2: Summary of GPC and DSC Analyses of 6-9

Compound	M _n ^a (kDa)	PDI ^a	T _g ^b (°C)	T _m ^b (°C)	T _c ^b (°C)
6	7.0	1.12	-55.2 -27.8	40.2	43.8
7	6.1	1.27	-57.8 54.9	--	--
8	6.8	1.09	N/A ^c	--	--
9	6.6	1.18	-32.7	--	--

^aDetermined by GPC analysis at 40 °C using polystyrene standards and THF as the eluent. ^bDetermined by DSC (second scan). ^cT_g not observed by DSC.

GPC indicated an increase in molecular weight and broadening of the polydispersity from the original OH-PAO and PPG homopolymers as expected after successful coupling. Interestingly, while the triblock copolymers containing aPMP and aPP end-blocks contained one or zero distinct glass transitions respectively, indicating miscibility between the blocks, the triblock copolymers containing PMCP and PMCH end-blocks each contained two distinct glass transition temperatures corresponding to the individual types of blocks as observed by DSC, which was a promising indication of phase-separation within a BCP.

2.5.2 Self-assembly

The self-assembly of compounds **6-9** in the bulk and thin-film states were investigated by SAXS and AFM respectively. For the triblock copolymers containing aPP (**8**) and aPMP (**9**) end-blocks, self-assembly was not expected due to the similarities between the A- and B-type blocks. For example, aPP and aPMP, like PPG, are low molecular weight, low T_g , amorphous materials. Thus, there should be little to no incompatibility between each block and the miscible blocks would not be microphase-separated. As expected, SAXS analysis before and after annealing at 60 °C of BCPs **8** and **9** confirmed this hypothesis and showed only a single broad peak characteristic of an amorphous polymer without a discernable structure (see Supplemental Results). Contrarily, SAXS analysis of the PMCP-containing BCP **6** at room temperature (Figure 2.8) showed the formation of a well-ordered lamellar morphology (q ratio of 1:2:3:4:5) with a domain spacing of 20.3 nm. Wide angle x-ray scattering (WAXS) conducted simultaneously showed the formation of PMCP crystalline domains with an chain-chain distance of 0.4 nm.

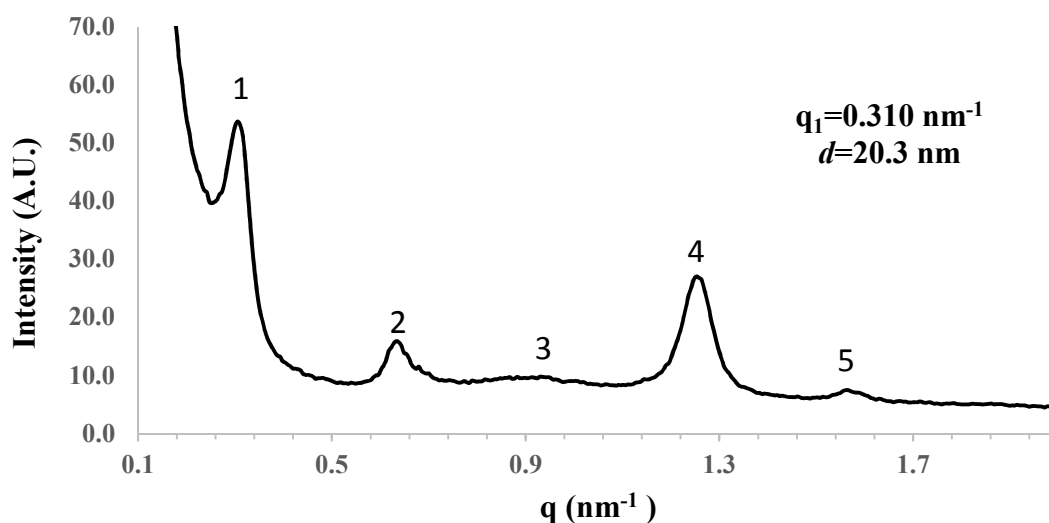


Figure 2.8: 1D SAXS analysis of **6** (unannealed) showing a lamellar morphology

Thin films of **6** were prepared by spin-casting of 0.5 % (w/v) solutions onto freshly cleaned Si (100) substrates. In an effort to eliminate any large crystallites, the solutions were filtered through a 0.2 micron pore filter before being used for spin-casting. Due to the crystalline nature of the PMCP blocks in **6**, different solvents were used in an attempt to minimize crystalline breakout during self-assembly. For example, it was found that crystallization dominated over microphase-separation during self-assembly when the film was spun-cast from toluene, as evidenced by the formation of dendrimeric PMCP crystals within a PPG matrix (Figure 2.9a). However, while spin-casting from a solution of acetone successfully suppressed the formation of these crystals, a significant amount of dewetting from the substrate surface occurred and no significant nanostructures were observed (Figure 2.9b). Ideal conditions for the thin film self-assembly of **6** must be explored further in the future.

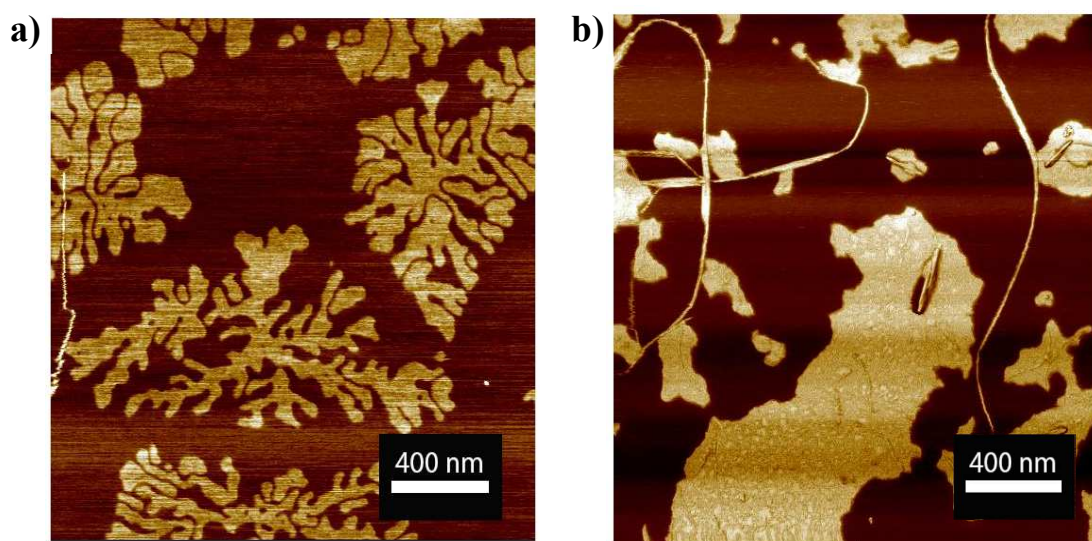


Figure 2.9: ps-tm AFM phase images of **6** spun-cast from a 0.5 % (w/v) solution in a) toluene and b) acetone

Similarly, thin films of **7** were prepared by spin-casting of a 0.5 % (w/v) solution in toluene onto freshly cleaned Si (100) substrates and were investigated by AFM (Figure 2.10). The presence of two distinct glass transitions for this material observed by DSC was promising in terms of the potential of this material to microphase-separate. Gratifyingly, the AFM phase map image after thermal annealing *in vacuo* at 60 °C for 10 h shows the presence of sphere-like structures approximately 20 nm in size embedded within an amorphous PPG matrix. These nanostructures confirmed that the triblock copolymer did not undergo macrophase-separation but instead formed microphase-separated nanostructures within thin films.

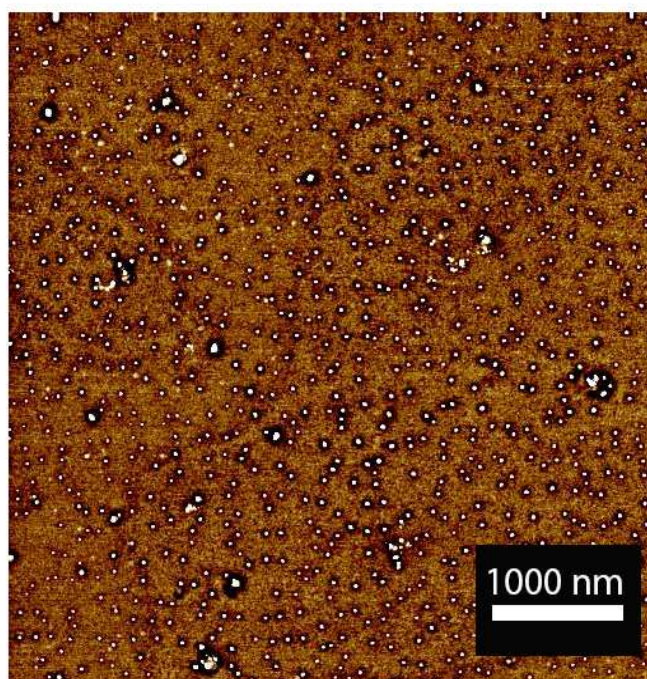


Figure 2.10: ps-tm AFM phase image of a thin film of **7** after thermal annealing at 60 °C for 10 h *in vacuo*

2.6 Conclusions

Living Coordinative Chain Transfer Polymerization (LCCTP) provided a method for expanding the currently available library of ‘precision polyolefins’ with controlled degrees of polymerization and narrow polydispersities. The LCCTP system was expanded to access a broad range of end-group functionalized poly(α -olefins) (x-PAOs). LCCTP was used for the cyclopolymerization and subsequent end-group functionalization of 1,5-hexadiene and 1,6-heptadiene to produce hydroxy-terminated poly(1,3-methylene cyclopentane) (OH-PMCP) and the first example of amorphous poly(1,3-methylene cyclohexane) (OH-aPMCH), respectively, with controllable molecular weights and extremely narrow polydispersities (<1.1). Thus, LCCTP was used to provide access to a new, broader range of polyolefin materials (x-PAOs) that can contain crystalline domains or relatively high glass transition temperatures, even at very low degrees of polymerization. Facile end-group functionalization enables x-PAOs to be used as non-polar building blocks for applications like the self-assembly of amphiphilic materials or new thermoplastic elastomers. This study served to demonstrate two of many examples of the utility of such x-PAO building blocks by using OH-PAOs as macroinitiators for the ring opening polymerization of ϵ -caprolactone to form PAO-*b*-polyester diblock copolymers, and through the coupling of OH-PAOs to a telechelic PPG midblock to create new thermoplastic elastomeric triblock copolymer materials that display microphase separation at low overall molecular weights. The versatility of LCCTP and x-PAOs is paramount in the quest to keep up with the ever-increasing global demand for new polyolefin materials.

2.7 Experimental Information

2.7.1 Materials

All manipulations were performed under an inert atmosphere of N₂ using standard Schlenk-line or glove-box techniques. Toluene and Chlorobenzene (ReagentPlus, 99%) were dried and deoxygenated by passage over activated alumina and GetterMax® 135 catalyst (purchased from Research Catalysts, Inc.) and collected under N₂ prior to use. Precatalyst, [Cp*HfMe₂{N(Et)C(Me)N(Et)}] (**I**) was synthesized as previously described by our group. N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate ([PhNMe₂H][B(C₆F₅)₄]) (**II**) and diethyl zinc was purchased and used as received from Boulder Scientific and Sigma Aldrich, respectively. 4-methyl-1-pentene monomer was purchased from Alfa Aesar and purified by stirring over Na/K amalgam in a Schlenk storage tube for at least 2 days followed by collection *via* vacuum transfer (freeze-pump-thaw) and transferred to a glovebox. Hydroxy-terminated atactic polypropylene (aPP-OH) (**4**) was provided by Precision Polyolefins LLC (*M_n*: 1.3 kDa; *D*: 1.09; T_g: -29.8 °C).

2.7.2 Instrumentation

Gel Permeation Chromatography (GPC): GPC analyses were performed using a Viscotek GPC system equipped with a column oven and a differential refractometer both maintained at 40 °C and four columns also maintained at 40 °C. THF was used as the eluent at a flow rate of 1.0 mL/min. *M_n*, *M_w*, and *M_w/M_n* values were obtained using a Viscotek GPC with OmniSEC software and ten polystyrene standards (*M_n*=580 Da to 3150 kDa) (Polymer Laboratories).

Nuclear Magnetic Resonance (NMR): ^1H NMR spectra were recorded at 500 MHz with chloroform-*d* at room temperature unless otherwise noted. $^{13}\text{C}\{\text{H}\}$ NMR spectra were recorded at 125 MHz with chloroform-*d* at room temperature unless otherwise noted.

Differential scanning calorimetry (DSC): DSC measurements were carried out using a TA DSC Q1000 system. Samples were sealed in hermetical pans with an average sample weight of 6 mg. An empty pan was used as a reference. A heat/cool/heat temperature program was used with a 10 °C/min ramp.

Atomic Force Microscopy (AFM): AFM images were obtained using a Nanoscope IIIa Multimode AFM in tapping mode equipped with Extender Electronics package (Veeco Inc., CA). Height and phase-shift data were recorded simultaneously under ambient conditions with a silicon-etched tip. Thin films of the polymer materials were spun cast (2000 rpm) from solutions onto cleaned silicon surfaces unless otherwise noted. Wafers were cleaned using Piranha solution (7:3 H_2SO_4 : H_2O_2), rinsed with deionized water, then isopropanol and dried under nitrogen gas. To anneal samples, films were placed in a vacuum oven for a given length of time unless otherwise noted. Film thickness was obtained using a Gaertner optical ellipsometer.

Small Angle X-ray Scattering (SAXS): For SAXS experiments, a Xenocs Xeuss system with a Cu $\text{K}\alpha$ X-ray source with a wavelength of 1.542 Å (GeniX3D Cu ULD, Xenocs, SA, France) was used. The two-dimensional scattering data were collected with semiconductor (CMOS) detectors (pixel size = 0.172 mm, Pilatus 300K, DECTRIS, Swiss). Samples were supported between two layers of Kapton film. The

acquisition time was 10 minutes for each frame. Two dimensional spectra were integrated using Igor Pro software (Version 6.3).

2.7.3 Synthesis

OH-PMCP via LCCTP (1)

In a 250 mL round bottom flask, 120.0 mL of dry and oxygen free toluene was cooled to 0 °C. 400 equivalents of 1,5-HXD was added to the round bottom flask. A solution of **(I)** (0.120 mmol) in 1.0 mL chlorobenzene at 0°C was added to **(II)** (0.120 x 1.1 mmol) and agitated until dissolved. 5.5 eq of diethyl zinc was added to the activated solution, agitated, then quickly added to the 250 mL round bottom flask. Stirring was maintained for the duration of the reaction (24 h). O₂ was then bubbled into the reaction solution for 18 hours and the reaction was quenched in acidic methanol to isolate the polymer product. The resulting polymer was collected and dried under vacuum and purified via silica column in hexanes.

Synthesis of OH-aPMCH via LCCTP (2)

In a 50 mL round bottom flask, 20.0 mL of dry and oxygen free toluene was cooled to 0 °C. 520 equivalents of 1,6-HXD was added to the round bottom flask. A solution of **(I)** (0.020 mmol) in 1.0 mL chlorobenzene at 0°C was added to **(II)** (0.020 x 1.1 mmol) and agitated until dissolved. 17 eq of diethyl zinc was added to the activated solution, agitated, then quickly added to the 20 mL round bottom flask. Stirring was maintained for the duration of the reaction (24 h). O₂ was then bubbled into the reaction solution

for 18 hours and the reaction was quenched in acidic methanol to isolate the polymer product. The resulting polymer was collected and dried under vacuum and purified via silica column in hexanes.

Synthesis of PMCP-b-PCL (3)

In a N₂ glove box, minimal (~5 mL) dry and oxygen free toluene was used to transfer OH-PMCP **2.A** into a 100 mL schlenk flask. 12 eq. of ϵ -caprolactone was added to the flask. The reaction mixture was brought out of the glove box and 1 eq of Sn(Oct)₂ was added to the flask using a gas-tight syringe. The reaction was allowed to reflux at 70°C for 12 hours under N₂ with rapid stirring. The resulting polymer was collected and dried under vacuum and purified via silica column.

Synthesis of OH-aPMP via LCCTP (5)

In a 50 mL round bottom flask, 20.0 mL of dry and oxygen free toluene was cooled to 0 °C. 900 equivalents of 4-methyl-1-pentene was added to the round bottom flask. A solution of (I) (0.025 mmol) in 1.0 mL chlorobenzene at 0°C was added to (II) (0.025x1.1 mmol) and agitated until dissolved. 30 eq of diethyl zinc was added to the activated solution, agitated, then quickly added to the 50mL round bottom flask. Stirring was maintained for the duration of the reaction. O₂ was bubbled into the reaction solution for 19 hours and the reaction was quenched in acidic methanol to isolate the polymer product. The resulting polymer was collected and dried under vacuum and purified via silica column in EtOAc.

General Synthesis of PAO-b-PPG-b-PAO (6-9)

The desired OH-PAO and 0.05 wt% dibutyltin dilaurate in 20.0 mL of dry and oxygen free toluene was added to a 100 mL schlenk flask. The appropriate amount of tolylene 2,4-diisocyanato-poly(propylene glycol) was added to the flask dropwise over approximately 30 minutes. The reaction was then refluxed for 8 h under N₂ with rapid stirring. The resulting polymer was cooled then collected and dried under vacuum and purified via silica column using a 9:1 chloroform/methanol mixture.

2.8 References

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Chapter 3: Conformational Asymmetry in Polyolefin

Copolymers

3.1 Background

A wealth of experimental and theoretical knowledge has been gained in the last three decades that has established BCPs as leading materials in a plethora of applications.¹⁻⁷ As described in Chapter 1, there are two major parameters that are said to control conformationally symmetric AB-type diblock copolymer phase behavior: χN , or the product of the Flory-Huggins interaction parameter and the total number of segments, and f_A , or the volume fraction of the A block.⁸ In purely polyolefin BCPs, microphase-separation can be difficult to achieve because of a low χ parameter between the two hydrophobic blocks, a complication which is especially significant at low values of N . However, it has been shown that introducing slight differences in statistical segment length or volumes of each block, thereby increasing conformational asymmetry, can significantly alter phase behavior. This study aimed to demonstrate how the LCP system could be further utilized to generate microphase-separated polyolefin BCPs by exploiting the wide variety of available monomers and the ability to control stereochemistry in order to maximize conformational asymmetry in crystalline-amorphous BCPs.

3.1.1 Conformational Asymmetry in BCPs

Polyolefins are saturated hydrocarbon polymers which contain only simple van der Waals interactions between chains. Though this would imply that simple solution

theory would be sufficient to approximate phase-behavior, that was found not to be the case due to the effects of subtle variations in chain architecture.⁹ In 1992, Bates and coworkers first reported on the theory and experiment of another significant parameter that affects BCP phase behavior: the degree of conformational asymmetry within the BCP.^{4, 10, 11} Conformational asymmetry refers to differences in the statistical segment lengths or chain stiffnesses of the constituents of an AB-type BCP and can be parameterized using the ratio of the A and B statistical segment lengths, α_A/α_B . Several theoretical and experimental studies have been done on this effect which indicate several consequences: 1) the microphase boundaries that are symmetric about $f_A=0.50$ for conformationally symmetric BCPs becomes asymmetric, such that 2) the dependence of morphology upon f_A (the stiffer block) shifts towards higher volume fractions of A, subsequently 3) shifting order-order transitions (OOT) and order-disorder transitions (ODT).^{10, 12-19} Studies have also suggested that a difference in chain stiffness between the A and B blocks contributes to conformational asymmetry in a BCP system.²⁰⁻²²

3.1.2 Conformationally Asymmetric BCPs via LCP

The Sita Group has recently demonstrated that living coordination polymerization (LCP) and cyclopolymerization of α -olefins and α,ω -nonconjugated dienes could be used to form conformationally asymmetric BCPs that phase separated into well-defined morphologies. In 2015, Crawford reported the design of “hard-soft” amorphous polyolefin BCP thermoplastic elastomers based on the sequential cyclic/linear/cyclic LCP of 1,6-heptadiene, propene, and 1,6-heptadiene to form a

stereo-irregular, amorphous poly(1,3-methylene cyclohexane)-*b*-atactic polypropene-*b*-poly(1,3-methylene cyclohexane) (PMCH-*b*-aPP-*b*-PMCH) polyolefin triblock copolymer.²³ This system took advantage of the size and stiffness differences between the PMCH and aPP blocks to form BCPs with well-defined cylindrical morphologies and superior thermoplastic elastomeric properties. Additionally, in 2017 Hwang reported the unusual dynamic mechanical behavior of a crystalline-amorphous diblock copolymer consisting of amorphous poly(1-hexene) (PH) and the relatively stiff, semi-crystalline poly(1,3-methylene cyclopentane) (PMCP). It was found that the PH-*b*-PMCP diblocks exhibited microphase separation into various morphologies. For the spherical BCPs, the large difference in chain stiffness between the PH and PMCP blocks contributed to a sharp increase in overall dynamic shear modulus upon melting of the crystalline PMCP block.²⁴ This study served to increase the scope of available polyolefin BCPs that exhibit microphase-separation based on conformational asymmetry.

3.2 PMCP-co-PMCH Random Copolymers

Poly(1,3-methylene cyclopentane), or PMCP, is a semi-crystalline, low T_g polyolefin with a rigid five-membered ring structure formed by the cyclopolymerization of 1,5-hexadiene. On the other hand, atactic poly(1,3-methylene cyclohexane), or aPMCH, is an amorphous, high T_g polyolefin with a more flexible six membered ring structure. The structural similarity of the two blocks likely leads to a low Flory-Huggins interaction parameter, χ , and at low molecular weights, the product of χN would likely be insufficient to cause microphase-separation. However, it was of

interest to determine if differences in chain stiffness could overcome this barrier to produce a microphase-separated PMCP-*b*-PMCH diblock copolymer. It was also of interest to determine if the incorporation of the slightly more flexible PMCH would alter the physical properties of PMCP.

3.2.1 PMCP-PMCH Homopolymer Blend

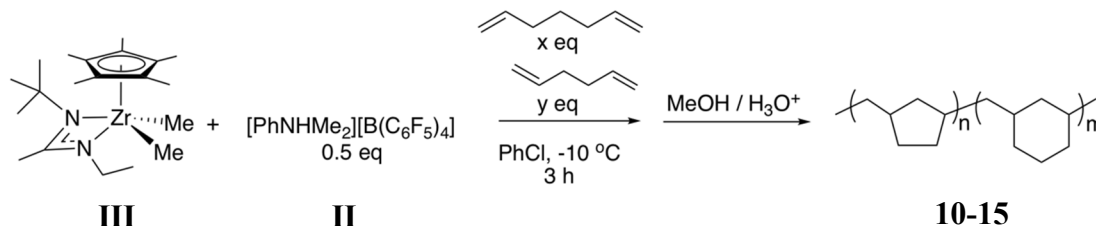
In order to qualitatively determine the likelihood of a PMCP-PMCH copolymer being able to microphase separate, a blend of the two homopolymers (M_n approximately 10 kDa) was analyzed. To prepare the blend, 1.0 % (w/v) solutions of each homopolymer were prepared in toluene and allowed to homogenize for 24 h before being combined. The thermal properties of the bulk blend were investigated by DSC.

For DSC, equal amounts of each homopolymer solution were combined and the solvent evaporated under reduced pressure to generate the 1:1 PMCP-PMCH blend. The blend was analyzed with a heat/cool/heat program over a temperature range of -70 °C to 250 °C. Unfortunately, only one T_m and one T_c were observed at 85.1 °C and 72.3 °C, respectively, which was associated with the melting of the semi-crystalline PMCP homopolymer. The absence of peaks associated with the PMCH homopolymer indicated a degree of miscibility between the two homopolymers within the blend, which is not promising for microphase separation within a PMCP-PMCH copolymer. Accordingly, these two interesting materials were utilized for a different purpose; it was of interest to determine the extent to which randomly incorporating PMCH into a PMCP material would affect the physical properties, such as T_g and crystallinity. Thus,

a series of PMCH-*co*-PMCP random copolymers was synthesized with varying percentages of PMCH.

3.2.2 Synthesis and Characterization

Scheme 3.1: General synthesis for PMCP-*co*-PMCH random copolymers via LCP



The random copolymers were synthesized via the simultaneous living coordination cyclopolymerization (LCP) of 1,5-hexadiene and 1,6-heptadiene (Scheme 3.1). In this case, pre-initiator **III** was activated by a substoichiometric amount of **II** to increase stereoirregularity within the polymer and produce amorphous PMCH. A series of random copolymers with an increasing percentage of PMCH were synthesized by simply varying the equivalents of 1,6-heptadiene relative to 1,5-hexadiene at the start of the polymerization while maintaining an overall target molecular weight of less than 30.0 kDa. The percent incorporation of PMCH was determined using integrations obtained from ^{13}C -NMR with inverse-gated proton decoupling (Figure 3.1 and Supplemental Results). A total of six polymers, including PMCP and PMCH homopolymers and four random copolymers with PMCH percentages of 0 % (**10**), 20 % (**11**), 54 % (**12**), 73 % (**13**), 77 % (**14**), and 100 % (**15**), were used in this study. Attempts to synthesize a random copolymer with a PMCH percentage less than 20 %

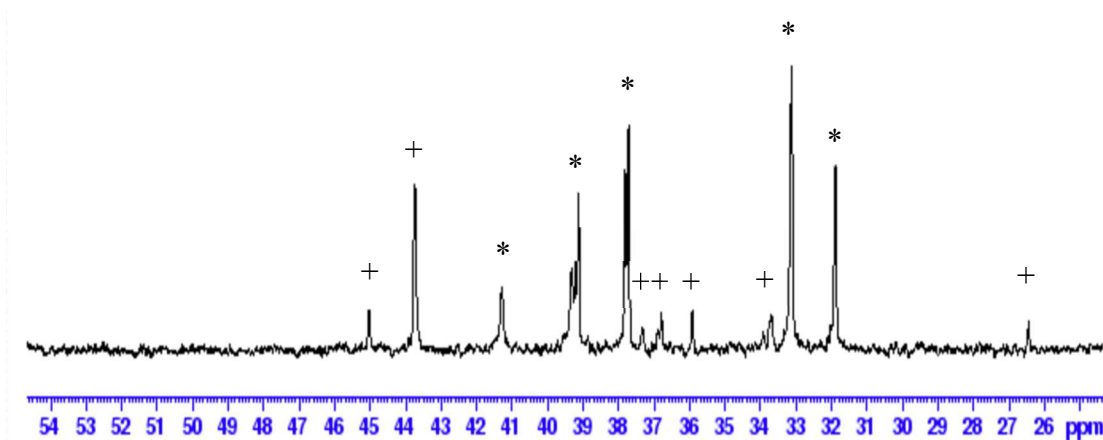


Figure 3.1: Partial inverse-gated ^{13}C -NMR (125 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 100 $^\circ\text{C}$) spectrum of **11**. PMCH resonances are marked with a plus (+) and PMCP resonances are marked with an asterisk (*). Integration provides a composition of 20 % PMCH and 80 % PMCP. Random copolymers **12-14** were analyzed in the same manner.

were unsuccessful due to the difference in relative reactivities between the two monomers. The polymers were characterized by ^1H -NMR, ^{13}C -NMR, GPC, and DSC.

3.2.3 Tuning Physical Properties

Regardless of conditions, the cyclopolymerization of 1,5-hexadiene via LCP or LCCTP produces semi-crystalline PMCP. While melting temperatures occur well above room temperature, the PMCP materials still possess low values of T_g (e.g. below 0 $^\circ\text{C}$). It was of interest to determine if these physical properties could be changed, or even controlled, by randomly incorporating PMCH into the PMCP chains. Table 3.1 summarizes the physical properties of the PMCP and PMCH homopolymers and the PMCP-*co*-PMCH random copolymers used for this study (**10-15**).

Table 3.1: Characterization of PMCP, PMCH, and PMCP-*co*-PMCH materials

Compound #	Fraction PMCH ^a	Total M _n ^b (kDa)	PDI ^b	T _g ^c (°C)	T _m ^c (°C)	T _c ^c (°C)
10	0.00	9.6	1.08	-13.8	96.3	81.3
11	0.20	27.9	1.05	12.6	--	--
12	0.54	17.8	1.09	39.1	--	--
13	0.73	10.9	1.23	60.1	--	--
14	0.77	22.4	1.10	88.5	--	--
15	1.00	10.4	1.10	98.8	--	--

^aDetermined using integral ratios from inverse-gated ¹³C-NMR. ^bDetermined by GPC at 40 °C using THF as an eluent. ^cDetermined by DSC using a heat/cool/heat cycle from -70 °C to 250 °C. Boxes marked with (--) indicate that a T_m or T_c were not observed.

Indeed, it was found that the incorporation of PMCH did alter the physical properties in an advantageous manner; the desirable high T_g of atactic PMCH was maintained and the undesirable crystalline properties of PMCP were eliminated while maintaining a low overall molecular weight. This effect was observed in all of the PMCP-*co*-PMCH copolymers, including copolymer **11** with a PMCH percentage of only 20 %. Thus, only small amounts of 1,6-heptadiene in the feed during polymerization are required to disrupt the PMCP crystal formation in within the PMCP-*co*-PMCH copolymers. Moreover, the T_g can be tuned by varying the percentage of PMCH, which can be valuable for applications in which a specific utility temperature is needed. The dependence of T_g on the percentage of PMCH is shown in Figure 3.2. Gratifyingly, the T_g was increased from -13.8 °C for pure, low molecular weight PMCP to 88.5 °C for copolymer **14** with 77 % PMCH. Thus, the desirable properties of atactic

PMCH (e.g. amorphous, high T_g) are maintained while using less of the relatively expensive 1,6-heptadiene monomer.

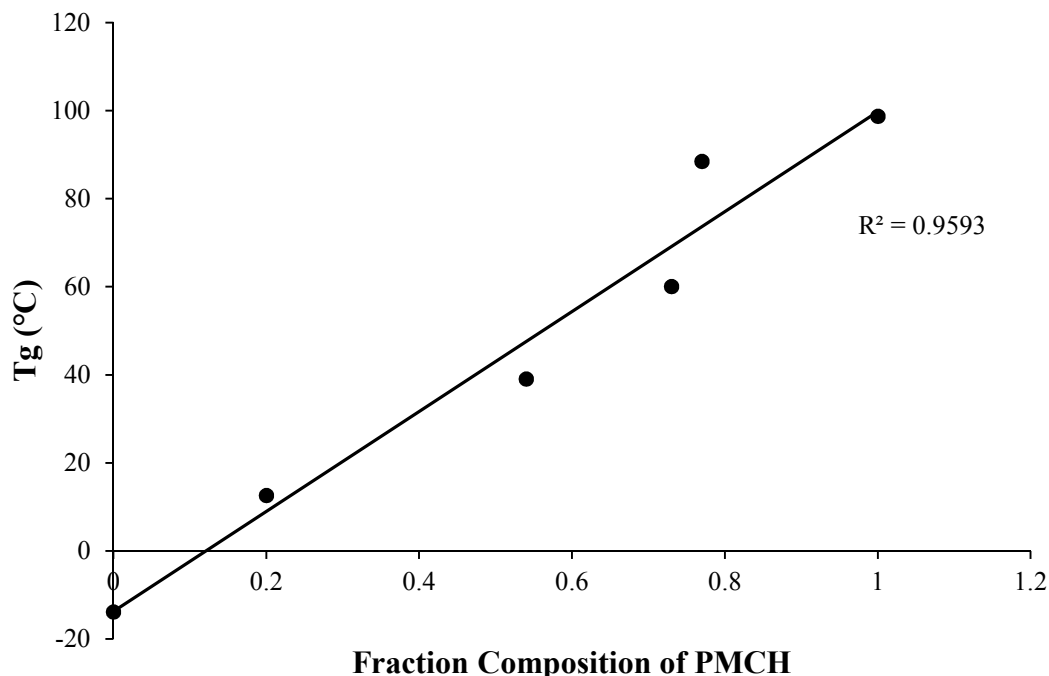


Figure 3.2: Increase in T_g dependent upon the amount of PMCH incorporated into PMCP-*co*-PMCH random copolymers **10-15**

3.3 Diblock Copolymers Containing Poly(4-methyl-1-pentene)

3.3.1 Design Considerations

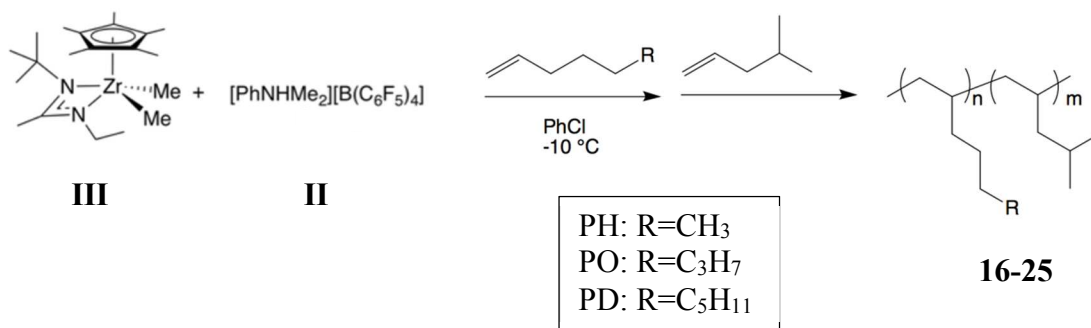
Though PMCP-PMCH copolymers exhibited interesting properties, the goal of obtaining new microphase-separated crystalline-amorphous polyolefin block copolymers was not reached. To this end, another series of BCPs was investigated which consisted of di- and tri-block copolymers containing poly(4-methyl-1-pentene) (PMP) with either poly(1-hexene) (PH), poly(1-octene) (PO), or poly(1-decene) (PD). It was of interest to determine if increasing the steric bulk of the side chain of block 1

would increase conformation asymmetry and prevent crystallization of PMP during self-assembly, thus creating a microphase-separated polyolefin BCP.

Though similar in size to PMP, PH is an amorphous polymer with a significant difference in chain stiffness from PMP. Contrarily, PO and PD are relatively rigid compared to other conventional saturated polymers but for a given contour length, the radius of gyration is much larger than other saturated systems.²⁵ This study targeted PMP as the minority block with fraction compositions of PMP, f_{PMP} , of 0.20-0.30 to target spherical or cylindrical morphologies and minimize the possibility of crystalline breakout by PMP domains.

3.3.2 Synthesis

Scheme 3.2: General synthetic method employed to synthesize PH-*b*-PMP, PO-*b*-PMP, and PD-*b*-PMP diblock copolymers



Scheme 3.2 summarizes the method used to synthesize the various diblock copolymers used for this study. The diblock materials were synthesized under LCP conditions using preinitiator **III** activated by a stoichiometric quantity of **II** in chlorobenzene at -10 °C. The block copolymers were made by living polymerization via the sequential addition of the 4-methyl-1-pentene monomer after complete

consumption of the initial 1-hexene, 1-octene, or 1-decene monomer to produce fully isotactic diblock copolymers **16-25** in high yield. Several variations of each type of diblock were synthesized in order to systematically investigate the effect of overall molecular weight and f_{PMP} on self-assembly. The results of these polymerizations are summarized in Table 3.2. The polymers were characterized by ^1H -NMR, ^{13}C -NMR (inverse-gated proton decoupled), and GPC. While still low, the polydispersities of

Table 3.2: Diblock materials synthesized via LCP

Material	Type	% Yield	M_n^a (kDa)	PDI^a	f_{PMP}^b
16	PH-PMP	84.9	54.8	1.19	0.12
17	PH-PMP	82.3	61.0	1.21	0.18
18	PO-PMP	91.1	39.2	1.09	0.26
19	PO-PMP	78.6	51.3	1.10	0.20
20	PO-PMP	82.9	51.4	1.11	0.28
21	PO-PMP	87.0	60.8	1.31	0.52
22	PO-PMP	86.9	73.5	1.20	0.23
23	PO-PMP	90.2	99.5	1.45	0.32
24	PD-PMP	74.9	35.0	1.12	0.18
25	PD-PMP	83.0	38.3	1.07	0.12

^aDetermined by GPC at 40 °C using THF as an eluent. ^bDetermined using integral ratios from inverse-gated proton decoupled ^{13}C -NMR (200 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 90 °C).

some of these diblock materials was slightly above the typical PDI seen with LCP (e.g. less than 1.1). This may be due to the poor solubility of isotactic PMP in tetrahydrofuran (THF), which is used as the eluent during GPC. This can lead to an inaccurately high value for PDI. This effect becomes more significant with increasing molecular weight of the PMP block.

3.3.3 Characterization and Self-assembly

The thermal properties of diblocks **16** and **17** containing PH were investigated by DSC. In both cases, the very low T_g of the PH blocks (c.a. -50 °C to -55 °C) were maintained, which is typical of PH (see Supplemental Results).²⁶ The isotactic PMP blocks formed crystalline domains with melting temperatures at 141.3 °C (**16**) and 164.0 °C (**17**), and crystallization temperatures at 104.4 °C (**16**) and 128.5 °C (**17**). As expected, the T_m/T_c of the material increased with increasing f_{PMP} due to the increase in crystalline domains.

It was of interest to determine if the incompatibility between the PH and PMP domains would be sufficient to cause microphase separation. Moreover, the ability of the PH domains to disrupt the crystal lattice of PMP and prevent crystalline breakout during self-assembly needed to be determined as well. To accomplish this, AFM was performed on thin films of **17** (film thickness=41 nm) before and after thermal annealing. Films were prepared by spin-casting of a 1.0 % (w/v) solution of **3.H** in toluene, a good solvent for both blocks, onto the native SiO₂ layer of freshly cleaned Si (100) substrates and analyzed by phase-sensitive tapping mode AFM (ps-tm AFM). Unfortunately in both cases, any potential microphase-separated morphology was

obscured by crystalline breakout of the PMP domains (Figure 3.3), which formed long, rod-like crystallites within the amorphous matrix. The crystallites increased in long-range order after being cooled from the molten state during annealing above the T_m .

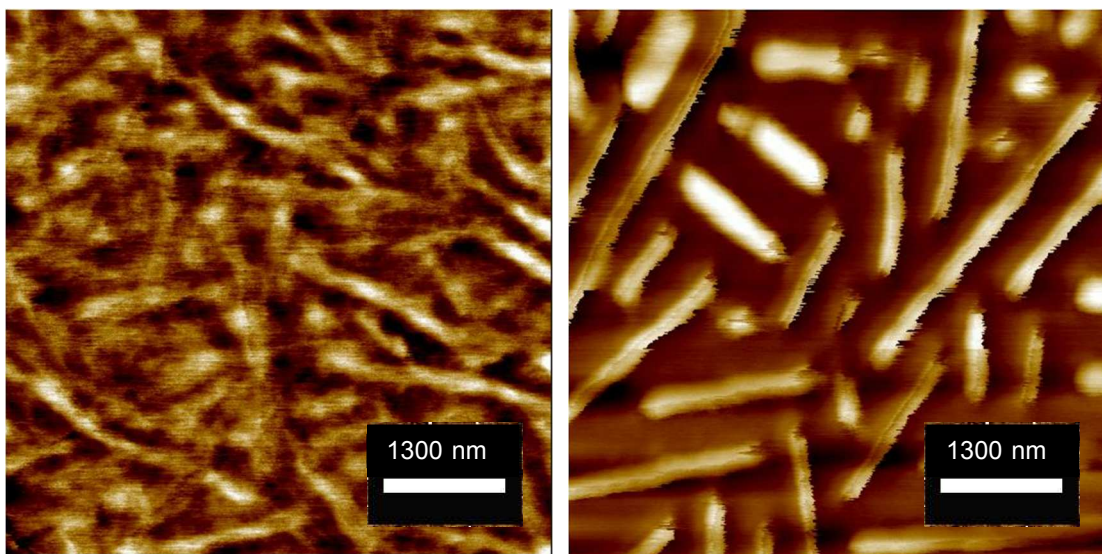


Figure 3.3: ps-tm AFM phase map images of a thin film (41 nm thick) of **17** from a 1.0 % (w/v) solution in toluene on Si (100) “as-cast” (left) and after thermal annealing (right) at 175 °C for 18 h *in vacuo*. The thermally annealed film was allowed to cool slowly over several hours and the AFM image was recorded at room temperature.

Since PH did not successfully disrupt PMP crystallization within the BCP, PO, with two additional carbons in the polymer side-chain, was utilized next in an attempt to increase conformational asymmetry and provide a microphase-separated BCP. A total of six PO-*b*-PMP diblock copolymers were synthesized with increasing molecular weight ranging from 39 kDa to 100 kDa and f_{PMP} ranging from 0.26 to 0.52. None of the PO-*b*-PMP materials had a T_g observable by DSC. The T_m and T_c values reported in Table 3.3 vary depending on molecular weight and composition, except for **20** and **22**, which surprisingly showed no first or second order thermal phase changes.

Table 3.3: Thermal properties of **18-23** measured by DSC

Material	T _m (°C)	T _c (°C)
18	113.0	79.7
19	143.6	125.4
20	--	--
21	92.7	26.2
22	--	--
23	120.5	48.4

Heat/cool/heat cycle from -70 °C to 250 °C at a flow rate of 10 °C/min

To begin, thin films (thicknesses $\approx$ 150 nm) of diblocks **18-23** were prepared in an identical manner as described for **17** and analyzed by ps-tm AFM. Gratifyingly, almost all of these PO-*b*-PMP diblock copolymers (except **20** and **21**) appeared to be microphase-separated into a weakly ordered hexagonally-packed cylindrical morphology before thermal annealing, which was consistent with the theoretical BCP phase diagram for the given f_{PMP} values. An example is shown below in Figure 3.4 for **18** in which a spherical or cylindrical morphology with an average domain spacing, d , of 29.3 ± 0.8 nm can be observed in the as-cast films (a, b). SAXS/WAXS analysis of these samples also confirmed the presence of weak microphase-separation above the T_m , which confirmed that these materials had sufficient incompatibility between the PO and PMP domains to form self-assembled domains both at room temperature and in the melt state in the absence of PMP crystals (see Supplemental Results).

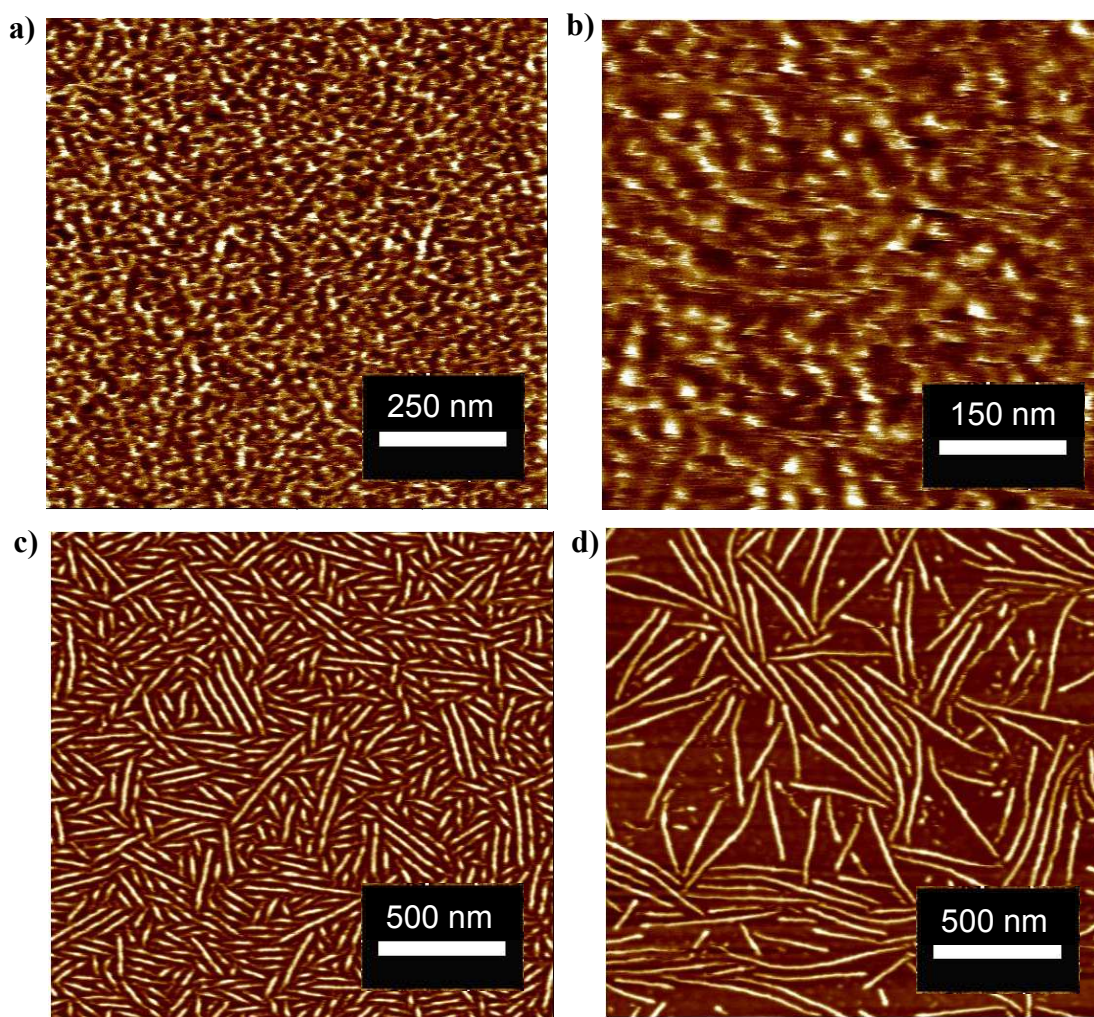


Figure 3.4: ps-tm AFM phase map images recorded at room temperature of thin films of **18** (thickness=158 nm) a,b) as-cast, and after thermal annealing *in vacuo* at c) 90 °C and d) 120 °C for 14 h.

Unfortunately, however, thermal annealing and subsequent cooling did not maintain these structures, and the nucleation of needle-like PMP crystals began upon cooling back below T_m/T_c (Figure 3.4c,d). Although it was unclear why **20** did not microphase-separate, the lack of morphology within thin films of **21** was attributed to the high f_{PMP} of 0.52. While this symmetric diblock was synthesized to form lamellae, the high content of crystalline PMP prevented the formation of microphase-separated domains. Instead, the formation of extremely well-defined, micron-sized crystalline-

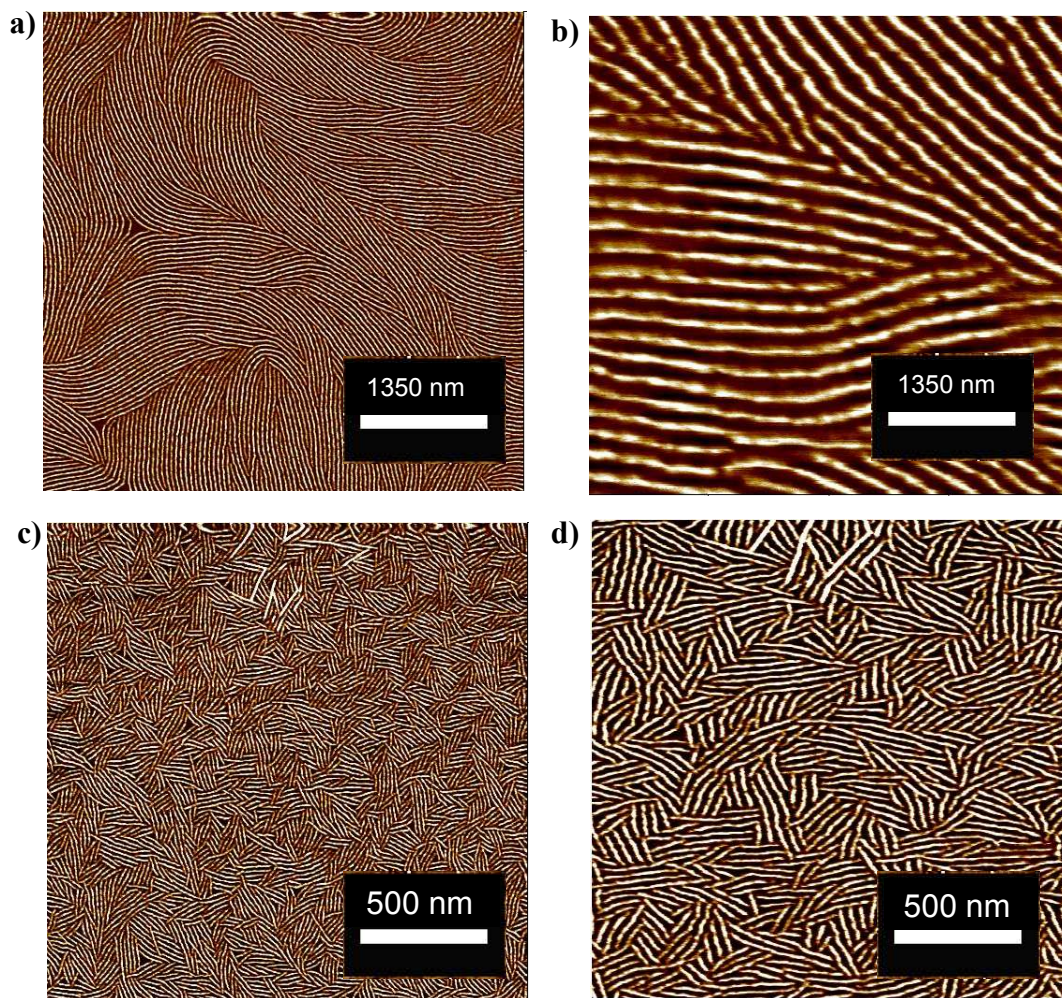


Figure 3.5: ps-tm AFM phase map images recorded at room temperature of thin films of **21** (thickness=144 nm) a,b) as-cast, and c,d) after being quickly cooled after thermal annealing *in vacuo* at 120 °C for 14 h.

lamellae was observed (Figure 3.5a,b). After thermal annealing above the T_m , a quick-cooling protocol was used to attempt to trap any morphology that existed in the melt-state; the films were removed from the vacuum oven while at a temperature above T_m and immediately plunged into a pool of liquid nitrogen. However, the crystallization kinetics were extremely fast and PMP crystals still dominated within the thermally annealed film (Figure 3.5c,d).

Finally, two PD-*b*-PMP BCPs, **24** and **25**, were investigated. The T_m and T_c values determined by DSC are listed in Table 3.4. The two distinct melting points, both below room temperature, can be attributed to the main and side chains of the PD block as described previously in the literature.²⁷⁻²⁹ Melting/crystallization temperatures at higher temperatures that would be expected from PMP crystals are notably absent in both PD-*b*-PMP samples, suggesting that the incorporation of PD in the diblock has sufficiently blocked the crystallization of PMP chains.

Table 3.4: Thermal properties of **24** and **25** measured by DSC

Material	T_{m1} (°C)	T_{m2} (°C)	T_c (°C)
24	5.7	14.4	--
25	5.8	22.9	29.1

Measured by heat/cool/heat cycle from -70 °C to 250 °C at a flow rate of 10 °C/min. Boxes marked with (--) indicate that the transition was not observed.

AFM analysis of “as-cast” thin films of **25** (thickness=152 nm) showed the formation of random crystalline lamellae in addition to areas of spheres or hexagonally packed cylinders (Figure 3.6). Before thermal annealing, the crystalline lamellae are significantly less ordered and less well-defined than those formed by PO-*b*-PMP **21**.

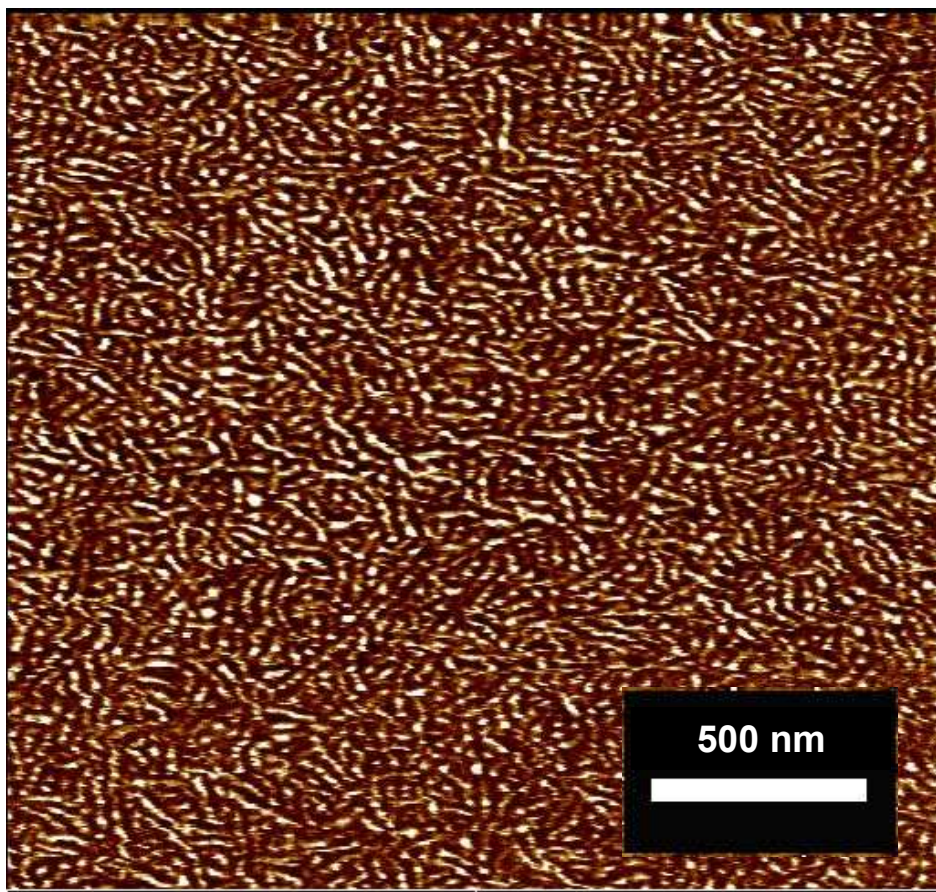


Figure 3.6: ps-tm AFM phase map image recorded at room temperature of an “as-cast” thin film of **25** spun-cast from a 1.0 % (w/v) solution in toluene onto Si (100) substrate

To investigate the effects of thermal annealing as well as the effect of cooling rate on self-assembly, thin films of **25** were thermally annealed *in vacuo* at 120 °C for 14 h and cooled either slowly while still *in vacuo* or very quickly by plunging into liquid nitrogen while hot. A significant difference was observed between the two cooling methods. The slow cooling method produced very long (e.g. > 1 μm), highly ordered crystalline lamellae (Figure 3.7, left), while the fast cooling method provided much shorter, less ordered regions of crystalline lamellae (Figure 3.7, right).

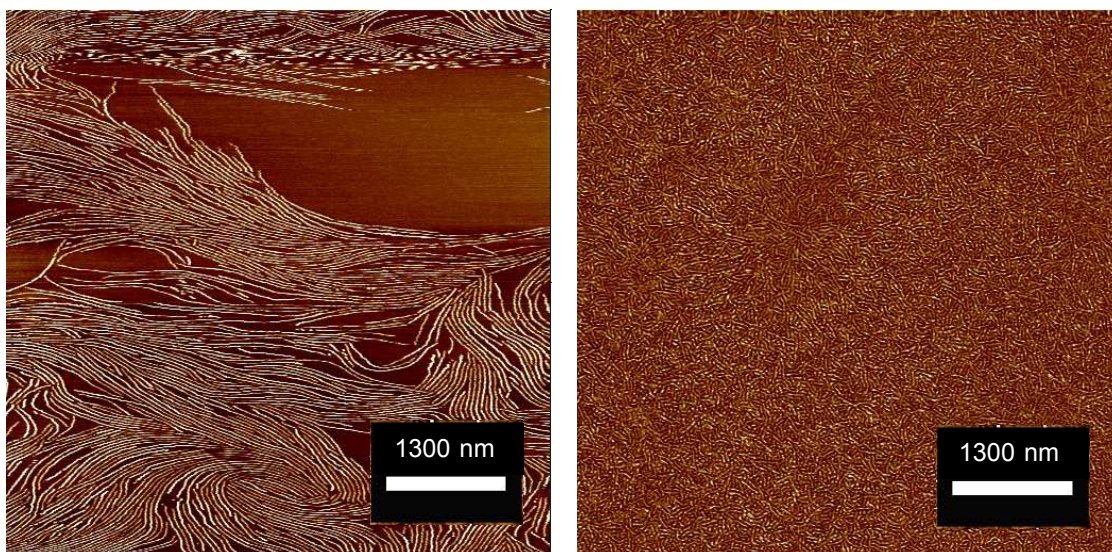


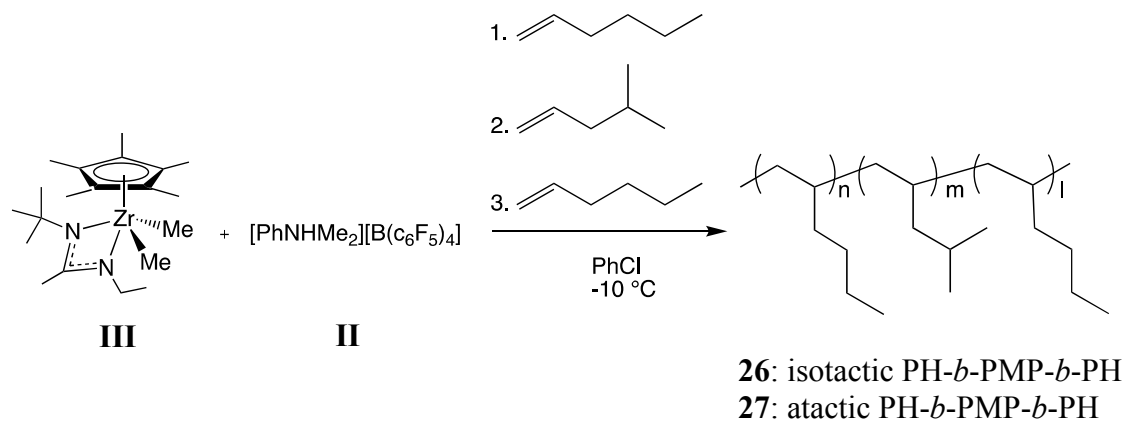
Figure 3.7: ps-tm AFM phase map images of a thin film (152 nm thick) of **25** after thermal annealing at 120 °C for 14 h *in vacuo* then cooled slowly *in vacuo* (left) or cooled quickly by plunging into liquid nitrogen while hot (right).

3.4 PH-*b*-PMP-*b*-PH Triblock Copolymers

Of the PH-*b*-PMP, PO-*b*-PMP, and PD-*b*-PMP diblocks described in the previous section, the PH containing diblocks were the only ones to show no indication of a microphase-separated morphology, instead showing only classic crystalline lamellae from the PMP domains. Isotactic and atactic PH-*b*-PMP-*b*-PH triblock copolymers were synthesized, which added an additional PH block and sandwiched the crystalline PMP domain between two amorphous PH blocks, in order to determine if this would sufficiently block PMP crystallization and create a microphase-separated BCP film.

3.4.1 Synthesis and Characterization

Scheme 3.3: Synthetic route to PH-*b*-PMP-*b*-PH via LCP



The fully isotactic triblock copolymer was synthesized under standard LCP conditions, while the atactic triblock copolymer was synthesized using substoichiometric activation of **III** by **II** (Scheme 3.3). The polymers were characterized by NMR, GPC, DSC, AFM, and SAXS. The characterization is summarized in Table 3.5. The thermal properties of the isotactic and atactic triblocks vary greatly from each other; while both triblocks had a low T_g from the amorphous PH end-blocks, the isotactic **26** had very strong T_m and T_c observed by DSC while the atactic **27** had a very weak T_m and no T_c . This was a potential sign that the amorphous PH end-blocks were sufficient to block crystallization of the atactic, less crystalline PMP mid-block during self-assembly. Thus, AFM was performed on thin films of the two triblocks.

Table 3.5: Properties of PH-*b*-PMP-*b*-PH triblocks **3.T** and **3.U**

Material	[II]/[III]	% yield	M _n (kDa) ^a	PDI ^a	f _{PMP} ^b	T _g (°C) ^c	T _m (°C) ^c	T _c (°C) ^c
27	0.5	74.1	51.0	1.28	0.47	-30.7	103.0	--
26	1.0	80.9	26.5	1.04	0.31	-45.7	197.1	172.0

^aDetermined by GPC at 40 °C using THF as an eluent. ^bDetermined using integral ratios from inverse-gated ¹³C-NMR. ^cDetermined by DSC using a heat/cool/heat cycle from -70 °C to 250 °C. Boxes marked with (--) indicate that the transition was not observed.

3.4.2 Self-Assembly

Thin films of **26** and **27** were prepared by spin-casting from 1.0 % (w/v) solutions in toluene onto the native SiO₂ layer of Si (100) substrates. The films were analyzed by AFM and the bulk materials were analyzed by SAXS. For the isotactic triblock **26**, crystallization of the PMP block completely dominated the self-assembly in the bulk and thin film states both before and after thermal annealing (Figure 3.8).

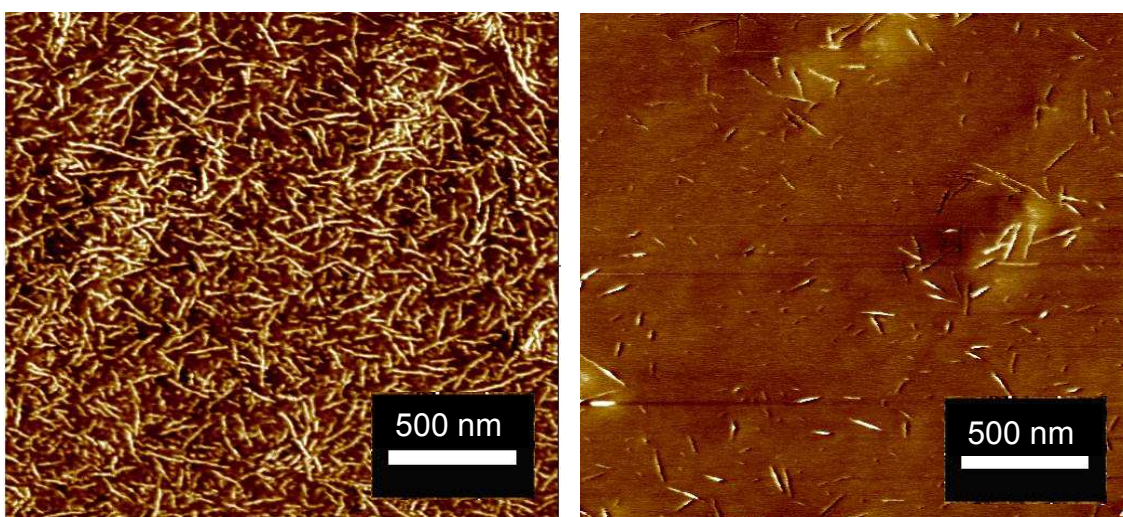


Figure 3.8: ps-tm AFM phase map images recorded at room temperature of thin films of **26** (200 nm thick) “as-cast” (left) and after thermal annealing at 210 °C for 14 h (right)

Notably, however, the film of **26** after thermal annealing above the T_m displays significantly fewer crystallites than the films of PH-*b*-PMP diblock copolymers. Thus, adding a PH block seemed to have contributed to preventing some PMP crystallization, though not completely. SAXS confirmed a lack of morphology above the T_m and ordering of crystalline lamellae during heating (below T_m) (see Supplemental Results).

Despite the very weak T_m and lack of T_c observed by DSC for the atactic triblock **27**, the self-assembly was still dominated by the semi-crystalline PMP. Highly ordered, well-defined crystalline lamellae were observed before and after thermal

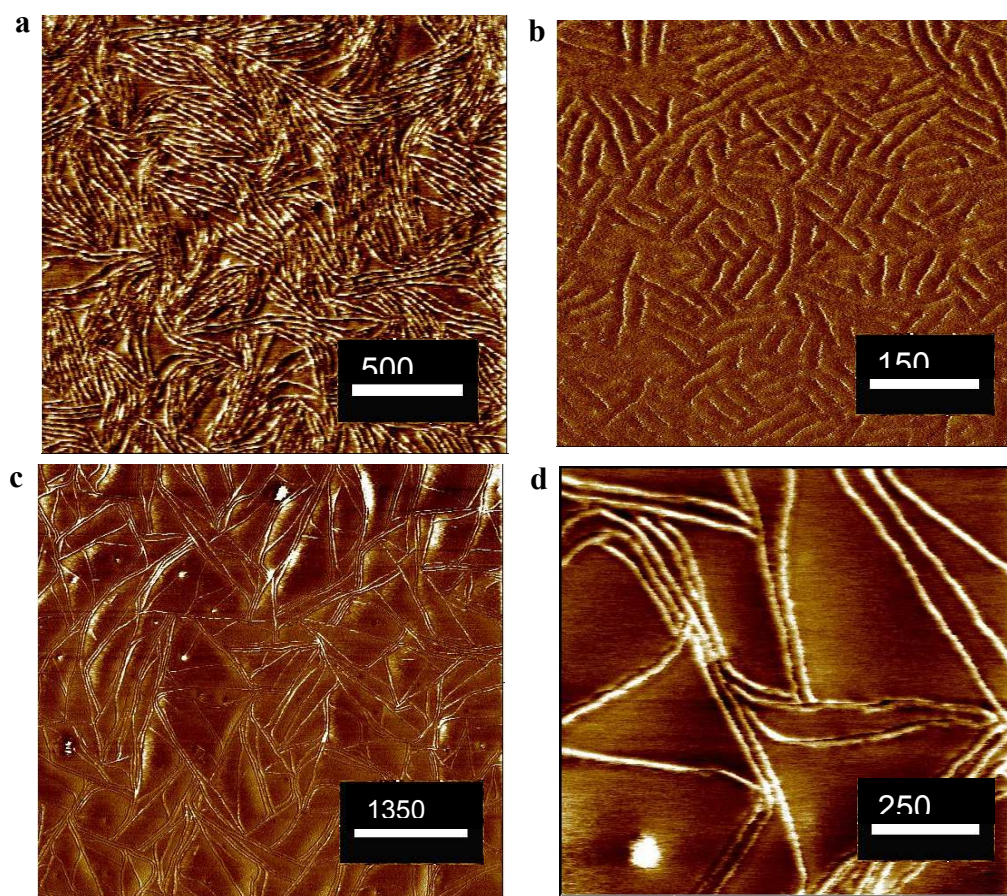


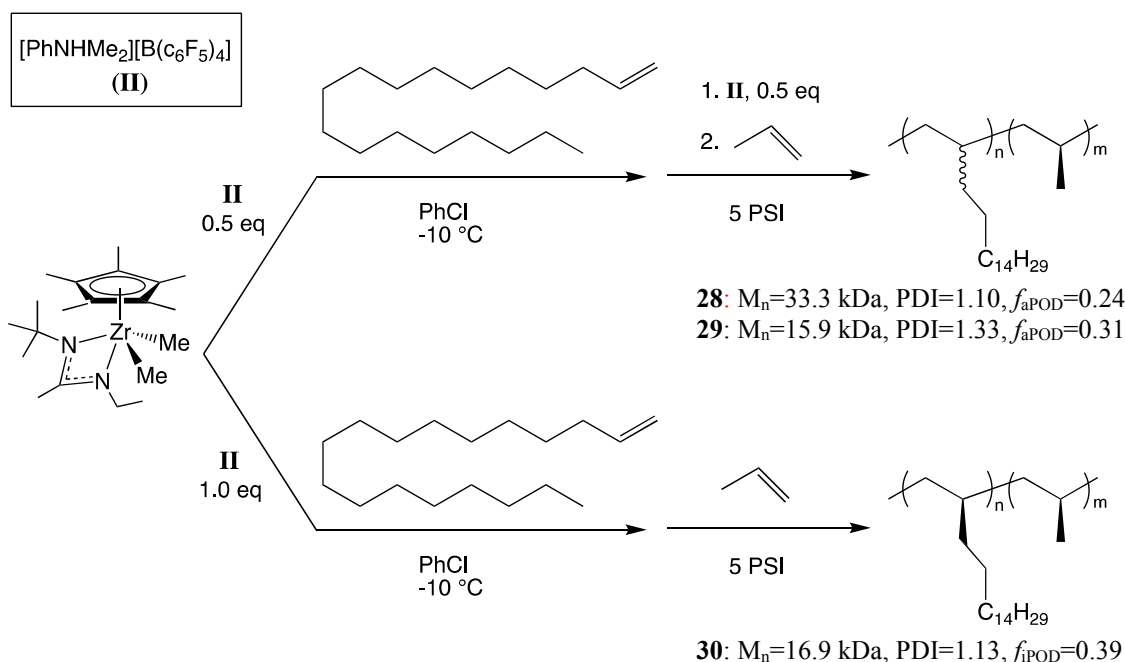
Figure 3.9: ps-tm AFM phase map images recorded at room temperature of thin films of **27** (thickness=184 nm) a,b) as-cast, and c,d) after thermal annealing *in vacuo* at 120 °C for 14 h.

annealing (Figure 3.9). Thus, attempts to obtain a microphase-separating PH-*b*-PMP-*b*-PH triblock copolymer were unsuccessful.

3.5 Poly(octadecene)-*b*-isotactic poly(propylene) Diblock Copolymers

3.5.1 Synthesis and Characterization

Scheme 3.4: Synthetic route to aPOD-*b*-iPP and iPOD-*b*-iPP via LCP



Scheme 3.4 presents the methods employed to synthesize POD-*b*-iPP diblock copolymers **28-30** in high yield. For the fully isotactic diblock (**30**), traditional LCP conditions were utilized. For the atactic POD/isotactic PP diblocks **28** and **29**, LCP under Methyl Degenerative Group Transfer (MeDeT) conditions were employed to create the stereoblock copolymers as previously reported by the Sita Group.^{30, 31} The diblock copolymers were characterized by GPC, DSC and SAXS using a synchrotron source. The thermal properties determined by DSC are summarized in Table 3.6.

Table 3.6: Thermal properties of **28-30** measured by DSC

Material	T_g (°C)	T_m(POD) (°C)	T_{m2}(iPP) (°C)	T_{c1}(POD) (°C)	T_{c2}(iPP) (°C)
28	2.95	--	107.1	--	67.7
29	--	26.3	106.3	15.5	74.5
30	--	45.5	108.6	19.2	76.8

Measured by heat/cool/heat cycle from -70 °C to 250 °C at a flow rate of 10 °C/min. Boxes marked with (--) indicate that the transition was not observed.

The goal for the aPOD-*b*-iPP materials was for the aPOD to display a low T_g while the iPP maintained a strong, relatively high T_m/T_c. This goal was obtained for **28** but not for **29**. This may be attributed to the difference in f_{aPOD} and the overall molecular weights of the two diblocks; **28** had a lower percentage of aPOD that may have prevented the crystallization of the aPOD side-chains.

The self-assembly of the bulk materials was investigated by SAXS using a synchrotron x-ray source at Brookhaven National Laboratory. All three POD-*b*-iPP diblock copolymers displayed weak, poorly ordered microphase-separation at room temperature, during heating below T_m, and above the T_m. For the isotactic POD diblock, a second order peak was visible, but a clear phase could not be identified based on literature values for the currently known phases. However, for the atactic POD diblocks, though the domain spacing calculated from the first peak, q_1 , was too large for the peak to be associated with iPP crystals, the lack of peaks higher than first order

in the SAXS data prevented the determination of a specific type of phase. The one-dimensional scattering plots for **28-30** are shown in Figure 3.10. Thus, though both polyolefins, the POD and iPP blocks were sufficiently incompatible to phase-separate.

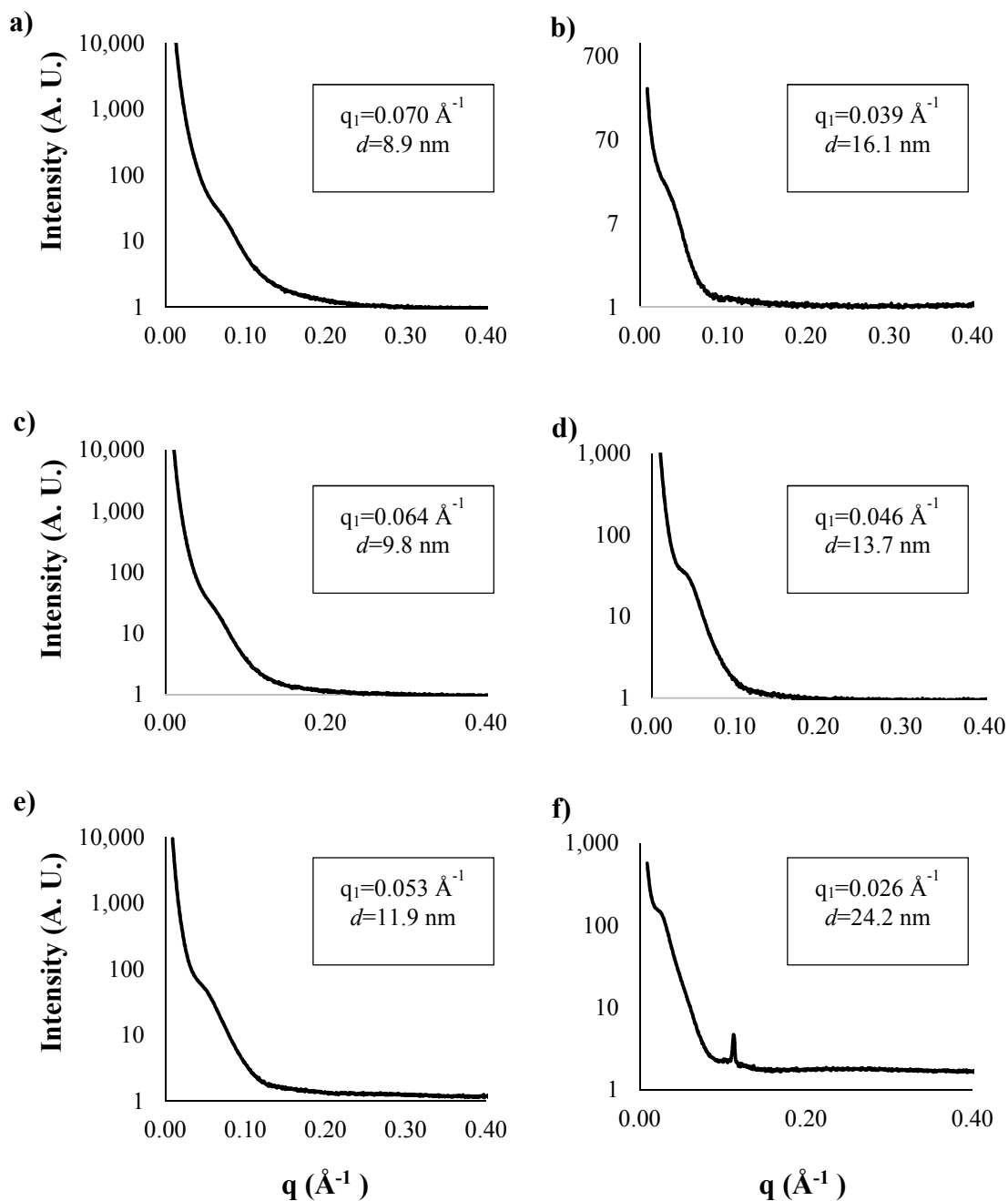


Figure 3.10: 1D SAXS plots for a) **28** at 38 °C; b) **28** at 120 °C; c) **29** at 38 °C; d) **29** at 120 °C; e) **30** at 38 °C; f) **30** at 120 °C

3.6 Conclusions

Living coordination polymerization (LCP) was successfully utilized for the synthesis of polyolefin di- and tri-block copolymers and random copolymers with narrow polydispersities. Since microphase-separation in BCPs is dependent upon the product of χN and χ is relatively small for two polyolefin blocks, this study served to demonstrate that amplifying conformational asymmetry between the blocks can create sufficient incompatibility to drive microphase-separation. Specifically, several crystalline-amorphous polyolefin BCPs displayed microphase separation in the melt state, including PO-*b*-PMP, PD-*b*-PMP, aPOD-*b*-iPP, and iPOD-*b*-iPP. Additionally, it was found that the thermophysical properties of PMCP materials could be tuned by the simple random incorporation of a given amount of PMCH during polymerization. These PMCP-*co*-PMCH random copolymers eliminated the undesirable crystalline properties of PMCP and maintained the relatively high T_g of PMCH materials desirable for applications, while using substantially less of the relatively expensive 1,6-heptadiene monomer than was required for PMCH homopolymers.

3.7 Experimental Information

3.7.1 Materials

All manipulations were performed under an inert atmosphere of N₂ using standard Schlenk-line or glove-box techniques. Toluene and Chlorobenzene (ReagentPlus, 99%) were dried and deoxygenated by passage over activated alumina and GetterMax® 135 catalyst (purchased from Research Catalysts, Inc.) and collected under N₂ prior to use. Precatalyst **III** was synthesized as previously described by our group. N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate (**II**) was purchased and used as received from Boulder Scientific and Sigma Aldrich, respectively. 1-hexene, 1-octene, 1-decene, 1,5-hexadiene, 1,6-heptadiene, and 4-methyl-1-pentene monomers were purchased from Alfa Aesar and purified by stirring over Na/K amalgam in a Schlenk storage tube for at least 2 days followed by collection *via* vacuum transfer (freeze-pump-thaw) and transferred to a glovebox. PMCP homopolymer **15** was synthesized by Kaitlyn Crawford.

3.7.2 Instrumentation

Gel Permeation Chromatography (GPC): GPC analyses were performed using a Viscotek GPC system equipped with a column oven and a differential refractometer both maintained at 40 °C and four columns also maintained at 40 °C. THF was used as the eluent at a flow rate of 1.0 mL/min. M_n , M_w , and M_w/M_n values were obtained using a Viscotek GPC with OmniSEC software and ten polystyrene standards (M_n =580 Da to 3150 kDa) (Polymer Laboratories).

Nuclear Magnetic Resonance (NMR): ^1H NMR spectra were recorded at 500 MHz with chloroform-*d* at room temperature unless otherwise noted. $^{13}\text{C}\{\text{H}\}$ NMR spectra were recorded at 125 MHz with chloroform-*d* at room temperature unless otherwise noted.

Differential scanning calorimetry (DSC): DSC measurements were carried out using a TA DSC Q1000 system. Samples were sealed in hermetical pans with an average sample weight of 6 mg. An empty pan was used as a reference. A heat/cool/heat temperature program was used with a 10 °C/min ramp.

Atomic Force Microscopy (AFM): AFM images were obtained using a Nanoscope IIIa Multimode AFM in tapping mode equipped with Extender Electronics package (Veeco Inc., CA). Height and phase-shift data were recorded simultaneously under ambient conditions with a silicon-etched tip. Thin films of the polymer materials were spun cast (2000 rpm) from solutions onto cleaned silicon surfaces unless otherwise noted. Wafers were cleaned using Piranha solution (7:3 H_2SO_4 : H_2O_2), rinsed with deionized water, then isopropanol and dried under nitrogen gas. To anneal samples, films were placed in a vacuum oven for a given length of time unless otherwise noted. Film thickness was obtained using a Gaertner optical ellipsometer.

Small Angle X-ray Scattering (SAXS): For SAXS experiments, a Xenocs Xeuss system with a Cu $\text{K}\alpha$ X-ray source with a wavelength of 1.542 Å (GeniX3D Cu ULD, Xenocs, SA, France) was used. The two-dimensional scattering data were collected with semiconductor (CMOS) detectors (pixel size = 0.172 mm, Pilatus 300K, DECTRIS, Swiss). Samples were supported between two layers of Kapton film. The

acquisition time was 10 minutes for each frame. Two dimensional spectra were integrated using Igor Pro software (Version 6.3).

3.7.3 Synthesis

General Synthesis of PMCP-*co*-PMCH (11-15)

In a 250 mL round bottom flask, 120.0 mL of dry and oxygen free PhCl was cooled to -10.0 °C. X equivalents of 1,5-hexadiene and Y equivalents of 1,6-heptadiene were added to the flask. A solution of **III** (0.025 mmol) in 1.0 mL chlorobenzene at -10.0 °C was added to **II** (0.025 x 0.5 mmol) and agitated until dissolved. Stirring was maintained for the duration of the reaction (3 h). The reaction was quenched in acidic methanol to isolate the polymer product. The resulting polymer was precipitated from acidic methanol for 14 h then collected and dried under vacuum.

General Synthesis of PH/PO/PD-*b*-PMP (16-25)

In a 250 mL round bottom flask, 100.0 mL of dry and oxygen free PhCl was cooled to -10.0 °C. X equivalents of monomer 1 (1-hexene/1-octene/1-decene) was added to the flask. A solution of **III** (0.025 mmol) in 1.0 mL chlorobenzene at -10.0 °C was added to **II** (0.025 x 1.1 mmol) and agitated until dissolved. Stirring was maintained for 3.5 h, then Y equivalents of 4-methyl-1-pentene (cooled to 0 °C) was added. The reaction was stirred for an additional 3.5 h. The reaction was quenched in acidic methanol to isolate the polymer product. The resulting polymer was precipitated from acidic methanol for 14 h then collected and dried under vacuum.

General Synthesis of PH -*b*-PMP-*b*-PH (26-27)

In a 250 mL round bottom flask, 100.0 mL of dry and oxygen free PhCl was cooled to -10.0 °C. X equivalents of 1-hexene was added to the flask. A solution of **III** (0.025 mmol) in 1.0 mL chlorobenzene at -10.0 °C was added to **II** (0.025 x 1.1 mmol for isotactic, 0.025 x 0.5 mmol for atactic) and agitated until dissolved. Stirring was maintained for 3.5 h, then Y equivalents of 4-methyl-1-pentene (cooled to 0 °C) was added. Stirring was maintained for 3.5 h, then Y equivalents of 1-hexene (cooled to 0 °C) was added. The reaction was stirred for an additional 3.5 h. The reaction was quenched in acidic methanol to isolate the polymer product. The resulting polymer was precipitated from acidic methanol for 14 h then collected and dried under vacuum.

General Synthesis of aPOD -*b*-iPP (28-29)

In a 250 mL Schlenk flask, 100.0 mL of dry and oxygen free PhCl was cooled to -10.0 °C. X equivalents of 1-octadecene was added to the flask. A solution of **III** (0.025 mmol) in 1.0 mL chlorobenzene at -10.0 °C was added to **II** (0.025 x 0.5 mmol) and agitated until dissolved. Stirring was maintained for 3 h. A solution of **II** in chlorobenzene (0.025 x 0.6 mmol) was cooled to -10 °C and added to the flask and the solution was allowed to stir for 10 minutes before propene gas was added to the flask at 5 psi. Stirring was maintained for 3.5 h. The reaction was quenched in acidic methanol to isolate the polymer product. The resulting polymer was precipitated from acidic methanol for 14 h then collected and dried under vacuum.

General Synthesis of iPOD -*b*-iPP (30)

In a 250 mL Schlenk flask, 100.0 mL of dry and oxygen free PhCl was cooled to -10.0 °C. X equivalents of 1-octadecene was added to the flask. A solution of **III** (0.025 mmol) in 1.0 mL chlorobenzene at -10.0 °C was added to **II** (0.025 x 1.1 mmol) and agitated until dissolved. Stirring was maintained for 3 h, then propene gas was added to the flask at 5 psi. Stirring was maintained for 3.5. The reaction was quenched in acidic methanol to isolate the polymer product. The resulting polymer was precipitated from acidic methanol for 14 h then collected and dried under vacuum

3.8 References

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Chapter 4: Synthesis and Preliminary Characterization of a Cellobiose-atactic Polypropylene Conjugate

4.1 Background

4.1.1 Thermoresponsive “Smart” Materials

“Smart” materials, or those which respond to external stimuli like temperature, light, pH, or solvent vapor, are of intense academic and industrial interest because of the plethora of applications and technologies for which they can be used.¹⁻⁴ In addition to block copolymers (BCPs), which are widely used in self-assembly, research interests have recently been shifting towards amphiphilic “hybrid” materials that can utilize the principles and advantages of both small molecule surfactants and block copolymers. For example, Cheng and coworkers reported a class of self-assembling “giant surfactants” containing large molecular nanoparticle “head” groups, like C₆₀ or POSS, and low molecular weight polymer “tails.”⁵ Borsali and Willson reported the formation of a high χ , low N hybrid system of natural-*b*-synthetic BCPs composed of oligosaccharide/silicon containing block copolymers.⁶ Despite the ability of these systems to form well-defined self-assembled nanostructures, they are not without limitations. For example, the versatility of the molecular nanoparticle head group of giant surfactants is limited by the cost and relatively difficult synthesis, and both giant surfactants and natural-*b*-synthetic BCPs utilize high glass-transition (T_g) polymers, such as polystyrene, making them relatively rigid systems.

4.1.2 Previous Work on Sugar-Polyolefin Conjugates

In an effort to design a self-assembling system utilizing x-PAOs made via LCCTP, the Sita Group recently reported a new class of hybrid smart materials from the coupling of a polar monosaccharide (β -galactose) head group to an atactic, very low molecular weight, low T_g x-PAO tail with an extremely narrow polydispersity (<1.1).⁷ The general structure of sugar-polyolefin conjugates is shown in Figure 4.1.

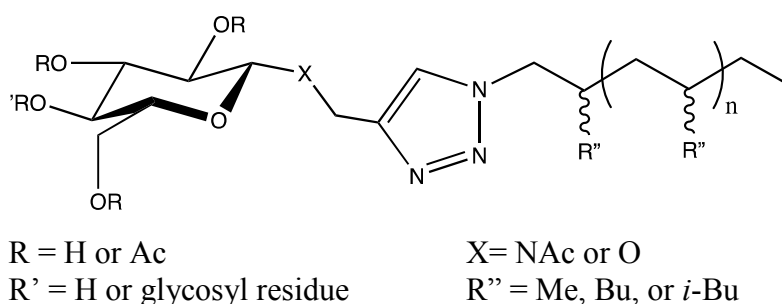


Figure 4.1: General structure of sugar-polyolefin conjugates

These sugar-polyolefin conjugates, especially the conjugate possessing an atactic polypropylene tail and oxygen linker (G-aPP), produced nanostructures with sub-10 nm periodicities within thin films, the morphology of which were seemingly governed by the occupied volume of the amorphous x-PAO tail. Low temperature thermal annealing of the thin films (at 60 °C) increased the long-range order of the self-assembled domains, which is typical of BCP films and is very useful in applications such as nanotemplating.⁸⁻¹⁰ The goal of this work was to design a more refined sugar-polyolefin conjugate that could display a richer and more complex phase behavior while maintaining a sub-10 nm periodicity.

4.2 Design Considerations

4.2.1 Establishing a high χ , low N System

Given the promising self-assembly behavior of the Gal-aPP conjugate previously reported, the goal of developing a new system with even more potential for self-assembly was established. As the field continues to trend towards smaller and smaller dimensionalities, the demand for the development of high χ , low N systems increases since dimensionality scales according to $d \approx N^{2/3}\chi^{1/6}$. In sugar-polyolefin conjugates, self-assembly arises as a result of the incompatibility between the hydrophilic sugar head-group and the hydrophobic x-PAO tail. Because the monosaccharide galactose, with four unprotected hydroxyl groups after conjugation, was able to self-assemble with low molecular weight atactic polypropylene, it was our belief that increasing the hydrophilicity (e.g. the number of hydroxyl groups) of the sugar group would significantly increase the value of χ for this system. To accomplish this, disaccharides, with seven unprotected hydroxyl groups after conjugation, would greatly increase the incompatibility between the two blocks while maintaining the small value of N of the polymer tail, thus creating a high χ , low N system for self-assembly with small dimensionality.

4.2.2 Selection of (D)-(+)-Cellobiose

Carbohydrates are the most abundant chemical compounds in nature.¹¹ Disaccharides are a group of carbohydrates formed when two monosaccharides are linked by a glycosidic bond. The ideal sugars for a high χ , low N system are ones that are both very hydrophilic and are able to undergo chemical transformations relatively easily. Disaccharides are also environmentally benign and are inexpensive, enabling the possibility of large-scale synthesis. To begin the study of disaccharide-sugar conjugates, (D)-(+)-Cellobiose (CB) was chosen as the first disaccharide for conjugation. CB is a homogeneous disaccharide with the formula $C_{12}H_{22}O_{11}$ consisting of two β -glucose residues linked by a $\beta(1\rightarrow4)$ glycosidic bond (Figure 4.2). It is obtained from the partial hydrolysis of cellulose, a plant-based material, and although it is not produced by the human body, it is found in some food products.¹²

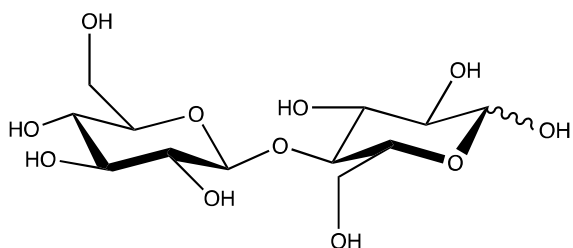


Figure 4.2: Structure of (D)-(+)-Cellobiose

CB has eight free hydroxyl groups with strong intra- and intermolecular hydrogen bonding capabilities. Additionally, CB is a reducing sugar containing a reactive hemiacetal center that can be chemically modified (e.g. substitution of -OH group).

4.2.3 Use of Low Molecular Weight Atactic Polypropylene

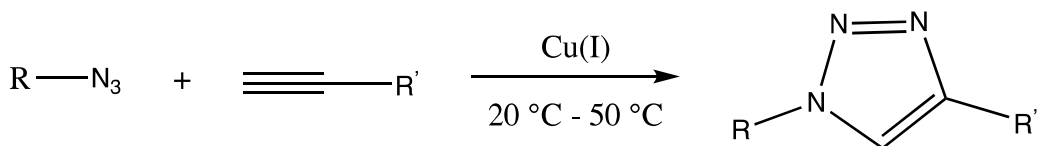
As previously described, LCCTP provides access to a wide range of x-PAOs with controlled molecular weights and extremely narrow polydispersities. Using this system, atactic polypropylene (aPP) was chosen as an ideal “tail” for the sugar-polyolefin conjugates. Polypropylene is the second highest produced plastic after polyethylene and has an extremely wide variety of applications, including biomedical, automotive, packaging, and clothing applications. The global demand for PP was approximately 55 million tons in the year 2013.¹³

In aPP, the methyl pendant groups on the tertiary carbon atoms along the polymer backbone are in random steric orientation. aPP is completely amorphous (no crystallinity) and is readily soluble in common organic solvents at ambient temperatures, unlike the semicrystalline isotactic polypropylene (iPP). Through LCCTP, scalable quantities of end-group functionalized aPP at various molecular weights are easily accessed. For the application of sugar-polyolefin conjugates, it was determined that the x-PAO most suitable would be one that is amorphous and low molecular weight (e.g. significantly below the chain entanglement molecular weight). By choosing such polyolefins, potential complications during self-assembly, for example crystallization-driven self-assembly^{14, 15} or limited molecular mobility due to

chain-entanglement^{16, 17} can be minimized while maintaining a high χ from the hydrophobic polyolefin tail.

4.2.4 Click Chemistry

“Click” chemistry, introduced by K. B. Sharpless in 2001, refers to a class of reactions that are versatile, high-yielding, can be performed in easily removable solvent or in the absence of solvent, and have few or no byproducts.¹⁸ The most widely accepted and utilized example of a click reaction is the 1,3-dipolar cycloaddition of azides and terminal alkynes, especially stereospecific Copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) reactions that give rise to 1,4-disubstituted 1,2,3-triazoles. (Scheme 3.1).^{19,20} Because CuAAC click reactions are easy to carry out and are tolerant of a wide variety of functional groups and solvents, they have been used in the synthesis of many different types of materials, such as dendrimers, block copolymers with complex architectures, surfactants, and macrocycles.²¹



Scheme 4.1: General scheme for a CuAAC click reaction. The 1,5-isomer is not formed.

In the case of sugar-polyolefin conjugates, the method employed for conjugation was the CuAAC click reaction of alkyne-terminated disaccharides and azido-terminated polyolefins. In 2003, Pérez-Balderas et al. reported the first synthetic

strategy to obtain *N*-propargyl mannosylamine from unprotected mannose, but the method required long reaction times with multiple steps and gave low yields.²² Several years later in 2008, Halila et al. reported a much simpler novel methodology for the multigram scale synthesis of alkyne-functionalized sugars using excess propargyl amine without requiring carbohydrate protecting groups, providing a pathway to click chemistry.²³ This method was used for the alkyne-functionalization of (D)-(+)-Cellobiose for click chemistry with azido-terminated PP, which is easily accessed by LCCTP (Figure 4.3). This method is more efficient and versatile than direct glycosylation methods at the anomeric position.²⁴

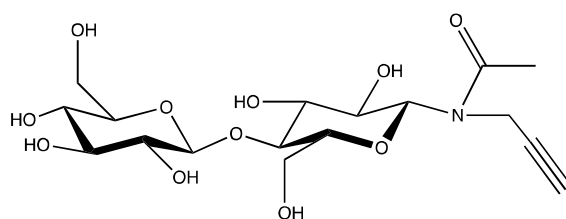


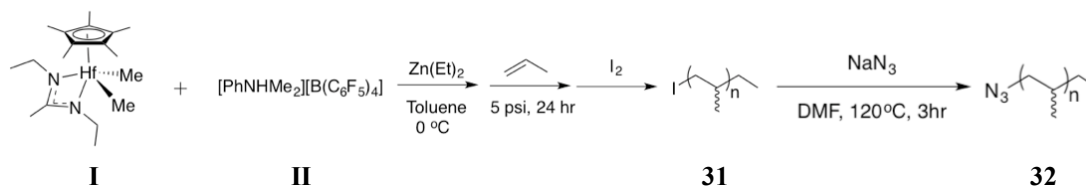
Figure 4.3: Structure of Cellobiose after alkyne-functionalization with propargyl amine

In addition to the ease of synthesis, this method was also chosen because of the nitrogen-atom linker between the sugar residue and the alkyne functionality. This nitrogen atom provides the opportunity for further functionalization. In the future, this will be explored as a potential method for the formation of sugar-polyolefin conjugates with more complex architectures, such as mikto-arm architectures, or for the conjugation of bioactive small molecules.

4.3 Synthesis and Characterization of CB-aPP Conjugate

4.3.1 Synthesis

Scheme 4.2: General synthetic route to azido-terminated atactic polypropylene (N₃-aPP) via LCCTP



As described in Section 4.2, the CB-aPP conjugate was synthesized via the click reaction of azido-terminated aPP (tail) and alkyne-terminated CB (head group). Scheme 3.2 summarizes the method used to make large quantities of iodo-terminated atactic polypropylene (I-aPP). Under LCCTP conditions, low molecular weight x-PAOs are exposed to excess iodine to quantitatively end-group functionalize the polymer chains and form I-PAOs.^{25, 26} This method can also be employed with ethylene, other higher α -olefins, and α,ω -nonconjugated dienes.²⁷⁻³² A molecular weight of approximately 1 kDa was targeted for this study (Table 4.1).³³

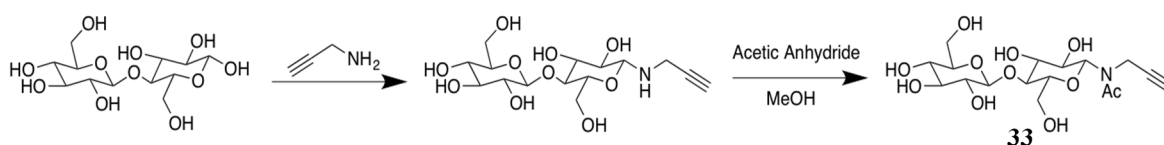
Table 4.1: Reaction conditions and characterization of I-aPP (**31**) used for the CB-aPP conjugate

Eq. ZnEt (relative to I)	Reaction time (h)	Yield (g)	M _n (kDa) by GPC	DP	Đ (M _w /M _n)
400	24	18.498	1.3	31	1.09

After purification via a silica gel plug, **Aa** was quantitatively transformed to azido-terminated atactic polypropylene (N₃-aPP) (**Ab**) by reflux with sodium azide to allow

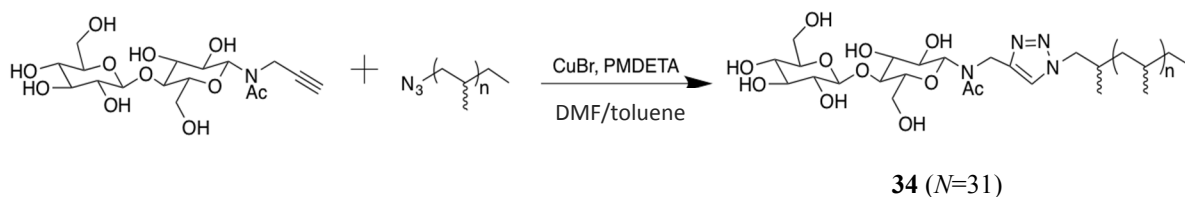
the x-PAO to be used in click chemistry. End-group analysis by ^1H -NMR using the diastereotopic protons in the α -position adjacent to the end-group was performed to confirm the I- and N_3 - termination of aPP.

Scheme 4.3: Synthetic route to *N*-acetylated propargyl cellobiose (**33**)



Scheme 4.3 summarizes the method used to obtain *N*-acetylated propargyl cellobiose (AcN-propargyl CB, **33**) for use as the sugar head-group in good yield (78%). In the presence of excess neat propargyl amine, the anomeric carbon (C-1) selectively undergoes a nucleophilic substitution. The newly formed C-N bond is then stabilized by selective acetylation of the N atom with acetic anhydride in methanol. The product is purified by precipitation from dichloromethane.

Scheme 4.4: Synthetic route to CB-aPP (**34**) conjugate via click chemistry



Finally, **32** and **33** are coupled using CuAAC click chemistry to produce the CB-aPP conjugate **34** in good yield (69.3 %) as shown in Scheme 3.4. Because of the extremely different polarities of the sugar head-group and the N_3 -PAO tail, a solvent

mixture of dimethylformamide (DMF) and toluene was required to solubilize both starting materials simultaneously.

4.3.2 Characterization

The success of the coupling reaction to form **34** was confirmed by ^1H -NMR through the disappearance of the alkyne proton (ca. 2.25 ppm) and the simultaneous emergence of the resonance from the proton of the triazole ring (ca. 8.25 ppm) as seen in Figure 4.4.

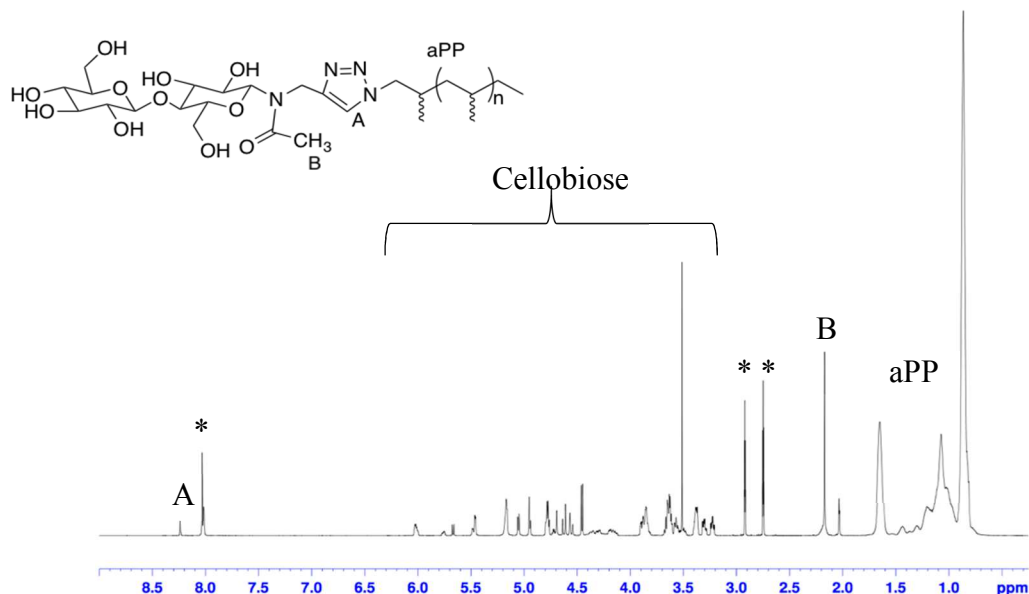


Figure 4.4: ^1H -NMR (600 MHz, $\text{DMF-}d_7$, RT, calibrated at 8.01 (COH) ppm) of **34**. Peaks labeled with an asterisk represent DMF.

It was predicted that switching from a monosaccharide head-group to a disaccharide head-group would make a greater contribution towards the establishment of more complex phase behavior by increasing the χ , or the immiscibility of the sugar head-group and x-PAO tail. Thermal analysis of **34** by differential scanning calorimetry

(DSC) indeed revealed two distinct glass transition temperatures (T_g)- one low temperature T_g at -20 °C associated with the aPP domain and one higher temperature T_g at 60 °C associated with the CB domain (Figure 4.5). Notably, there is no such transition observable in the DSC analysis of pure (D)-(+)-Cellobiose. This result was promising in terms of CB-aPP as a potential thermoresponsive material because it is what one would expect of microphase-separated block copolymers in the bulk state.

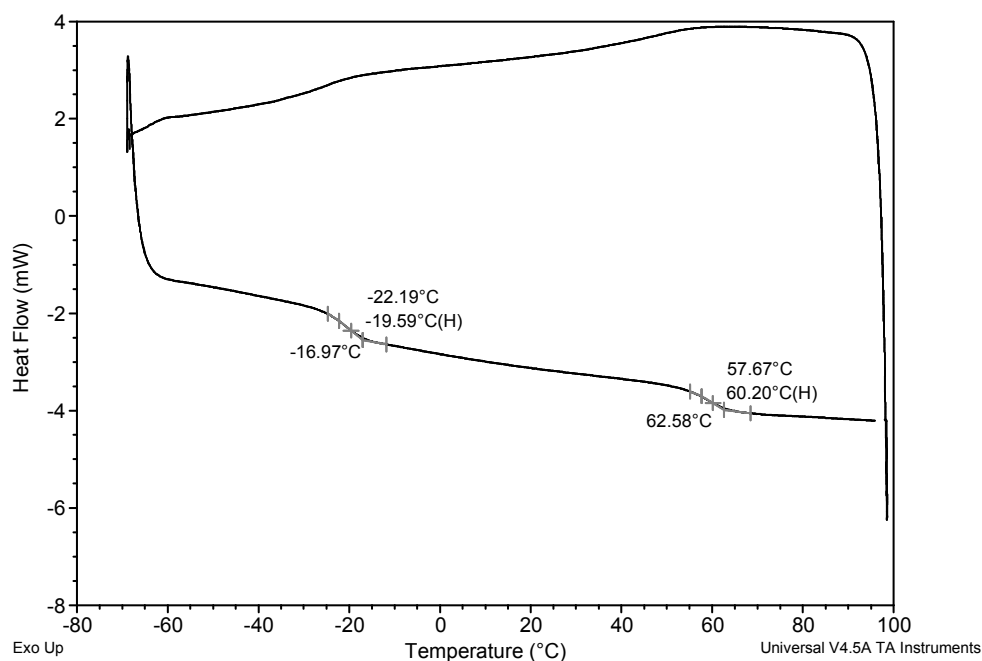


Figure 4.5: DSC analysis of **34** (Heat/Cool/Heat 10 °C/min from -70 °C to 100 °C)

4.4 Bulk and Thin Film Self-assembly of CB-aPP Conjugate

Upon successful synthesis of the CB-aPP conjugate **34**, it was of significant interest to explore the use of this material as a thermoresponsive “smart” material. To this end, the self-assembly behavior, both in the bulk and thin film states, was investigated by several methods to elucidate the phase behavior. Based on the design

considerations of the CB-aPP conjugate, including a very high value of χ , it was anticipated that this material would self-assemble in order to minimize contact between the two incompatible segments.

4.4.1 Self-assembly in the Bulk State

Small angle x-ray scattering (SAXS) is an invaluable tool in the characterization of materials that can determine the shape and size of nanostructures in ordered systems. It requires only minimal sample preparation, is non-destructive, and has a plethora of applications not only in polymer characterization, but in colloids, proteins, metals, and pharmaceuticals.³⁴ To determine which, if any, nanostructure exists in the bulk phase of the CB-aPP material, SAXS was performed on an unannealed sample of **34** on a lab-scale instrument at the University of Maryland (Figure 4.6).

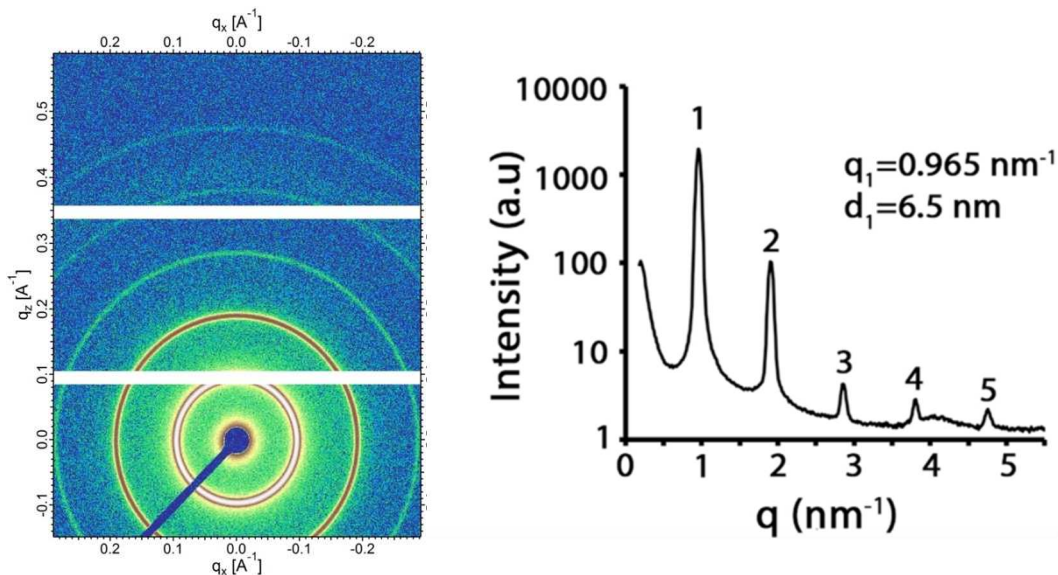


Figure 4.6: 2D (left) and 1D (right) SAXS analysis of an unannealed sample of **34**

In SAXS, the ratios of the peak positions reveal the symmetry of an ordered system. In this case, the ratio of the scattering rings (1:2:3:4:5) indicate a highly ordered lamellar morphology consisting of alternating CB and aPP domains. From the q_1 peak position, the domain spacing was calculated to be 6.5 nm.

Preliminary data on the bulk self-assembly was also collected for a 0.1% (w/v) solution of **34** (in a 1:1 butanol/hexane mixture) using dynamic light scattering (DLS). DLS is a powerful tool for studying the diffusion behavior of macromolecules in solution; the hydrodynamic radius can be calculated from the diffusion coefficient determined by DLS.³⁵ The data showed that a population of self-assembled structures existed with an average size of 6.2 nm (Figure 4.7), similar to the domain size of the lamellae seen by SAXS. This size distribution is consistent with the formation of micelles, which typically form in the range of 2 nm to 20 nm.³⁶ The self-assembly of CB-aPP in solution was not studied further, but will be in the future.

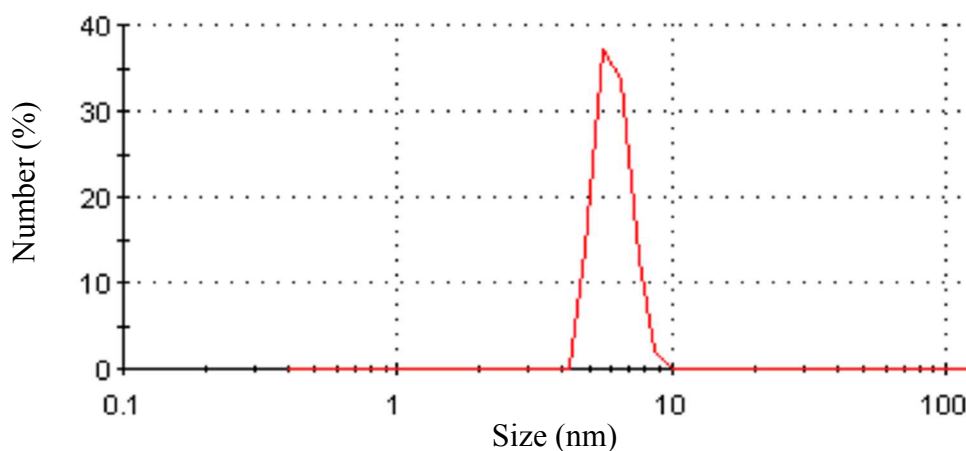


Figure 4.7: DLS of a 0.1 % (w/v) solution of **34** in 1:1 BuOH/Hexanes.

4.4.2 Self-assembly in the Thin Film State

The formation of highly ordered lamellae in the bulk material led to the investigation of the self-assembly of **34** within thin and ultrathin films. Ultrathin films (with film thickness, h , less than 100 nm) were obtained on the native SiO₂ layer of Si(100) substrates through spin-casting at 2000 rpm of a 0.1% (w/v) solution of **34** in a 1:1 butanol/hexane mixture. In order to probe the surface of these ultrathin films and determine if it was nanostructured, atomic force microscopy (AFM) was utilized. However, unlike the G-aPP conjugate described previously, this surface did not provide well-ordered nanostructured films. In 2008, Fuss et al. reported the three-dimensional self-assembly of carbohydrate multilayers on highly-ordered pyrolytic graphite (HOPG) substrates based solely on weak carbohydrate-carbohydrate interactions.³⁷ Based on this, AFM analysis was also done on ultrathin films of **34** on HOPG substrates after being prepared in an identical manner. Figure 4.9a presents an AFM phase map image of this “as-cast” ultrathin film ($h=30$ nm) showing a classic fingerprint nanostructured morphology with domain spacing of 6.60 ± 0.68 nm. This fingerprint morphology is typically indicative of lamellae, in this case alternating CB and aPP domains, that are oriented perpendicular to the substrate.³⁸ Grazing incidence small angle x-ray scattering (GISAXS) was used to confirm both the morphology and orientation of the nanostructured thin-films on carbon-coated silicon (C-Si) substrates (Figure 4.8b). The out-of-plane peaks confirm that the domains are oriented mostly perpendicular to the substrate, while the ring connecting the two peaks shows that the lamellae are somewhat isotropic.

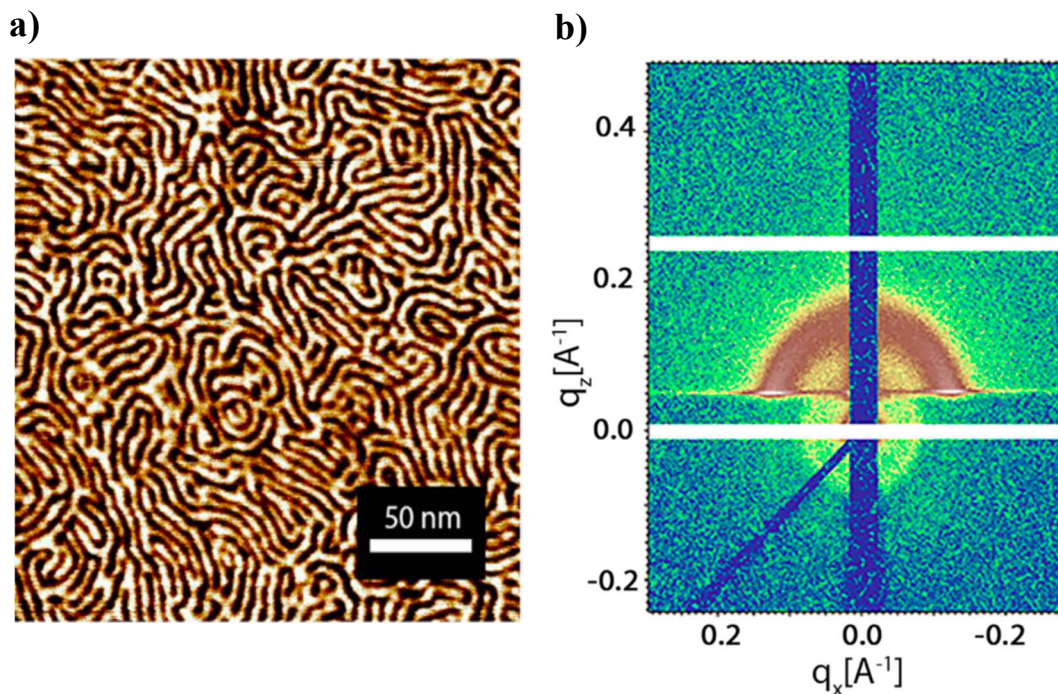


Figure 4.8: a) ps-tm AFM phase map of “as-cast” ultrathin film ($h=30$ nm) of **34** on HOPG substrate; b) 2D GISAXS of **34** ($h=65$ nm) on C-Si substrate showing perpendicular lamellae.

To investigate the effect of thermal annealing on the self-assembly of **34**, the films were annealed in a vacuum oven at 60 °C for 14 h. Quite surprisingly, in contrast to the **G-aPP** conjugate that simply increased in long-range order after thermal annealing, a distinct structural change occurred in the films of **34** which suggest that the alternating CB and aPP domains are now oriented parallel to the substrate (Figure 4.9b) with an average step-height of 6.4 nm.^{39, 40} In order to determine the effect of thermal annealing time on this newly observed morphology, the same film of **34** was annealed at 60 °C for increasing periods of time. This time-dependent series of ps-tm AFM phase map images is presented in Figure 4.9. After 14 h (Figure 4.9b,c) a distinct shift from the initial perpendicular lamellae (seen in Figure 4.9a)

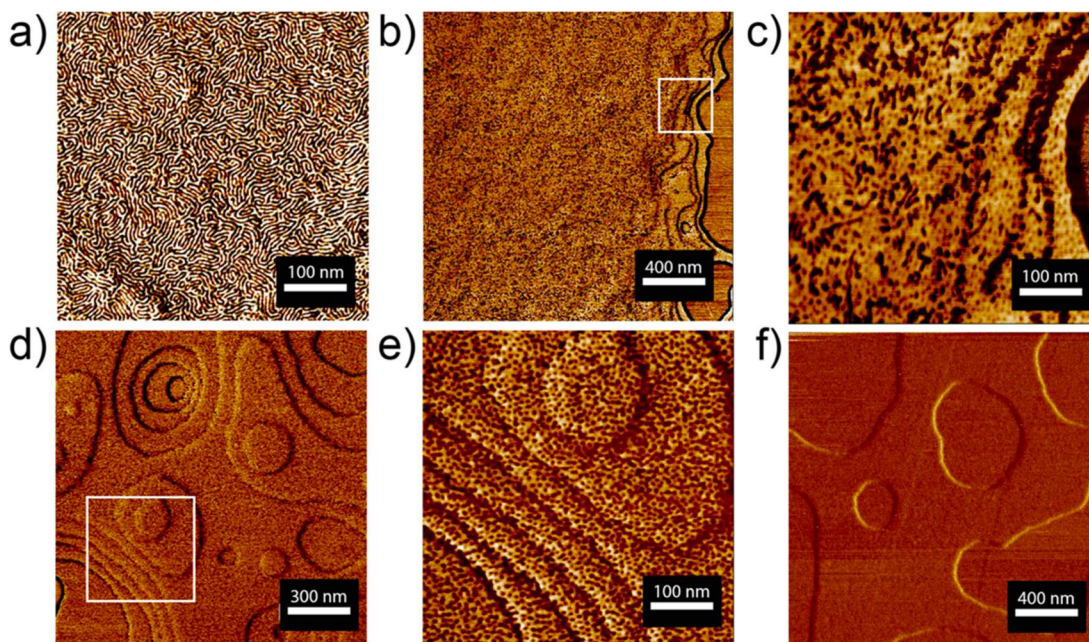


Figure 4.9: Time-dependent series of ps-tm AFM phase map images recorded at 25 °C of an ultrathin film ($h = 30$ nm) of **34** on HOPG that was thermally annealed (in vacuo) at 60 °C for different lengths of time. (a) As-cast ultrathin film of **34**, (b) same film annealed for a total of 14 h, (c) zoomed-in region within white square of b), (d) same film annealed for a total of 24 h, (e) zoomed-in region within white square of (d), (f) same film annealed for a total of 48 h. Figure used with permission from reference 38.

into nascent underlying parallel stacked bilayers can be observed. There is no apparent long- or short-range order for the CB and aPP domains, which appear to be heterogeneously mixed. After annealing this same film for a total of 24 h, this stacked bilayer structure is more well defined; the average repeating step height was determined to be 6.29 ± 0.11 nm using a cross section of the corresponding height map to the phase map in Figure 4.9d. Notably, as clearly evident in Figure 4.9e, what appeared to be spherical anomalies appeared after 24 h of thermal annealing. These spherical “spots” were uniformly 1 nm in size and evenly dispersed in a close-packed assembly within an aPP matrix. The underlying structure associated with these spherical spots could not be elucidated by AFM and were further investigated using a synchrotron light source.

The details of this investigation are presented in Chapter 5. Finally, after thermal annealing at 60 °C for a total of 48 h (Figure 4.9f), AFM showed a uniform parallel-stacked film with no evidence of CB and aPP phase segregation at the air-film interface. Thus, the assumption at the time of this work was that the thermodynamically favorable nanostructure for **34** on HOPG consisted of a tail-head-head-tail bilayer assembly for which the substrate-film and film-air interfaces both favor the aPP tail, as was seen with the Gal-aPP system by x-ray photoelectron spectroscopy.⁴¹

The dependence of self-assembly on annealing time (while keeping the temperature constant at 60 °C) prompted the investigation on the effect of annealing temperature as well. A series of lab-scale GISAXS experiments were done on ultrathin films of **34** on C-Si substrates ($h \approx 65$ nm). Each image was captured after holding the film isothermal at the given temperature for 1 h (Figure 4.10). Although the reorientation from perpendicular to parallel nanostructures was not observed in this series, a significant narrowing of the scattering ring can be observed as the temperature increases from room temperature through 100 °C. In GISAXS, the orientation of nanostructures and the degree to which it is oriented can be determined by the scattering pattern. When the scattering pattern has equal intensities along concentric circles around the beam, as seen in Figure 4.10, the sample is isotropic. As this ring decreases, the sample orientation is increasing in order. Therefore, as expected with thermal annealing, increasing the temperature serves to increase the rate at which the lamellae order.⁴²

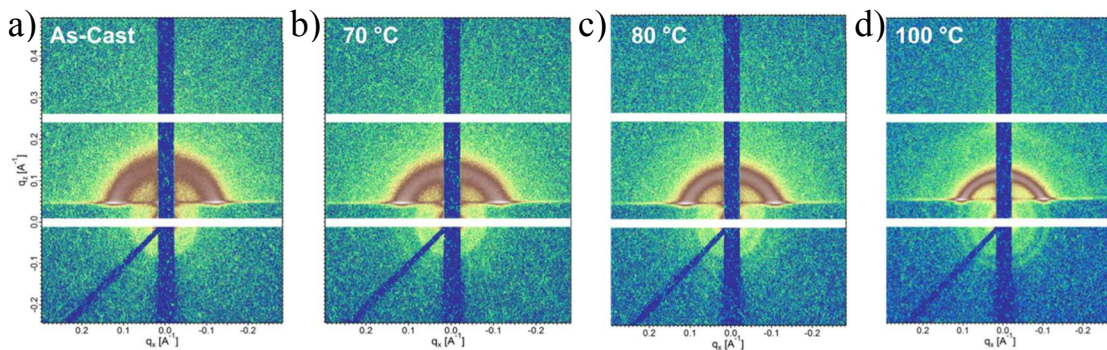


Figure 4.10: GISAXS of ultrathin films of **34** ($h=65$ nm) on C-Si substrate taken at a) room temperature and after holding for 1 h at b) 70 °C, c) 80 °C, and d) 100 °C

Consequently, it was of interest to determine if the same reorientation previously observed at 60 °C was possible at both lower and higher temperatures after varying the annealing time. For this study, films were annealed in a vacuum oven at the given temperature for various periods of time and GISAXS was recorded periodically throughout. This showed that the new nanostructure can be obtained relatively quickly when heated above the highest T_g (at 60 °C) of the material, for example after 3 h at 100 °C (Figure 4.11c). Gratifyingly, this dynamic behavior is also possible after simple thermal annealing well below the transition temperature, for example at the physiologically relevant 38 °C for 72 h (Figure 4.11a). This result demonstrates the potential for **34** as a thermoresponsive material for use in biomedical nanodevice applications. Notably, to the best of our knowledge, this report demonstrates the lowest temperature at which the solid-state dynamic behavior of a sub-10 nm nanostructured ultrathin film of an amphiphilic BCP or giant surfactant undergoes an order-to-order structural transition.

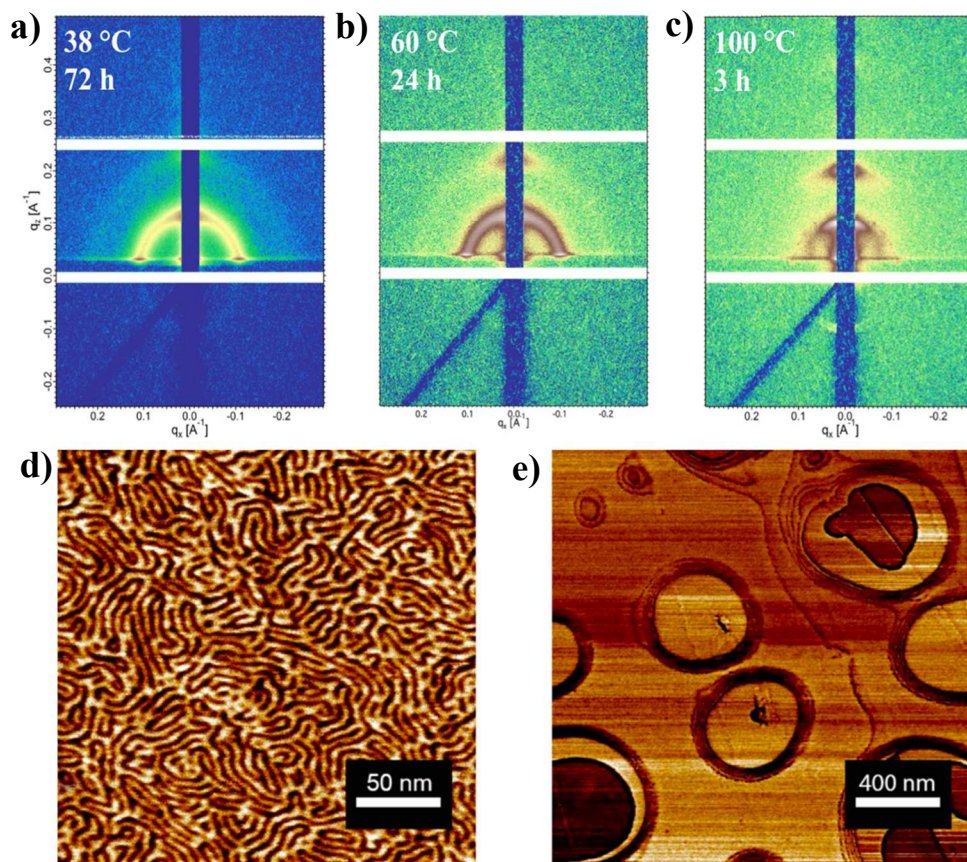


Figure 4.11: a-c) GISAXS of ultrathin films of **34** ($h=65$ nm) on C-Si substrate taken after thermal annealing in a vacuum oven; ps-tm AFM phase map images recorded at room temperature of d) an as-cast ultrathin film of **34** on HOPG and e) the same ultrathin film in d) that was thermally annealed at 38 °C for 72 h.

4.5 Conclusions

This study provides further support for the targeted use of x-PAOs as a new class of hydrophobic building block for self-assembly. In this case, low molecular weight amorphous polypropylene was chosen as a “tail” for a hydrophilic disaccharide “head-group” to form a novel sugar-polyolefin conjugate (CB-aPP). This conjugate did not only display well defined microphase separation in the bulk and thin film states

with sub-10 nm domains, but it was thermoresponsive and dynamic. This is most likely a result of the fluidity and molecular mobility of the x-PAO tail. These results serve to establish sugar–polyolefin conjugates as a new platform that can be used for the design and development of stimuli-responsive, nanostructured smart materials for applications at exceptionally low temperatures, including physiological temperatures.

4.6 Experimental Information

4.6.1 Materials

All manipulations of air and moisture sensitive compounds were carried out under an inert atmosphere of N₂ with standard Schlenk or glovebox techniques. N,N-dimethylformamide (DMF) was dried over molecular sieves and distilled before use. Anhydrous dichloromethane and methanol were dried over CaH (N₂ atmosphere) and distilled before use. Chlorobenzene and Toluene (ReagentPlus, 99%) were dried and deoxygenated by passage over activated alumina and GetterMax® 135 catalyst (purchased from Research Catalysts, Inc.) and collected (N₂ atmosphere) prior to use. All other solvents and reagents were used as received unless otherwise noted. Precatalyst (I) was synthesized as previously described by our group.⁴³ N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate ([PhNMe₂H][B(C₆F₅)₄]) (II) was purchased from Boulder Scientific and used as received.

4.6.2 Instrumentation

Gel Permeation Chromatography (GPC): GPC analysis was used to obtain molecular weight (M_n and M_w) and polydispersity (PDI) of polymers using a Viscotek GPCMax

equipped with 4 columns (T2500, T3000, T4000, and T5000) in a column oven and differential refractometer (maintained at 40 °C). Tetrahydrofuran (HPLC Grade) was used as the eluent with a flow rate of 1 mL/min). Polystyrene standards (from Polymer Laboratories Inc., 580 Da – 3,150 kDa) were used for calibration.

Nuclear Magnetic Resonance (NMR): ^1H and ^{13}C ⁴⁴ nuclear magnetic resonance (NMR) spectroscopy was carried out with a Bruker AVIII-600 MHz Varian spectrometer. Chloroform-*d* was used as the solvent for polymer samples and DMF-*d*7 was used as the solvent for conjugates.

Differential scanning calorimetry (DSC): DSC was used to obtain T_g values using a TA DSC Q1000 system. Samples were run in sealed hermetical pans with an empty pan as reference. A heat/cool/heat temperature program was used at a flow rate of 10 °C/min from -70 °C – 200 °C.

Small angle X-ray scattering (SAXS) and grazing incidence small angle X-ray scattering (GISAXS): Analyses were carried out using a Xenocs SAXS system at a wavelength of 1.542 Å with a CMOS detector (Pilatus 300K, pixel size 0.172×0.172 mm). Silver behenate (AgBe) was used as a reference sample. For GISAXS, incidence angle was 0.15-0.20 ° and data was collected at 600 seconds per frame with 1-hour isotherms, unless otherwise noted. For SAXS, data was collected at 300 seconds per frame. Image processing was done with Igor Pro with Nika 2D macro (provided by Advanced Photon Source, Argonne National Lab).

Atomic Force Microscopy (AFM): AFM images were obtained using a Nanoscope IIIa Multimode AFM in tapping mode (ps-tm-AFM) equipped with a silicon etched tip along with Extender Electronics package (Veeco Inc., CA). Height and phase-shift data

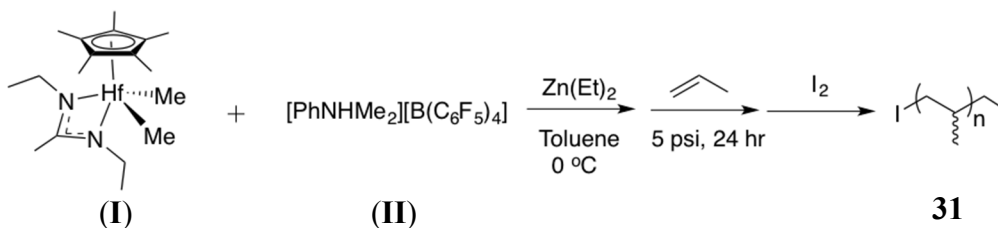
were recorded simultaneously under ambient conditions. Thin films of the conjugate were spun-cast (2000 rpm) from a 0.1% (w/v) solution (in 1:1 BuOH/Hexane) onto various substrates. Silicone substrates were cleaned using Piranha solution (7:3 H₂SO₄: H₂O₂), rinsed with DI water and isopropanol, and dried under N₂. Graphite and mica substrates were prepared by cleavage with tape. Film thicknesses were obtained using a Gaertner optical ellipsometer. To anneal samples, films were placed in a vacuum oven overnight unless otherwise noted.

Transmission electron microscopy (TEM): images were obtained using a JEOL JEM 2100 LaB₆ TEM on a carbon grid. The TEM grids were spun-cast (2000 rpm) from a 0.1 wt% (w/v) solution (in 1:1 BuOH:Hexane). The samples were stained with 0.5% aqueous RuO₄ for 30 minutes. Images were examined at 200 kV.

Dynamic Light Scattering (DLS): The size and intensity of samples were monitored using DLS on a Malvern Zetasizer Nano ZS90. The light source was a standard He-Me 4 mW laser at 633 nm at a scattering angle of 90 °C. Samples were prepared from a 0.1% (w/v) solution in a 1:1 butanol/hexane mixture.

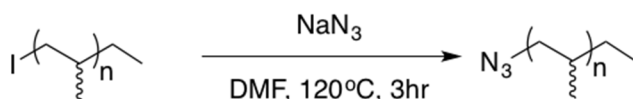
4.6.3 Synthesis

Scheme S4.1: Iodo-terminated atactic poly(propylene) (aPP-I) via living coordinative chain transfer polymerization (LCCTP) (**31**)



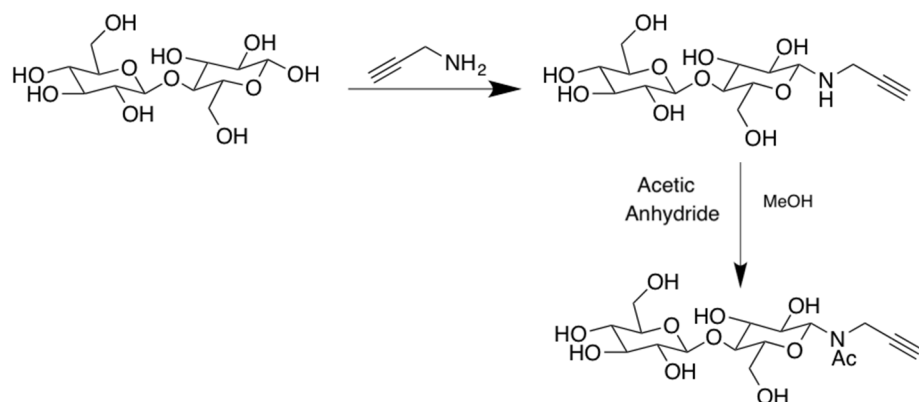
In a 250 mL Schlenk flask, 50.0 mL of toluene was cooled to 0 °C. Diethyl zinc (400 eq. relative to **I**) was added to the flask. A solution of **I** (11.4 mg, 0.025 mmol) in 1.0 mL chlorobenzene at 0 °C was added to **II** (22.0 mg, 0.0275 mmol) which was agitated until dissolved then quickly added to the Schlenk flask. The flask was charged with propene gas at 5 psi while stirring for 24 hours. The reaction was quenched with excess iodine until a light pink color appeared. The resulting polymer was dried in vacuo and purified using a silica column to remove excess iodine yielding 18.498 g of aPP-I. The polymer was characterized by ¹H NMR.

Scheme S4.2: Synthesis of azido-terminated atactic polypropylene (aPP-N₃) (**32**)



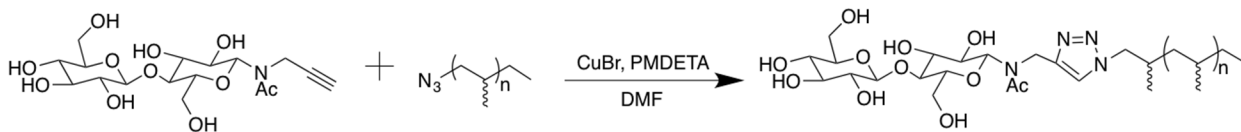
In a N₂ glovebox, aPP-I was dissolved in minimal toluene (2-4 mL) and added to a 100 mL round bottom flask with 10.0 mL DMF. NaN₃ (1.2 eq.) was added to the flask. The flask was brought out of the glovebox and set to heat at 120 °C for 3 hours under reflux while stirring. The resulting polymer was dried in vacuo and purified using a silica column to yield 2.734 g of aPP-N₃ (72.7%). The polymer was characterized by ¹H NMR and GPC.

Scheme S4.3: Synthesis of Acetal-N-propargyl cellobiose (**33**)



Using Schlenk line techniques, D-(+)-Cellobiose (3.00 g, 8.76 mmol) was added to a 100 mL Schlenk flask. Neat propargyl amine (11.7 mL, 180.6 mmol) was added to the flask using a gas-tight syringe and the mixture was stirred rapidly at room temperature for 24 hours. Excess propargyl amine was removed under reduced pressure at 35 °C then co-evaporated with a 9:1 toluene:methanol mixture (v/v). The yellow solid was dissolved in methanol and precipitated in dichloromethane. The precipitate was filtered and washed with a 1:4 methanol:dichloromethane mixture (v/v). The resulting white solid was added to a 50 mL bottom flask and a mixture of 1:5 acetic anhydride:methanol (v/v) was added. The reaction was stirred at room temperature for 16 hours. The solvent and traces of acetic anhydride were removed in vacuo then co-evaporated with a 1:1 mixture of methanol and toluene (v/v) to yield 2.340 g white solid (78.0%). The product was characterized by ¹H NMR.

Scheme S4.4: Synthesis of cellobiose-aPP conjugate



In a N₂ glovebox, acetal-N-propargyl cellobiose (**33**) (1 eq.) dissolved in 5 mL DMF, aPP-N₃ (1 eq.) dissolved in minimal toluene (3-5 mL), and N,N,N',N'',N''-Pentamethyldiethylenetriamine (0.5 eq.) were added to a 50 mL heart-shaped flask. While stirring, copper (I) bromide (0.5 eq.) in 5 mL of DMF was added to the flask drop-wise. The reaction stirred for 16 hours and was quenched with methanol. Solvents were removed in vacuo at 40 °C and the product was purified by flash column chromatography using a 9:1 chloroform/methanol mixture to yield a white solid (1.244 g, 69.3%).

4.7 References

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Chapter 5: Dynamic Phase-Behavior of Sugar-Polyolefin

Conjugates: *In Situ* Synchrotron Studies

5.1 Background

As discussed in Chapter 4, it was previously determined that the CB-aPP conjugate **34** displayed well-defined, dynamic self-assembly within thin films using a combination of atomic force microscopy (AFM) and a laboratory-scale grazing-incidence small angle x-ray scattering (GISAXS) instrument.¹ In this study, sugar-polyolefins were investigated using a synchrotron x-ray source at Brookhaven National Laboratory in Upton, NY in order to gain a better and more detailed understanding of their dynamic self-assembly. This chapter will describe the self-assembly of several sugar-polyolefin conjugates in the bulk and thin film states as investigated with *in-situ* synchrotron x-ray scattering. Analysis of the SAXS/GISAXS data was done in collaboration with Dr. Kevin Yager at the NSLS-II 11-BM Beamline.

5.1.1 Small Angle X-ray Scattering (SAXS)

Although AFM and transmission electron microscopy (TEM) are both extremely useful techniques in the characterization of BCP materials and thin films, they are not without limitations. Although new technological advances in AFM have greatly broadened the scope of information that can be gained from the technique, including *in-situ* studies,²⁻⁴ it is limited to only the surface of a thin film. TEM can be used to visualize both the surface and bulk of a material, but it cannot be used to observe

dynamic processes, such as morphological transitions as a function of temperature, as it cannot monitor changes in microstructure in real-time.

Small angle x-ray scattering (SAXS) is a powerful analytical method and characterization technique that can be used for the characterization of BCPS and other structured systems. Although the first report of SAXS for amorphous materials was as early as the late 1920s,⁵ the technique remained a challenge for the next several decades. However, more recently, advances in the design of x-ray collimation systems,^{6, 7} tunability of x-ray wavelength, and the use of high power density/small beam divergence synchrotron x-rays,⁸ have enabled the design of time-resolved SAXS experiments on a wide range of samples.⁹

Among a wide variety of applications, SAXS can be used for the elucidation of polymer structure, order, size, and shape. In order to obtain this information, x-rays are used to irradiate a sample. As a result, all atoms scatter the incident radiation in all directions, giving a background radiation that is constant at small angles. Additional scattering is produced by particles (e.g. clusters of atoms) inside the sample with a different electron density that in the size-range of the x-ray wavelength. Measuring the intensity of the scattered radiation allows many conclusions to be drawn about the average structure. When x-rays are scattered they produce constructive or destructive interference which produce a two-dimensional interference pattern at the detector. This interference pattern is representative of the material's internal structure.¹⁰ The scattering pattern in reciprocal space relates the length of the maximum scattering vector, q_l (1/nm or 1/Å, with the domain spacing, d (in nm or Å), by the equation:

Equation 5.1:

$$d = \frac{2\pi}{q_1}$$

In SAXS, short-range order causes a build-up of a structure factor, or additional scattering from neighboring particles, in the SAXS pattern. The peaks in the structure factors become more well-defined as short-range order increases. It has been shown that lattices with different symmetries (e.g. lamellar, cubic, hexagonal, etc.) produce peaks with characteristic q -value ratios. The orientation, and the degree to which the system is oriented, can also be determined using the two-dimensional scattering pattern by observing the intensity modulation around the incident beam.¹⁰

Herein, SAXS on sugar-polyolefin conjugates was conducted using a powerful synchrotron x-ray source in order to capture meaningful SAXS patterns on the time-scale of seconds, as opposed to hours using the laboratory-scale SAXS instrument at the University of Maryland. This enabled us to visualize extremely detailed structural characteristics and observe changes in nanostructure in real-time.

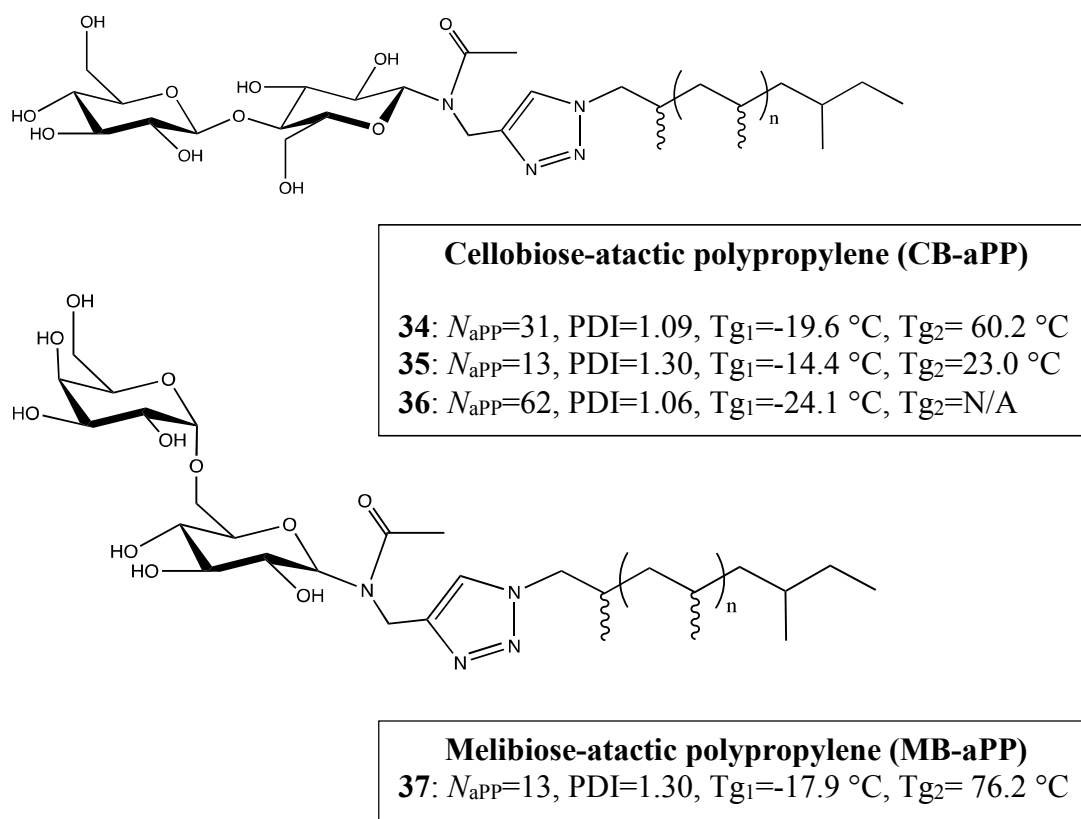
5.1.2 Grazing-Incidence Small Angle X-ray Scattering (GISAXS)

Grazing-incidence small angle x-ray scattering (GISAXS) applies the principles of SAXS to materials in the form of thin films. GISAXS has emerged as an extremely useful method for analyzing the nanostructure and orientation of structured thin films, especially those consisting of block copolymers.¹¹⁻¹⁸ GISAXS is a surface-sensitive technique that operates via a reflection-mode in SAXS. A typical GISAXS experiment directs an x-ray beam to the surface of a thin film that is supported on a flat substrate. The angle at which the beam hits the surface is carefully controlled by a sample stage;

depth-profiling of the film can be achieved by varying the incident angle. There exists a critical angle, θ_c , below which x-rays are completely reflected and only a few nanometers into the film can be probed. When the incident angle is much greater than θ_c the beam is essentially transmitted through the sample. Accordingly, measurements above and below the θ_c can be used as method of depth profiling, providing structural information about the surface of the film and the bulk of the film.¹⁵ This method was also used for the characterization of sugar-polyolefin conjugates.

5.2 Sugar-Polyolefin Conjugates Investigated

Scheme 5.1: Structure and characteristics of sugar-polyolefin conjugates investigated



In addition to CB-aPP conjugate **34**, several additional conjugates were made in order to gain a broader understanding of the self-assembly of sugar-polyolefin conjugates in the bulk and within thin films. First, two additional conjugates with the same (D)-(+)-Cellobiose head-group were synthesized with aPP tails of varying chain length (see Chapter 4.3 for details of synthesis). Second, an analogous conjugate was synthesized using Melibiose as the head-group to begin to investigate the role of the sugar head-group during self-assembly. The structure and details of each conjugate are shown in Scheme 5.1.

5.3 Thermal Stability of CB-aPP Conjugates

In 2012, Otsuka et al. reported cylinder to cubic phase transitions in hybrid BCPs consisting of an oligosaccharidic maltoheptaose (MH) block and a poly(ϵ -caprolactone) (PCL) block.^{19, 20} The authors attributed the OOTs to “caramelization” (e.g. thermal degradation or decomposition) of the sugar block when heated above ~200 °C, which caused the volume fraction of the MH block to change and structural rearrangements to occur. In the case of sugar-polyolefin conjugates **34-36**, the self-assembly was explored at temperatures up to 240 °C. Accordingly, the thermal stability of the conjugates was investigated by thermogravimetric analysis (TGA) to ensure that any results observed were not due to degradation of the conjugate materials (Figure 5.1). Indeed, at 240 °C, conjugates **34**, **35**, and **36** had remaining mass percentages of 97 %, 98 %, and 94 %, respectively. At 300 °C a substantial percentage of the weights were still present.

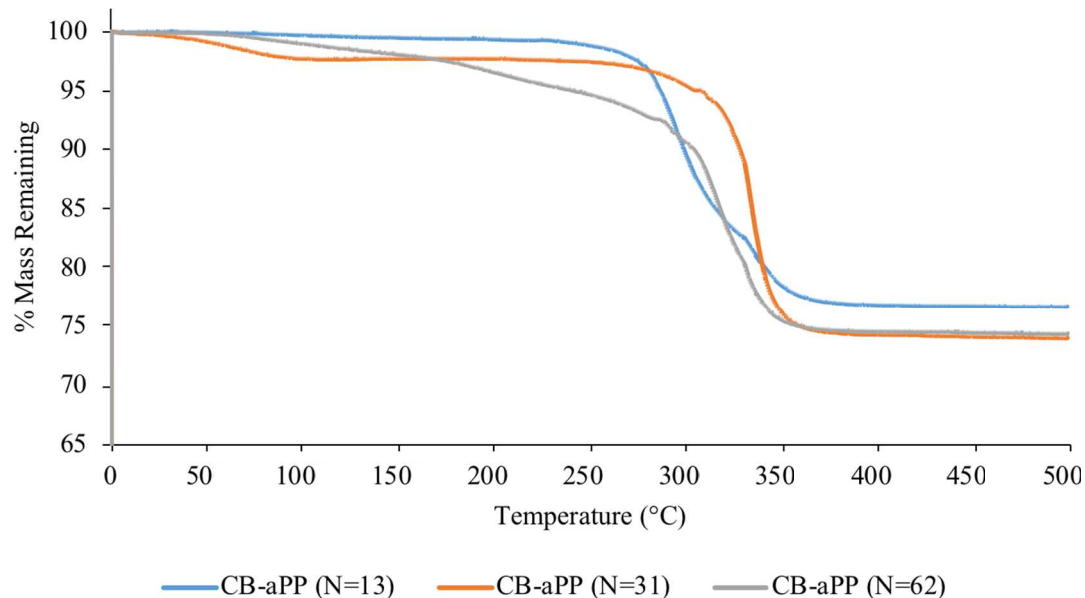


Figure 5.1: TGA profiles of **34-36**

5.4 Self-assembly of CB-aPP in the Bulk State

To determine the thermotropic self-assembly behavior of conjugates **34** and **35**, *in-situ* SAXS studies using a synchrotron light source were performed on the bulk samples while heating. The real-time SAXS profiles of the materials varied drastically upon heating, indicating multiple phases and OOTs during the heating process, including LAM, HPL, GYR, and HEX phases. The 1D scattering plots showed remarkably sharp principal scattering peaks and higher order peaks, indicating highly ordered phases. The temperature ranges over which the ordered phases (and mixture of ordered phases) coexisted for **34** and **35** are summarized in Table 5.1 and will be discussed in more detail in the following Section.

Table 5.1: Summary of OOTs observed during SAXS upon heating of **34** and **35**.

	Temp. Range (°C)							
Mater-ial	LAM	LAM + HPL	HPL	HPL + GYR	GYR	GYR + HEX	HEX	DIS
34	30-90	90-115	115-117	117-151	151-214	214-225	225-240	--
35	30-115	115-130	130-168	168-186	186-230	230-240	--	--

(--) indicates that the phase/transition was not observed.

5.4.1 Lamellar Morphology

To begin, a highly ordered LAM structure was identified at room temperature for **34**; a LAM structure was identified for **35** as well but significantly less ordered due to increased isotropy. The SAXS patterns shown in Figure 5.2 show the characteristic diffraction peaks with a q -value ratio of 1, 2, 3, and 4 for **34** and a ratio of 1, 2 for **35**. The small shoulders on the high q -value side of the q_1 and q_2 peaks in Figure 5.2a indicated a small percentage of isotropic lamellae in the nanostructure.²¹ The LAM phase present before annealing was consistent with the results discussed in Chapter 4 from AFM and SAXS experiments conducted at the University of Maryland.

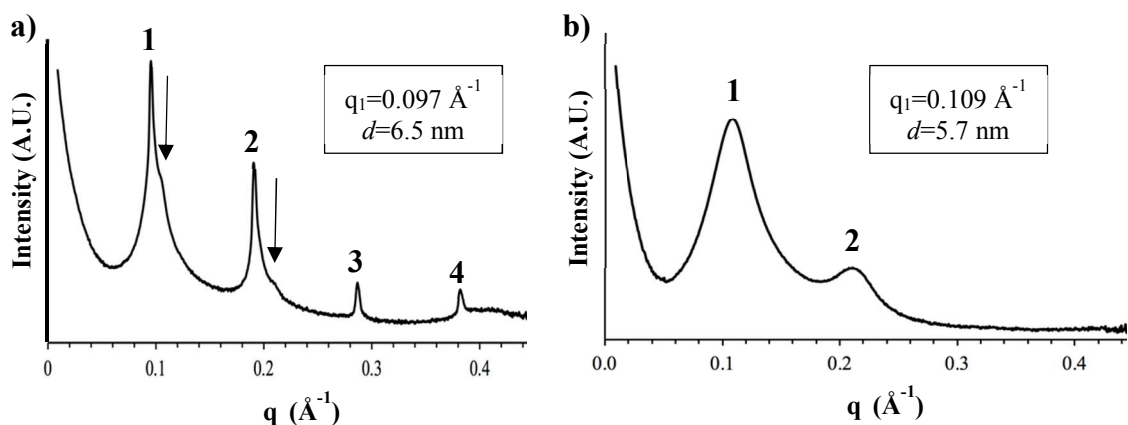


Figure 5.2: 1D SAXS profiles of a) **34** and b) **35** recorded at 30 °C indicating a LAM phase. The arrows indicate a small degree of isotropy within the lamellar domains.

5.4.2 Lamellar to Hexagonally Perforated Lamellar Phase Transformation

To investigate the temperature dependence of the self-assembly, the materials were heated from room temperature to 240 °C at 0.5 °C/min. The change in the first order and higher order peaks (e.g. broadening and change in q -value) was observed in the temperature range of approximately 90 °C to 115 °C that was attributed to an OOT. At

no point during the transformation did the material become disordered. Figure 5.3a shows the SAXS profiles recorded during the heating ramp for conjugate **34** from 57.1 °C to 115.5 °C, at which point a full OOT had occurred to form what was identified as the hexagonally perforated lamellar (HPL) phase. The HPL phase was remarkably well-ordered with characteristic q -values of q , $1.09q$, $1.18q$, $1.73q$, $1.90q$, $2.05q$, $2.18q$, and an additional higher-order peak at $3.31q$. Conjugate **35** underwent an analogous LAM $\rightarrow$ HPL transition at a higher temperature range of approximately 115 °C to 130 °C (see Supplemental Results). The SAXS profile of **34** in the HPL phase is shown in Figure 5.3b with the corresponding (hkl) indices.²² The fully formed HPL phase persisted over a temperature range of 100 °C to 120 °C for **34** and 120 °C to 170 °C.

The HPL structure in BCPs is an exceptionally long-lived nonequilibrium phase that has been a topic of great interest since its initial reports due to its interesting topology.²³⁻²⁷ Similar to the typical LAM phase, each component in the HPL structure is continuous in the plane of its lamellae. However, unlike LAM, hexagonally packed perforations are formed by the minority component through the lamellae, giving the majority component three-dimensional continuity. In HPL systems that are well-ordered, the preferred pore spacing and stacking of the hexagonally packed perforations (e.g. ABAB... versus ABCABC...) can be experimentally determined.²⁸ In the case of **34**, SAXS analysis showed peaks in excellent agreement of an ABCABC... stacking arrangement, which was confirmed by the strong scattering peak at $q=0.12 \text{ \AA}^{-1}$ (102) which would be absent for ABAB... stacking. The spacing between perforations (a) and the lamellar repeat distance (c) were determined to be 6.4 nm and 16.4 nm

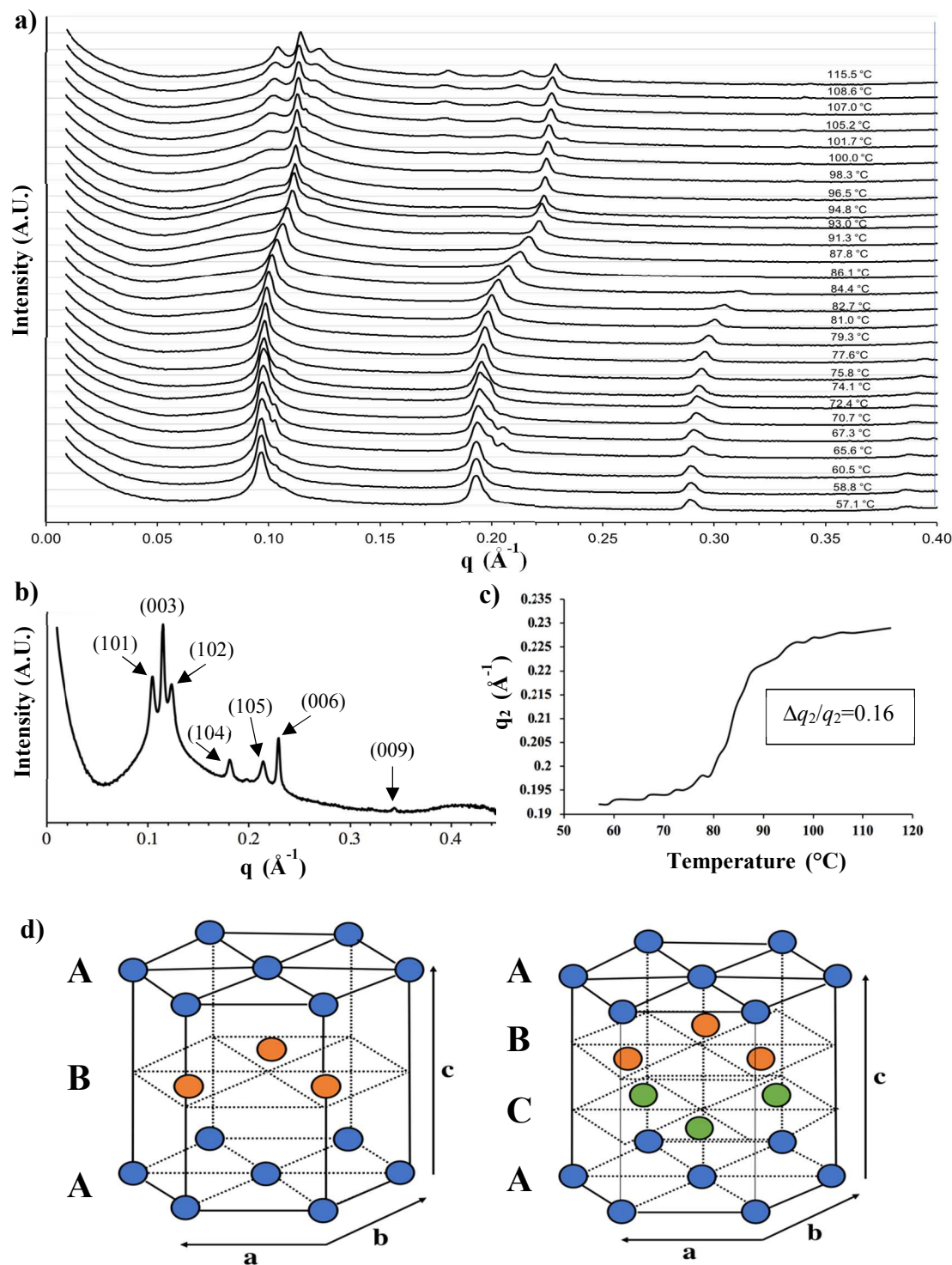


Figure 5.3: a) SAXS profiles for **34** during a heating ramp at the given temperatures showing a LAM $\rightarrow$ HPL OOT. Successive profiles are shifted in intensity for clarity. b) same material at 120 °C showing well-defined HPL phase. Indices (hkl) on top of peaks are according to an ABCABC... stacking of the perforations as illustrated in d).²² c) the increase in q_2 (decrease in d) as a function of temperature during the transition.

respectively. The hexagonal lattices associated with ABAB... and ABCABC... stacking are illustrated in Figure 5.3d.

Also of note during the LAM $\rightarrow$ HPL transition is a large decrease in interlayer spacing upon formation of the HPL phase, as evidenced by the increase in q_2 positions during heating (Figure 5.3a,c). Previous research of this phase transformation in literature has determined that the LAM $\rightarrow$ HPL involves a major rearrangement of the structure and a change in the number of layers, with an overall reduction in layer spacing of up to 9 %.^{29, 30} However, in the case of **34**, a much more pronounced decrease in layer spacing of 16 % was observed (Figure 5.3c).

5.4.3 Hexagonally Perforated Lamellar to Gyroid Phase Transformation

Upon further heating, an additional OOT was observed for both **34** and **35** that can be attributed to a HPL $\rightarrow$ GYR transition. The HPL phase as discussed in the previous section is known to facilitate the transition from LAM to GYR in BCPs through sequential OOTs of LAM $\rightarrow$ HPL and HPL $\rightarrow$ GYR in an epitaxial manner.^{31, 32} The GYR phase consists of two interpenetrating tubular networks of the minority component in a matrix of the majority component, forming a bicontinuous, three-dimensional structure. Förster et al. first described the factors that account for the relationship between HPL and GYR phases.³³ First, the topology of both structures can be simplified into a planar tripod; in HPL these tripods are connected in a planar fashion and in GYR they are connected in the Ia3d space group at a 70.5° angle. Second, there is an epitaxial relationship between the (211) planes of the GYR phase and the layers of the HPL phase.³¹

Figure 5.4 shows the SAXS profiles for the temperature range during which the HPL $\rightarrow$ GYR OOTs for **34** and **35** occurred. As observed with the LAM $\rightarrow$ HPL OOT, the HPL $\rightarrow$ GYR transition occurred over a wider, lower temperature range for **34** (117 °C to 151 °C) than it did for **35** (168 °C to 186 °C). This may indicate that the higher molecular weight of the aPP tail in **35** (with N_{aPP} more than double N_{aPP} of **34**) caused slower transformation kinetics. The highly ordered GYR phase formed during the OOT was confirmed by the appearance of strong peaks at the characteristic q -value ratios of $\sqrt{6}$, $\sqrt{8}$, $\sqrt{16}$, $\sqrt{20}$, $\sqrt{22}$, $\sqrt{24}$, $\sqrt{26}$, $\sqrt{30}$, $\sqrt{32}$, $\sqrt{38}$, $\sqrt{42}$, $\sqrt{46}$, $\sqrt{48}$, and $\sqrt{50}$ (Figure 5.5 and Supplemental Results) and lasted from 151 °C to 214 °C for **34** and 186 °C to 230 °C for **35**.³⁴ The domain spacing calculated from q_1 is 5.2 nm.

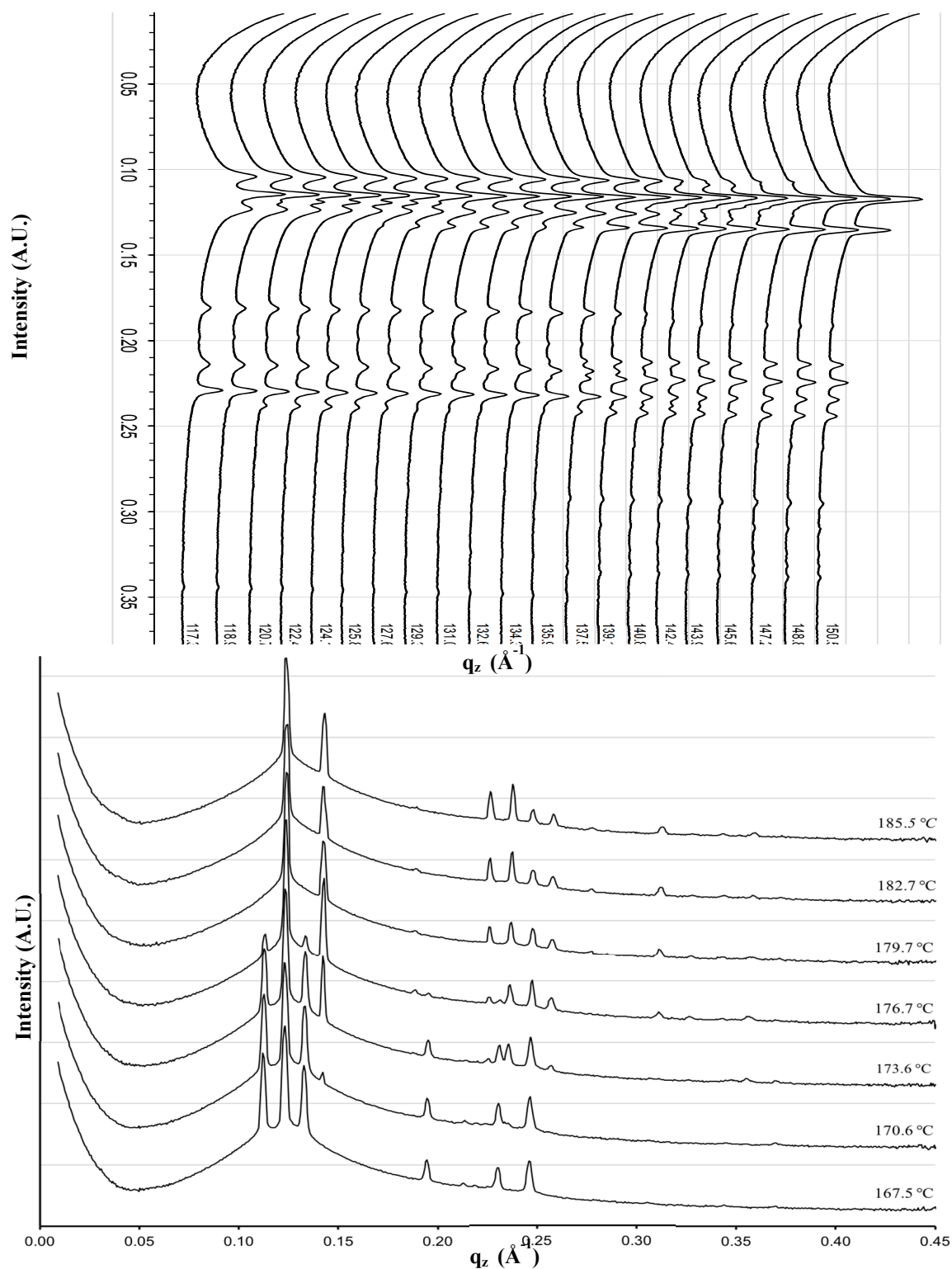


Figure 5.4: SAXS profiles for **34** (top) and **35** (bottom) during a heating ramp at the given temperatures showing HPL $\rightarrow$ GYR OOTs. Successive profiles are shifted in intensity for clarity.

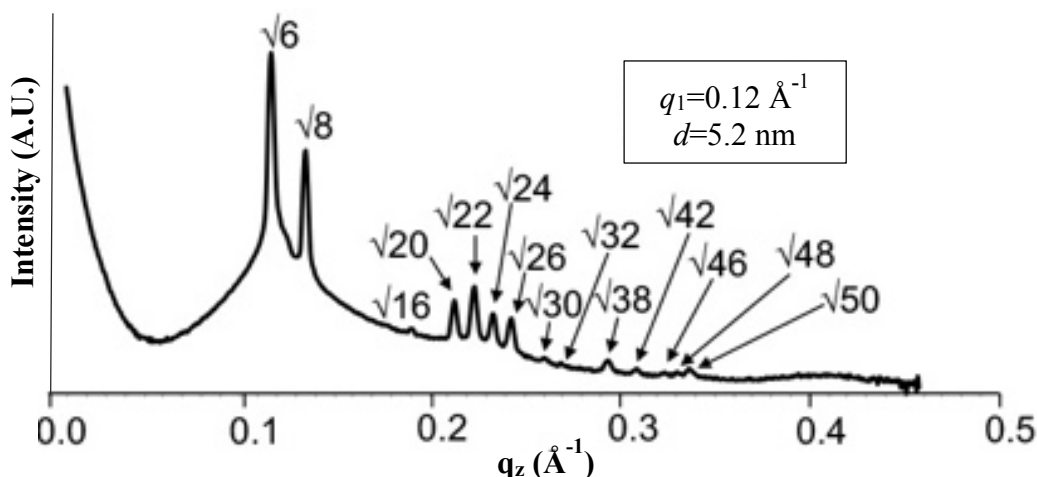


Figure 5.5: SAXS profile of **34** (GYR) recorded during a heating ramp at 160 °C

Due to the wealth of potential applications, it was of interest to determine the stability of the GYR phase upon cooling to room temperature. To accomplish this, a bulk sample of **34** was rapidly heated to 160 °C, held isothermal for 20 minutes, then cooled back down slowly *in vacuo*. The SAXS profile was then recorded again at room temperature. Gratifyingly, no loss of order or phase transitions occurred upon cooling. The GYR phase was highly ordered, accessible over a wide temperature range, and was a stable structure.

5.4.4 Gyroid to Cylinder Phase Transformation

Another OOT that has been investigated in BCPs is the GYR → HEX transition, which also occurs in an epitaxial manner. Several different mechanisms for this transformation have been reported, but in general, an axis of the GYR structure is converted to the cylinder axis of the HEX structure, and the tripodal skeletons of two gyroids connect to form a cylinder.^{35, 36} **34** underwent this OOT upon heating past the

stable gyroid phase, showing a transitional temperature range from 214 °C to 225 °C, and a stable HEX phase from 225 °C to 240 °C (Figure 5.6). Unfortunately, a T_{ODT} was not able to be determined because the maximum temperature of the heating stage was 240 °C. For **35**, the first indication of a phase transition was observed at 225 °C by the broadening of the principle scattering peak, however at 240 °C the material was still a weak, less-ordered GYR phase (Figure 5.6c). The hexagonally packed cylinders

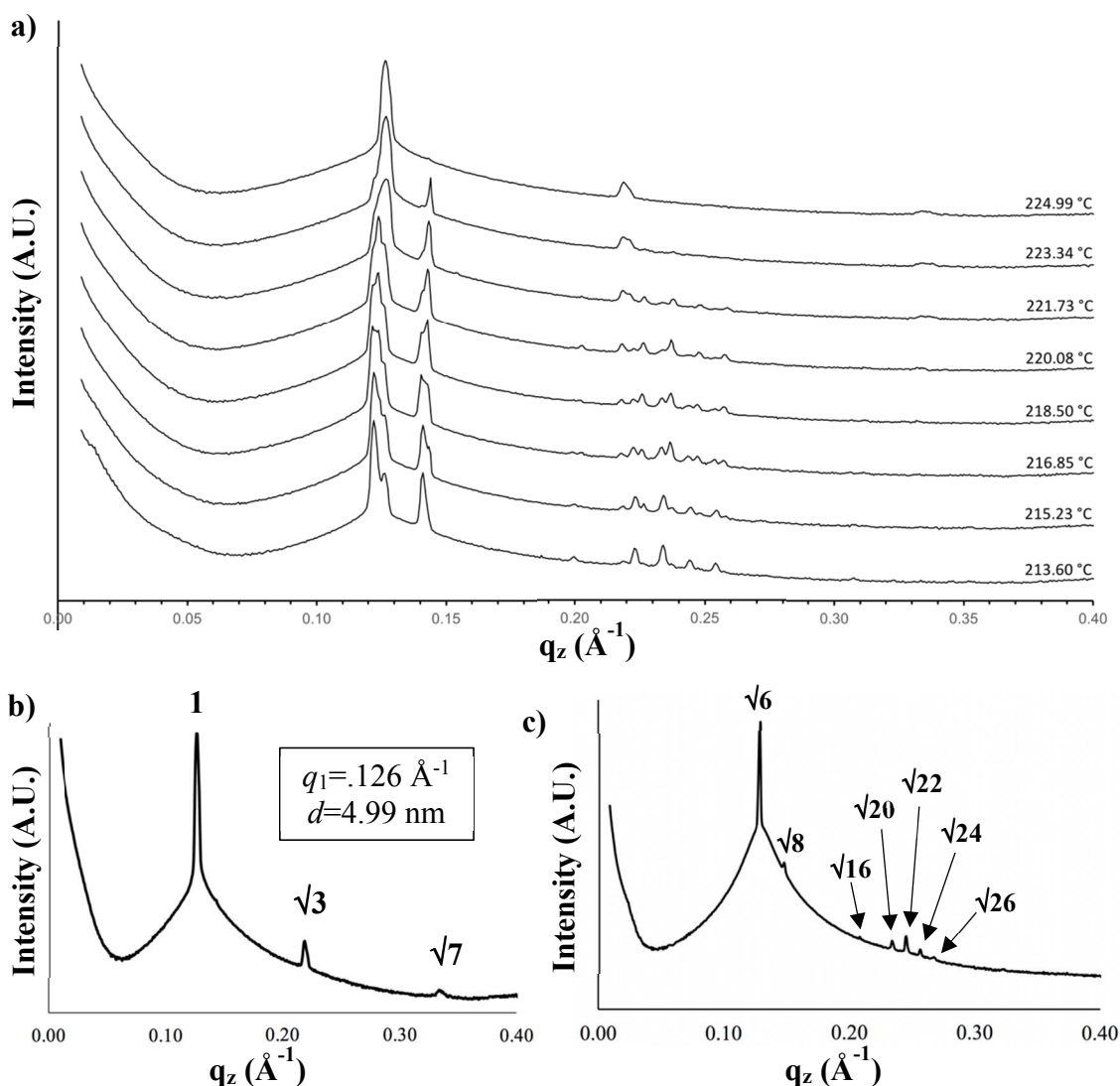


Figure 5.6: a) SAXS profiles for **34** during a heating ramp at the given temperatures showing GYR $\rightarrow$ HEX OOT. Successive profiles are shifted in intensity for clarity; SAXS profiles of b) **34** (HEX) and c) **35** (GYR) at 240 °C

were identified in **34** by the peaks at the characteristic q -value ratios at 1, $\sqrt{3}$, and $\sqrt{7}$. The characteristic peak at $2q$ was not observed, but the two higher order peaks were sufficient to conclusively determine morphology. The cylinders had a domain spacing of 4.99 nm.

5.5 Thin Film Preparation

Previous studies conducted at the University of Maryland described in Chapter 4 investigated the phase behavior of **34** at low temperatures (e.g. < 100 °C). However, given the discovery of several order-to-order transitions during thermal annealing of the bulk material to produce an incredibly rich phase behavior, there was significant motivation to explore the thin film self-assembly at higher temperatures as well. Thin films of **34-37** were prepared by spin-casting from solutions in 1:1 butanol/hexanes onto carbon-coated Si (100) substrates. For the experiments described here, films of three different thicknesses were made by spin-casting from either 0.25 %, 1.0 %, or 3.0 % (w/v) solutions to produce films with average thicknesses of 15 nm, 65 nm, and 150 nm respectively. All GISAXS experiments were performed in a vacuum chamber on an automatic temperature-controlled heating stage.

5.6 GISAXS Linear Temperature Ramp Experiments

In the context of this document, a linear temperature ramp refers to an increase in temperature at a constant ramping rate of 1°C/min. Replicates of thin film samples were probed during the heating ramp to provide details about the *in-situ* phase behavior of the conjugates. The first film investigated was that of **35** with a thickness of 65 nm.

As observed with the SAXS experiments of the same material in the bulk phase, the thin films exhibited remarkably rich phase behavior. A series of order-to-order transitions (OOTs) were observed during heating from 30 °C to 240 °C, including LAM $\rightarrow$ HPL $\rightarrow$ GYR $\rightarrow$ HEX as shown in Figure 5.7. Given the maximum temperature

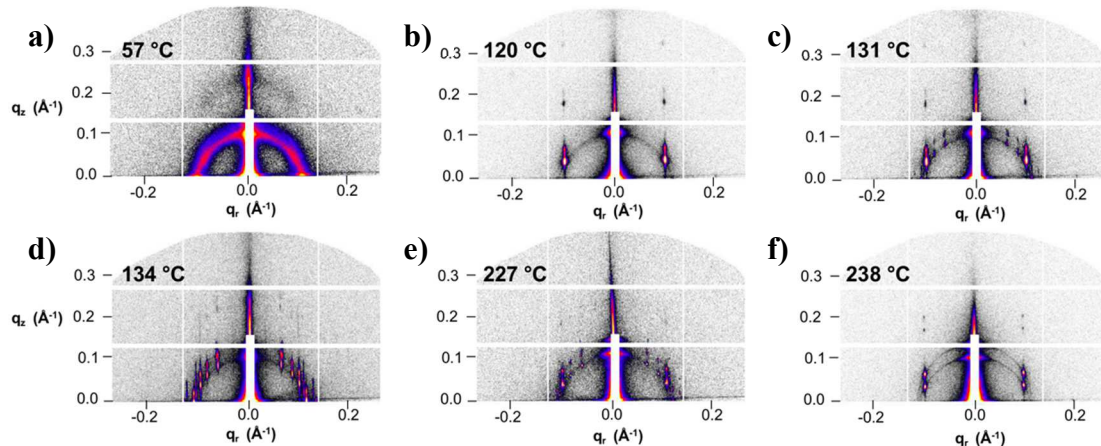


Figure 5.7: 2D GISAXS patterns at the incidence angle of 0.15° with a 10 s exposure time of thin films of **35** (65 nm thick) taken during a linear temperature ramp (1 °C/min from 30 °C to 240 °C) at the given temperatures showing the formation of a) isotropic LAM, b) HPL, c) a mixture of HPL and G, d) G, e) a mixture of G and C, and f) C phases.

capacity of the heating stage at 240 °C, further heating was not possible. Thus, the order-to-disorder transition temperature (T_{ODT}) for this material is greater than 240 °C but currently undetermined. Each phase formed during heating displayed extremely well-defined, highly ordered domains, with small temperature ranges during which two phases coexisted. The temperature ranges at which each phase/mixture of phases exists are summarized in Table 5.2. These results will be discussed in more detail in the subsequent sections of this chapter.

Table 5.2: Temperature ranges for morphologies and OOTs observed by GISAXS during linear temperature ramp of **35** (65 nm thick)

Phase	LAM	LAM + HPL	HPL	HPL +GYR	GYR	GYR + HEX	HEX
Range (°C)	30-74	74-78	78-129	129-134	134-219	219-224	224-240+

5.7 Factors Affecting Thin Film Self-assembly

5.7.1 Film Thickness and aPP Chain Length

As described in Chapter 1, in both BCP and surfactant self-assembly the occupied volume of the block or tail plays an important role in determining the shape and size of self-assembled structures. Therefore, in an effort to gain a better understanding of the rich phase behavior of sugar-polyolefin conjugates, CB-aPP conjugates with varying aPP chain lengths were synthesized as previously described. In addition to conjugate **35** described thus far with N_{aPP} of 13, thin films of conjugates **34** and **35** with N_{aPP} of 31 and 62, respectively, were investigated by GISAXS. Additionally, three different film thicknesses (15 nm, 65 nm, and 150 nm) of each conjugate were investigated as well. Figure 5.8 illustrates the phases and their respective transition temperatures for a total of nine films (**34**, **35**, and **36** at three film thicknesses each).

There are several trends to take note of when considering the effects of film thickness and aPP chain length. First and most notably, doubling the degree of polymerization from 31 (**34**) to 62 (**36**) caused a significant decrease in the richness of phase-behavior within the thin films. For the 15 nm and 65 nm films of **36** only two phases were observed (isotropic LAM and HPL) before becoming disordered upon heating.

Increasing the film thickness, which allows the thin film to behave more like the bulk material by decreasing confinement effects (e.g. film thickness and substrate interactions), showed the emergence of a short-lived, weakly ordered mixed GYR phase before becoming disordered. This phenomenon has been observed before in classic PS-*b*-PI BCPs, which favored layered structures such as LAM and HPL in thinner films (less than eight times the domain size).³⁷ The lack of nanostructural diversity in this case was attributed to a lack of molecular mobility due to the higher molecular weight of the aPP tail.

For **34** and **35**, the LAM, HPL, GYR, and HEX phases were present for all film thicknesses. The significance of observing stable GYR phases in such films will be discussed in detail in Section 5.8. However, the transition temperatures and the ranges over which certain phases existed changed for each conjugate and film thickness. For conjugate **35** with the shortest N_{aPP} , the complex phases (HPL and GYR) were longer-lived than the layered structures. Additionally, it was observed that the T_{ODT} decreased with both increasing N_{aPP} and increasing film thickness.

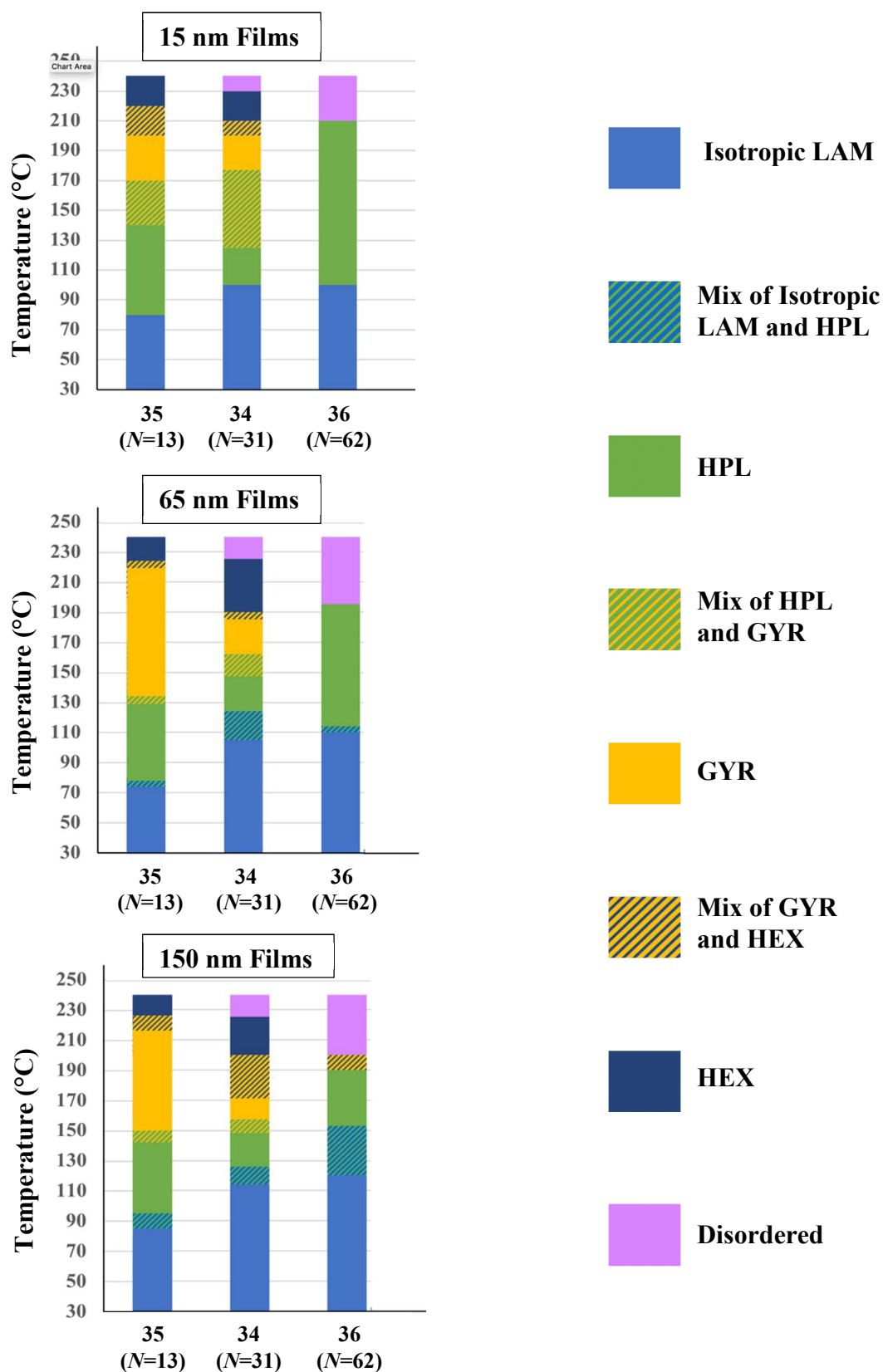


Figure 5.8: Phases and their respective transition temperatures for 34-36

5.7.2 Processing History

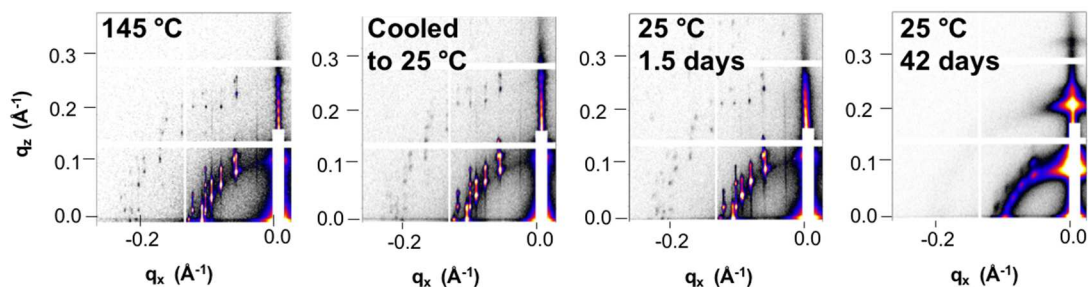


Figure 5.9: 2D GISAXS patterns at the incidence angle of 0.15° with a 10 s exposure time of thin films of **35** (150 nm thick). The thin film was heated quickly to 145 °C (GYR range) and cooled *in vacuo* to room temperature. The films were then stored under ambient conditions for 1.5 days and 42 days and GISAXS was recorded. The films showed a stable GYR structure on the time-scale of days with some loss of order over longer time-scales.

The thin film self-assembly of the sugar-polyolefin conjugates was found to be heavily influenced by a kinetic component. For example, Figure 5.9 shows that an observed phase was stable at room temperature for days, although some loss of order was seen at longer time-scales (e.g. months), which may be attributed to other factors such as dewetting from the substrate.³⁸ A given phase could be targeted simply by heating to the appropriate temperature and holding/quenching and generally, no OOTs were observed upon cooling. This may be due to kinetic trapping of the given morphology.

The kinetics of the OOTs and phase behavior was somewhat complicated and are currently being explored further by another member of the Sita Group. Preliminary investigations found that the thin film self-assembly was highly pathway-dependent, implying strong kinetic effects. For example, in a series of experiments this effect was probed by jumping/cooling as quickly as possible to various temperatures that were

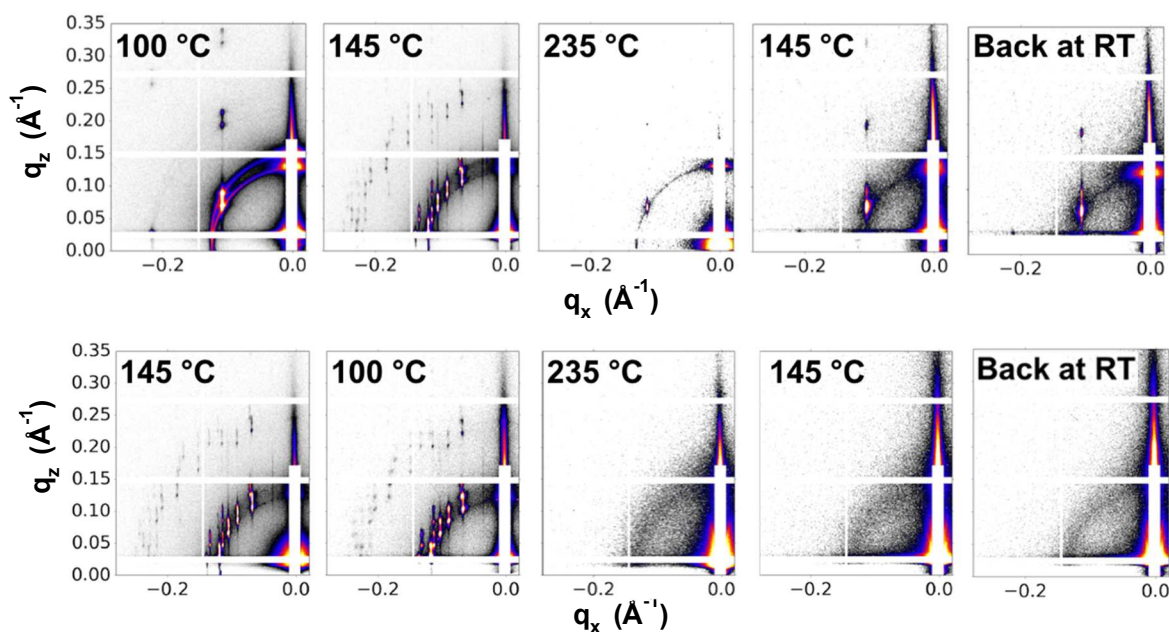


Figure 5.10: 2D GISAXS patterns at the incidence angle of 0.15° with a 10 s exposure time of thin films of **35** (150 nm thick) during different temperature jump sequences. The temperatures labelled on the patterns indicate the temperature sequence for each experiment from left to right (top and bottom represent two separate experiments).

corresponding to different phases and measuring the GISAXS in different sequences. For the first series shown in the top of Figure 5.10, the temperatures were chosen (in increasing order) to target specific phases based on the results from the linear temperature ramp experiments as shown in Figure 5.7. Indeed, each phase appeared as expected, including HPL at 100°C , GYR at 145°C , and HEX at 235°C . The last phase obtained during heating was retained upon cooling back to 25°C . However, when this experiment was repeated with a different temperature sequence (bottom of Figure 5.10), the phases that corresponded with each temperature were altered, showing GYR at 145°C as expected, but also GYR at 100°C and disordered at 235°C , which were inconsistent with the phases expected from the linear temperature ramp.

Another important characteristic of the self-assembly kinetics noted during the *in-situ* GISAXS experiments was the evidence of both rapid and slow responses to increasing temperature. For example, for **34** the emergence of new phases was quite slow, spanning up to 30 °C upon heating at 1 °C/min. If held at an intermediate temperature, the conversion from one phase to another could take more than 10 hours. On the other hand, a preferred phase appeared and coarsened extremely rapidly (e.g. less than 1 minute) when the appropriate temperature was reached quickly (Figure 5.11). While the slow response observed typically indicates limitations in molecular mobility, this was considered unlikely in this case because of the simultaneous rapid response. Thus, it was possible that either the phases were nearly degenerate in energy, or that there was some other energy barrier to phase-transformation, such as head-group interactions.

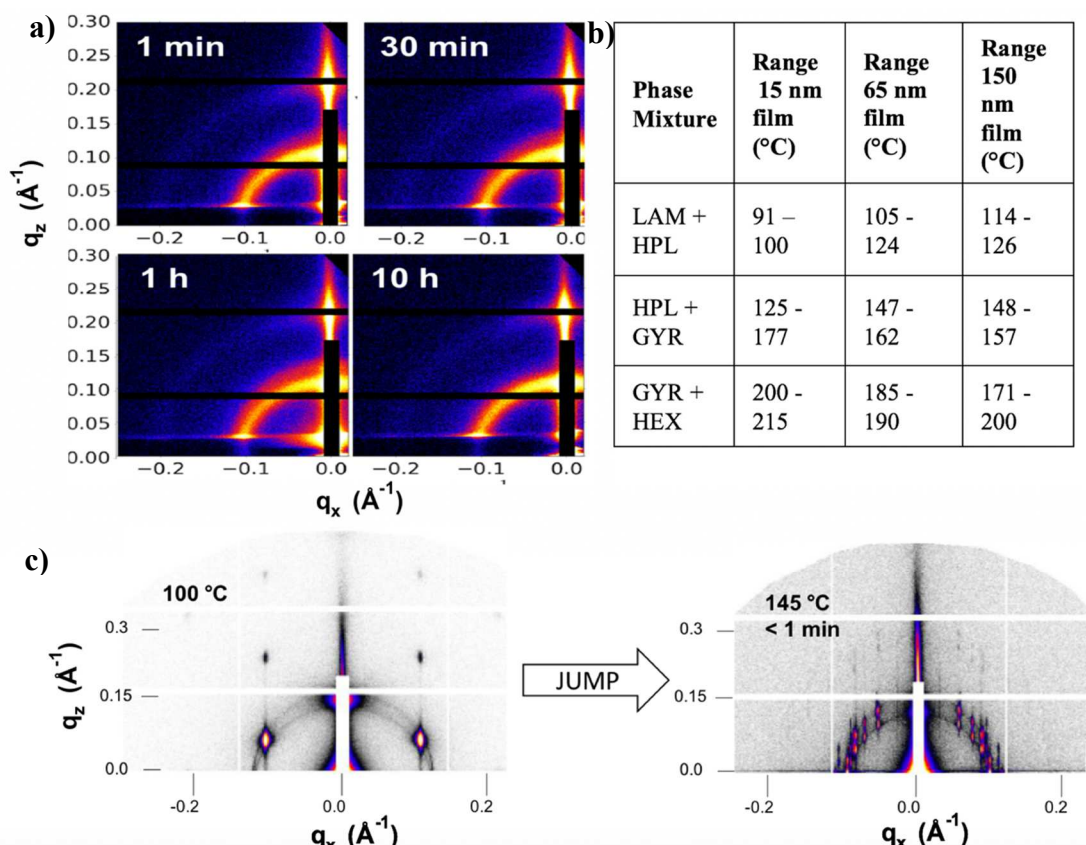


Figure 5.11: a) 2D GISAXS patterns at the incidence angle of 0.15° with a 10 s exposure time of thin films of **34** (65 nm thick) taken while being held isothermal at 60°C for 10 h. The phase is consistently isotropic LAM. b) Temperature ranges at which there was a coexistence of phases during linear temperature ramps of **34**. c) Rapid emergence of new phase (GYR) from HPL in thin film of **34** (65 nm thick) after jumping from 100°C to 145°C

5.7.3 Changing Sugar Head-Group

As previously discussed, it was suspected that the sugar head-group played a large role in the self-assembly of the CB-aPP conjugates. Thus, to qualitatively study this effect, an analogous conjugate to **35** was synthesized using Melibiose as the sugar head-group (**37**). The aPP used for the tail of this conjugate was from the same experimental batch as that used for the synthesis of conjugate **35** and the films were

prepared and analyzed in identical manners, thus any changes in self-assembly behavior could be exclusively attributed to differences in the sugar head-group.

(D)-(+)-Cellobiose is a reducing disaccharide consisting of two glucose residues with a $\beta(1\rightarrow4)$ linkage, while Melibiose is a reducing disaccharide consisting of galactose and glucose residues with a [D-Gal- $\alpha(1\rightarrow6)$ -D-Glc] linkage (Figure 5.12). Although there are other reducing disaccharides that more closely resemble (D)-(+)-Cellobiose (e.g. Maltose, Lactose), Melibiose was chosen for two main reasons. 1) it is available in the non-hydrated form for an inexpensive cost and 2) the major differences in stereochemistry and linkages would likely result in a change in self-assembly behavior. In 2011, Hashim et al. described that in the self-assembly of glycolipids,

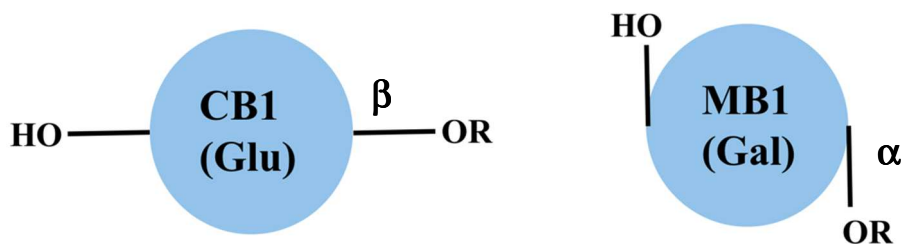


Figure 5.12: Schematic of the relative orientation between the C4 and anomeric OH groups in the first residues of (D)-(+)-Cellobiose (left) and Melibiose (right). Figure adapted from reference 39.

although similar phases were seen during self-assembly, the temperature range at which the ordered phases existed was wider for the α -galactosides, implying that axial C4 hydroxyl groups (e.g. in MB) effectively strengthen hydrogen bonding in the hydrophilic region better than equatorial C4 hydroxyl groups (e.g. in CB).³⁹

Figure 5.13 shows GISAXS patterns of unannealed thin films of **37** revealed the formation of isotropic lamellae similar to **35**. However, unlike with **35**, upon heating with a linear temperature ramp no OOTs were observed. Instead, the scattering ring continues to narrow upon heating indicating that lamellae are increasing in order. A T_{ODT} was observed at 175 °C, which is at least 65 °C cooler than the unreachd T_{ODT} of **35**. This is consistent with the observations of Hashim et al. that more energy is needed to break the hydrogen bonding interactions in α -galactosides than β -glucosides, hence a much wider temperature range for the existence of lamellae in the MB conjugate than the CB conjugate. Although this study definitely concluded that the architecture of the sugar head-group plays a significant role in self-assembly, further

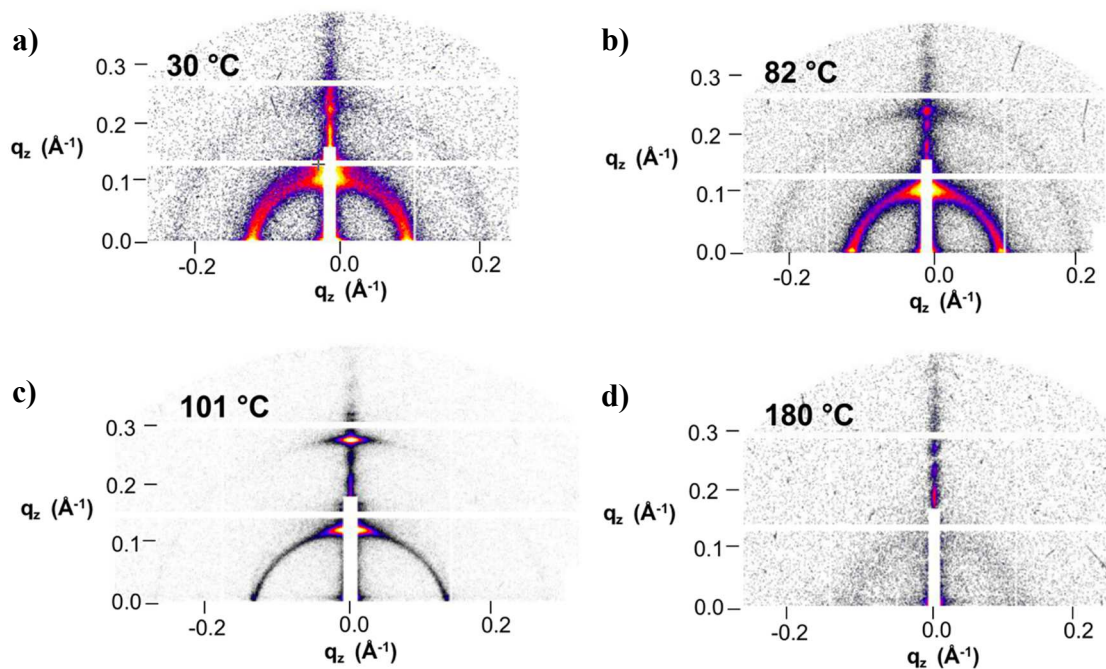


Figure 5.13: 2D GISAXS patterns at the incidence angle of 0.15° with a 10 s exposure time of thin films of **37** (65 nm thick) taken during a linear temperature ramp (1 °C/min from 30 °C to 240 °C) at the given temperatures showing the formation of a-c) LAM phase and d) disordered film

investigations are currently being performed by Group members with other disaccharide head-groups in order to more quantitatively establish the exact mechanisms of such effects.

5.8 Unprecedented Access to Gyroid Nanostructured Films

5.8.1 Current Examples in Literature

The self-assembly of soft-materials is of intense scientific interest because it can provide access to a range of morphologies with increasingly small feature-sizes and a high degree of order.⁴⁰⁻⁴² Among the various phases, e.g. lamellae (LAM), body-centered-cubic spheres (BCC), and hexagonally packed cylinders (HEX), the three-dimensional double gyroid (GYR) morphology is one of the most highly sought-after. The unique GYR phase consists of a bicontinuous, interpenetrating network within a cubic lattice and is extremely useful for practical applications in nanotechnology.⁴³⁻⁴⁵ Many applications, including nanoporous membranes, solar cells, and coatings, require nanostructured thin films (film thickness, h , $< 1\ \mu\text{m}$) or ultrathin films ($h < 100\ \text{nm}$). In this case, however, the morphology is also heavily influenced by surface effects, such as “hard” or “soft” confinement, differences in interfacial energy, and annealing method.⁴⁶ Although the GYR morphology has been extensively studied in the bulk state of BCPs and other amphiphilic materials, examples within thin films are relatively limited, and even more so within ultrathin films.^{12, 47, 48} As film thickness decreases, surface effects play an increasingly larger role in self-assembly, and it is thus challenging to obtain GYR structured thin-films even from materials that are GYR structured in the bulk. It is especially difficult to obtain GYR nanostructures within

ultrathin films because the nanostructure is destabilized when the film thickness is smaller than the unit cell parameter, a_G , of the GYR structure. GYR structured films have been reported in films with thicknesses of at least several hundred nanometers. Recently, Ryu et al. reported the stabilization of the gyroid morphology of a polystyrene-*block*-polydimethylsiloxane (PS-*b*-PDMS) BCP in solvent-vapor annealed films with a thickness range of 100-300 nm by controlling the interfacial energy of the film using a poly(vinyl acetate)-*random*-poly(vinyl alcohol) (PVAc-*r*-PVA) layer as a neutral top coat ($a_G=43.7$ nm).⁴⁹ Aissou et al. reported the stabilization of the GYR morphology in sub-100 nm films of PS-*b*-PDMS using a templated substrate and solvent-vapor annealing ($a_G=63.4$ nm).⁵⁰ Additionally, several Giant Surfactants/Giant Molecules reported by Cheng et al. form a GYR phase in the bulk,^{34, 51-55} but only one was reported to form a GYR nanostructured thin film.⁵⁶ However, the GYR film was observed after a HPL $\rightarrow$ GYR OOT only in films thicker than 200 nm, while films thinner than 200 nm underwent HPL $\rightarrow$ HEX OOTs. In a 2009 review on BCP mesostructures, Hillmyer et al. reported that the GYR has not yet been seen in BCP films with thicknesses of less than twice the bulk domain periodicity.⁵⁷ To the best of our knowledge, the GYR nanostructured films reported herein are the first to overcome this limitation in addition to not requiring external stabilization through templated substrates, matching interfacial energies, etc.

5.8.2 GYR Phase in Sugar-Polyolefin Conjugate Films

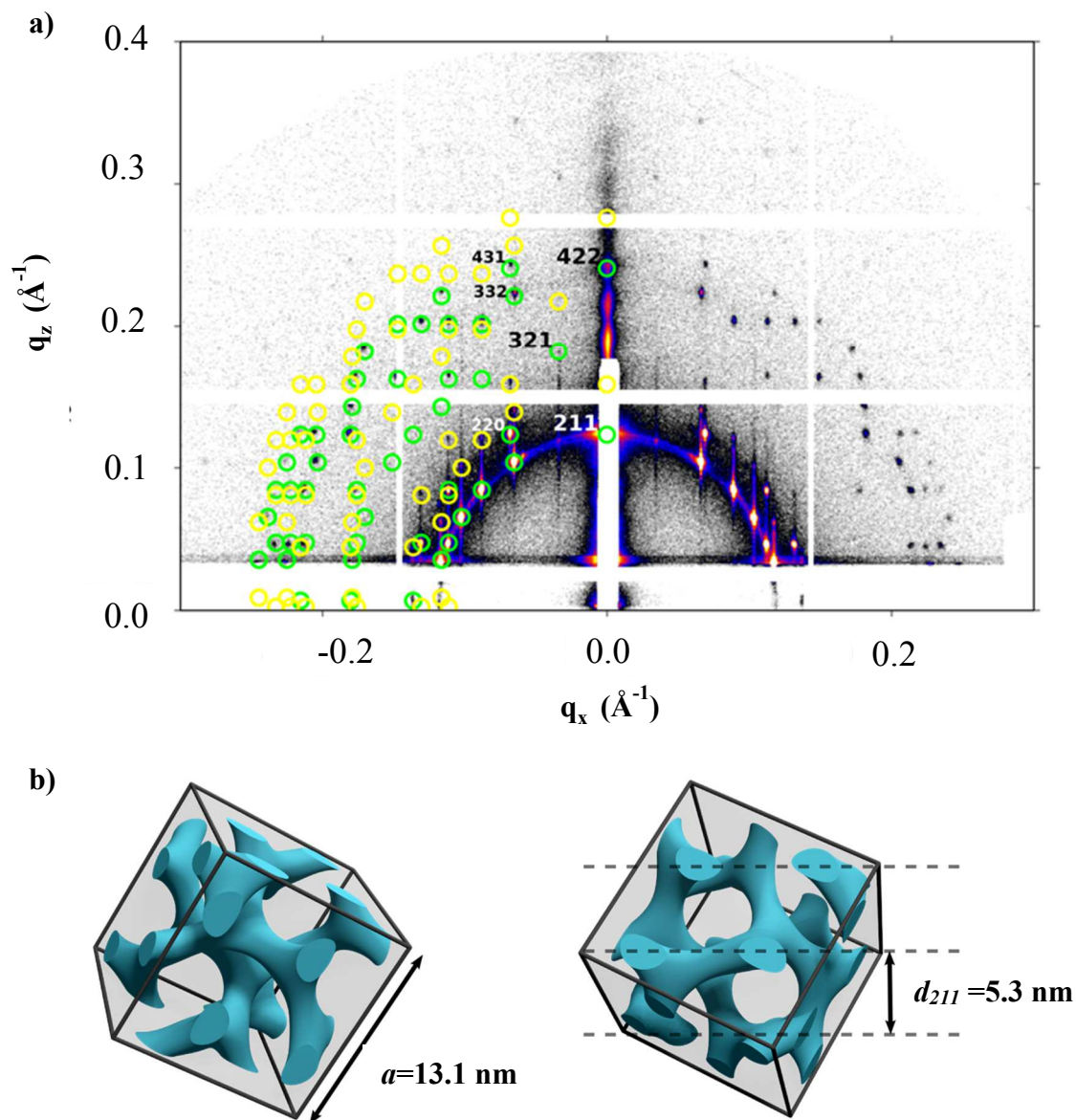


Figure 5.14: a) indexed 2D GISAXS pattern of a GYR nanostructured 150 nm thick film of **35** after thermal annealing at 145 °C for 20 min. The scattered and reflected peaks are marked by green and yellow circles respectively. b) Cartoon representations of the GYR phase with the (211) direction pointing up (in the film normal direction).

Stable, well-defined, and highly-ordered GYR nanostructures were observed in films of **34** and **35** at all three film thicknesses, including the 15 nm film. This is the thinnest GYR film to date. It was also found that the conjugate with the shortest aPP chain had the widest temperature ranges (for all three film thicknesses) at which the GYR structure existed. Figure 5.14a shows the fully indexed 2D GISAXS pattern of a representative GYR film of **35** that is in good agreement with simulated patterns.⁵⁶ The observed GYR structure is composed of a cubic unit cell with $Ia\bar{3}d$ symmetry where $a=b=c=13.1$ nm. The bright spot along the q_z axis corresponding to the (211) is indicative of the layering of this structure and showed that the nanostructures are oriented with the (211) direction pointing up (Figure 5.14b). This orientation was consistent in all film thicknesses. The coexistence of HPL and GYR phases suggest the epitaxial growth of the GYR phase from the HPL phase upon heating.^{32, 48, 58} As seen in Figure 5.9, the HPL $\rightarrow$ GYR transition was irreversible; the GYR structure was stable after being cooled to room temperature and remained stable for a time-scale of weeks.

5.9 Conclusions

The self-assembly behavior of four different sugar-polyolefin conjugates in the bulk and thin film states were investigated via x-ray scattering techniques using a synchrotron x-ray source. Three conjugates consisted of (D)-(+)-Cellobiose (CB) as the sugar head-group with aPP tails of lengths $N=31$ (**34**), $N=13$ (**35**), and $N=62$ (**36**), while one conjugate consisted of a Melibiose (MB) head-group and an aPP tail of $N=13$ (**37**). The bulk self-assembly of the CB-aPP conjugates **34** and **35** were investigated via *in-*

situ small angle x-ray scattering (SAXS) and exhibited remarkably rich, dynamic self-assembly behavior. Upon heating, conjugate **34** exhibited several irreversible OOTs including LAM $\rightarrow$ HPL $\rightarrow$ GYR $\rightarrow$ HEX. Each phase was highly ordered and contained extremely small feature sizes. Conjugate **35** displayed similar phase-behavior but the OOTs occurred at higher temperatures and over narrower temperature ranges than **34**; the final GYR $\rightarrow$ HEX transition was not observed due to the upper limit of the temperature-controlled sample stage.

The thin film self-assembly behavior of all four conjugates was also investigated via *in-situ* grazing-incidence small angle x-ray scattering (GISAXS). For **34** and **35**, analogous phase-behavior was observed in the films as in the bulk; the LAM, HPL, GYR, and HEX phases were observed in films of 15 nm, 65 nm, and 150 nm thicknesses. Again, transition temperatures varied with aPP chain length as well as film thickness, and the T_{ODT} was not observed for any films of **35**. Increasing the chain length of the aPP tail to $N=62$ (**36**) caused a decrease in the richness of phase-behavior, showing only the LAM $\rightarrow$ HPL $\rightarrow$ DIS transitions. Changing the sugar head-group to MB caused an even further reduction in phase complexity, showing only a well-ordered LAM morphology throughout heating. Of particular interest was the unprecedented formation of a stable GYR structure with extremely small feature sizes in films as thin as 65 nm and even 15 nm. Additionally, these nanostructures were stable without the aid of external stabilizing efforts (e.g. a neutral polymer top-coat or matching interfacial energies). These results demonstrated the utility of sugar-polyolefin conjugates as thermoresponsive materials with exceptionally rich self-assembly

behavior; the materials can be used to access a wide variety of stable nanostructures with exceptionally small feature sizes.

5.10 Experimental Information

5.10.1 Materials

All manipulations of air and moisture sensitive compounds were carried out under an inert atmosphere of N₂ with standard Schlenk or glovebox techniques. N,N-dimethylformamide (DMF) was dried over molecular sieves and distilled before use. Anhydrous dichloromethane and methanol were dried over CaH (N₂ atmosphere) and distilled before use. Chlorobenzene and Toluene (ReagentPlus, 99%) were dried and deoxygenated by passage over activated alumina and GetterMax® 135 catalyst (purchased from Research Catalysts, Inc.) and collected (N₂ atmosphere) prior to use. All other solvents and reagents were used as received unless otherwise noted. Precatalyst (**I**) was synthesized as previously described by our group. N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate ([PhNMe₂H][B(C₆F₅)₄]) (**II**) was purchased from Boulder Scientific and used as received.

5.10.2 Instrumentation

Gel Permeation Chromatography (GPC): GPC analysis was used to obtain molecular weight (M_n and M_w) and polydispersity (PDI) of polymers using a Viscotek GPCMax equipped with 4 columns (T2500, T3000, T4000, and T5000) in a column oven and differential refractometer (maintained at 40 °C). Tetrahydrofuran (HPLC Grade) was

used as the eluent with a flow rate of 1 mL/min). Polystyrene standards (from Polymer Laboratories Inc., 580 Da – 3,150 kDa) were used for calibration.

Nuclear Magnetic Resonance (NMR): ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy was carried out with a Bruker AVIII-600 MHz Varian spectrometer. Chloroform-*d* was used as the solvent for polymer samples and DMF-*d*7 was used as the solvent for conjugates.

Differential scanning calorimetry (DSC): DSC was used to obtain T_g values using a TA DSC Q1000 system. Samples were run in sealed hermetical pans with an empty pan as reference. A heat/cool/heat temperature program was used at a flow rate of 10 °C/min from -70 °C – 200 °C.

Small angle X-ray scattering (SAXS) and grazing-incidence small angle X-ray scattering (GISAXS): GISAXS experiments were performed at the Complex Materials Scattering (CMS) 11-BM beamline of the National Synchrotron Light Source II at Brookhaven National Laboratory. The x-ray energy was set to 13.5 keV (x-ray wavelength 0.9184 Å) using a double multilayer monochromator. Beam size was adjusted to 200 µm horizontal by 50 µm vertical using a two-slit system. Beam flux at the sample position was approximately 5×10^{10} photons/s. Small-angle scattering was collected using a photo-counting pixel-array detector (Dectris Pilatus 2M, pixel size 172 µm) positioned 2.012 m downstream of the sample. Detector data was converted to reciprocal-space (q) by calibrating using measurements of a standard sample (silver

behenate). We define q_z to be the vertical (film normal) direction, and q_x to be the orthogonal horizontal (in-plane) direction.

Samples were measured under vacuum, using a typical exposure time of 10 s. GISAXS data was collected across a range of incident angles (0.08° to 0.20°), with measurements both below and above the film critical angle. The critical angle was estimated to be 0.10° based on material makeup and density, which is consistent with the experimental position of the Yoneda scattering at small incident angle. A selection of samples was measured in grazing-incidence transmission (GTSAXS) geometry, where the beam is aligned with the downstream edge of the sample at a large incident angle (0.80°), allowing undistorted sub-horizon scattering to exit from the substrate.

For kinetic measurements during thermal annealing, measurements were conducted using an incident angle of 0.15° ; at this angle, the beam vertical spread is projected to ~ 19 mm across the sample, thereby over-illuminating the sample and averaging over a large sample area (3.8 mm^2). Samples were translated horizontally between each measurement, to prevent accumulation of x-ray induced beam damage.

Indexing of GISAXS data was performed by computing the 3D reciprocal-space positions of peaks for a candidate unit cell (at a candidate orientation), rotating peaks about the vertical (q_z) to account for in-plane isotropy (in-plane powder), projecting these peaks onto the detector (accounting for Ewald sphere curvature, and applying GISAXS refraction corrections to shift the q_z peak positions).

Atomic Force Microscopy (AFM): AFM images were obtained using a Nanoscope IIIa Multimode AFM in tapping mode (ps-tm-AFM) equipped with a silicon etched tip

along with Extender Electronics package (Veeco Inc., CA). Height and phase-shift data were recorded simultaneously under ambient conditions. Thin films of the conjugate were spun-cast (2000 rpm) from a 0.1% (w/v) solution (in 1:1 BuOH/Hexane) onto various substrates. Silicone substrates were cleaned using Piranha solution (7:3 H₂SO₄: H₂O₂), rinsed with DI water and isopropanol, and dried under N₂. Graphite and mica substrates were prepared by cleavage with tape. Film thicknesses were obtained using a Gaertner optical ellipsometer.

5.10.3 Synthesis

Synthesis of conjugates 35-37

The conjugates were prepared as described in Chapter 4 and as previously reported by our group.¹ First, I-aPP was synthesized via LCCTP with chain lengths of 13, 31, and 62, then converted to N₃-aPP. Then, click chemistry was utilized to conjugate the aPP tails to the desired propargyl-terminated disaccharide. For conjugates with aPP tails greater than 2.0 kDa, the reactions were performed at a slightly elevated temperature of 40 °C. Yields: **35** (71.1 %), **36** (41.9 %), **37** (67.3 %).

Table 5.3: Summary of I-aPP synthesis for conjugates **35-37**

Run	Eq. ZnEt ₂	Reaction time (h)	Yield (g)	M _n (kDa) ^a	PDI ^a
N=13	240	4	5.86	0.53	1.09
N=62	200	4	7.09	2.6	1.06

^aDetermined by GPC at 40 °C using THF as the eluent

5.11 References

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Chapter 6: Conclusions and Future Work

Living coordination polymerization (LCP) and living coordinative chain transfer polymerization (LCCTP) have already been demonstrated by the Sita Group to be extraordinarily useful techniques for the precise design and synthesis of polyolefin homopolymers and copolymers. As such, this research focused on two main ideas: first, to expand the LCP and LCCTP systems, and second, to explore new ways in which to utilize these valuable precision polyolefins and x-PAOs. Specifically, it was of interest to determine how simple hydrocarbon polymers can contribute to complex phase-behavior of various self-assembling systems, both amphiphilic and hydrophobic.

To induce microphase separation in hydrophobic polyolefin block copolymers, a common technique is to introduce conformational asymmetry between the components. To this end, the LCCTP system was expanded for the first time to include end-group functionalized poly(1,3-methylene cyclopentane) (PMCP) that was semicrystalline in nature and poly(1,3-methylene cyclohexane) (PMCH) that had a higher glass transition temperature than any other x-PAO available from LCCTP. These OH-PAOs were applied in a variety of ways to show their utility as nonpolar building blocks for self-assembling materials. Amphiphilic polyolefin-*b*-polyester diblock copolymers that self-assembled into various nanostructures were synthesized using OH-PAOs as macroinitiators for the ring opening polymerization of lactides and lactones, and elastomeric triblock copolymers were synthesized via the coupling of “hard” PMCH blocks and a “soft” polypropylene glycol block. It was also shown that

the undesirable crystalline properties of PMCP could be eliminated while maintaining the desirable high glass transition of PMCH by using LCP to synthesize PMCP-*co*-PMCH random copolymers with varying compositions of PMCH. Additionally, LCP was utilized to create purely polyolefin block copolymers with high degrees of conformational asymmetry with large differences both in the relative sizes of each block and of the chain stiffness of each block. Gratifyingly, several of the polyolefin block copolymers designed for this study were able to microphase-separate into ordered structures. These materials were characterized by a host of techniques, including NMR, DSC, GPC, AFM, SAXS, and GISAXS.

The Sita Group previously reported the formation of a novel monosaccharide-polyolefin conjugate system that could self-assemble into a well-defined nanostructure and gain long-range order upon thermal annealing. Using this as a foundation, new disaccharide-polyolefin conjugates were designed and synthesized in an effort to maximize the incompatibility between the two components of the conjugate while maintaining the extremely low overall degree of polymerization, and thus, the molecular mobility of the system. Not only did the CB-aPP conjugates self-assemble into well-defined nanostructures with sub-10 nm domains, but they displayed an incredibly rich and dynamic phase-behavior. The conjugates underwent multiple order-to-order transitions upon simple thermal annealing in the bulk and thin film states as revealed by SAXS/GISAXS with a synchrotron x-ray source. Because these conjugates utilize readily accessible x-PAOs that can be synthesized with precisely controlled molecular weights, a series of CB-aPP conjugates with varying chain lengths was synthesized and it was found that increasing the degree of polymerization causes a

reduction in the number of ordered phases present during annealing. Thus, an upper limit of chain length theoretically exists for the appearance of nanostructures with these systems.

Sugar-polyolefin conjugates appear to be an entirely new class of amphiphilic materials for self-assembly. They are more diverse and robust than small molecule surfactants, they are not traditional or natural-*b*-synthetic block copolymers because only one component is polymeric (nor do they do not follow the theoretical phase diagram for block copolymers), and they are smaller and more readily accessible than Giant Surfactants. The work presented here is merely the tip of the iceberg when it comes to studying these sugar-polyolefin conjugates. Let alone synthesizing a library of conjugates using various x-PAOs and sugars, the CB-aPP system must still be studied in greater detail. In order to predict and control the relationship between structure and function in sugar-polyolefin conjugates, the self-assembly behavior must be understood on a deeper level, which will come with time as more members of the Sita Group investigate this system in collaboration with experts at Brookhaven National Laboratory. Additionally, the potential applications in nanotechnology can still be explored. For example, using the nitrogen-linker as a site for functionalization for the formation of miktoarm polymers, or using the self-assembled structures, such as the bicontinuous gyroid phase, to host drug molecules or nanoparticles. These initial studies showed the ability of ultralow molecular weight x-PAOs, specifically the simple amorphous polypropylene, to dictate self-assembly on remarkably small length scales. These materials opened a window of opportunity and provided a path forward to the exploration of sugar-polyolefin conjugates.

Appendix

Included are supplemental data relevant to Chapters 2-5.

Figure S2.1: GPC Trace of 1

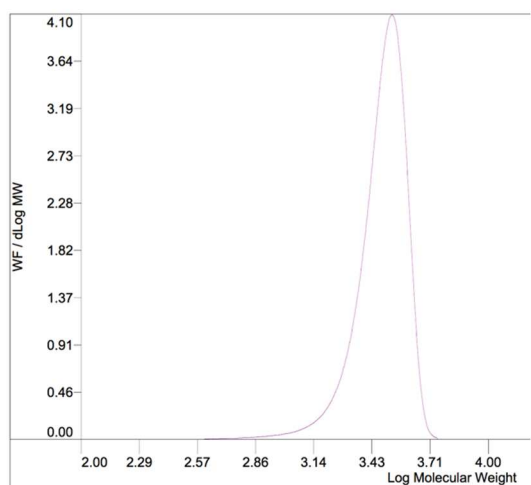


Figure S2.2: GPC Trace of 2

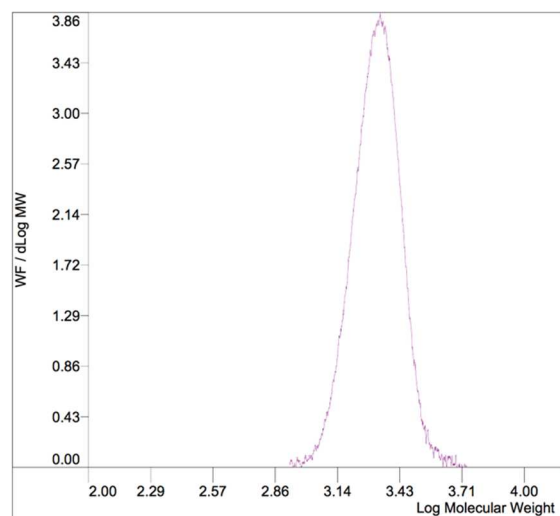


Figure S2.3: GPC Trace of 5

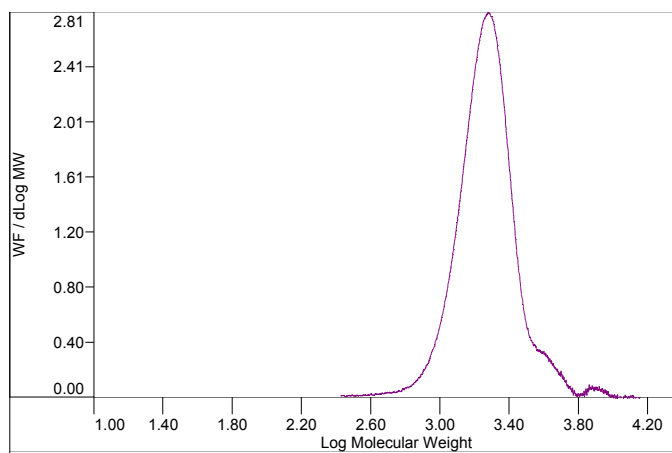


Figure S2.4: GPC Trace of **4**

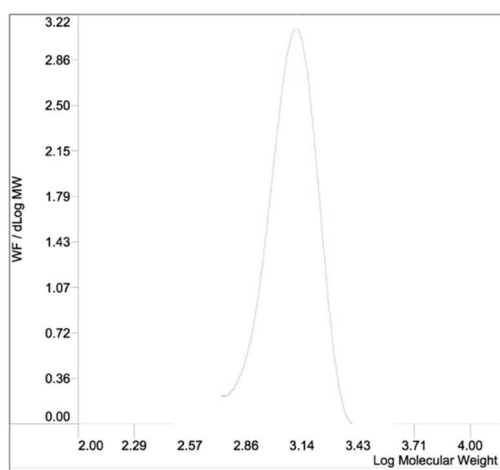


Figure S2.5: GPC Trace of **6**

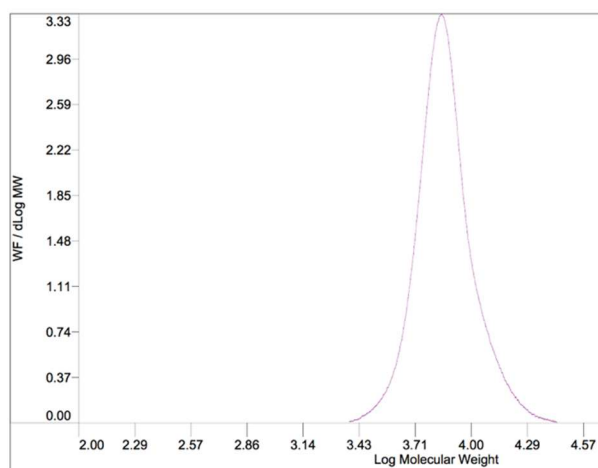


Figure S2.6: Trace of **7**

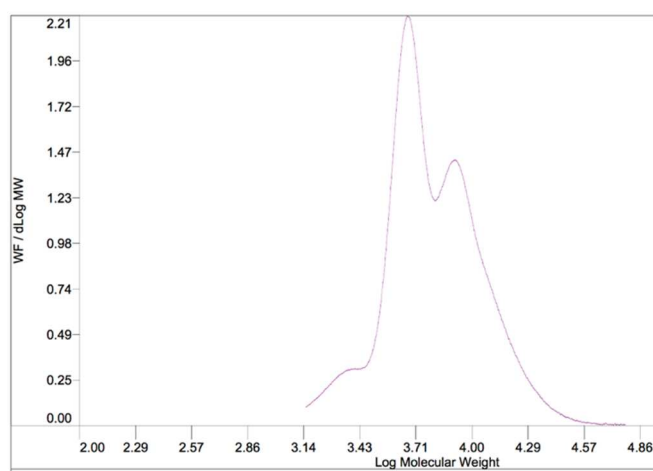


Figure S2.7: Trace of 9

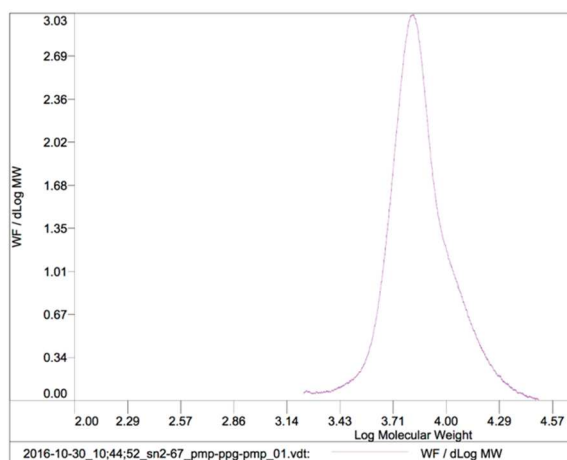


Figure S2.8: Trace of 8

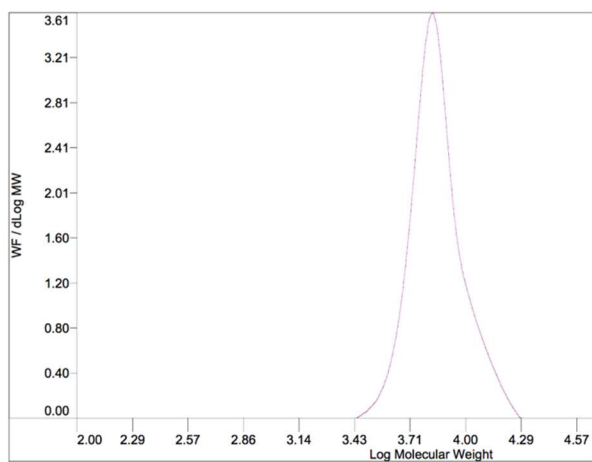


Figure S2.9: GPC Trace of 3

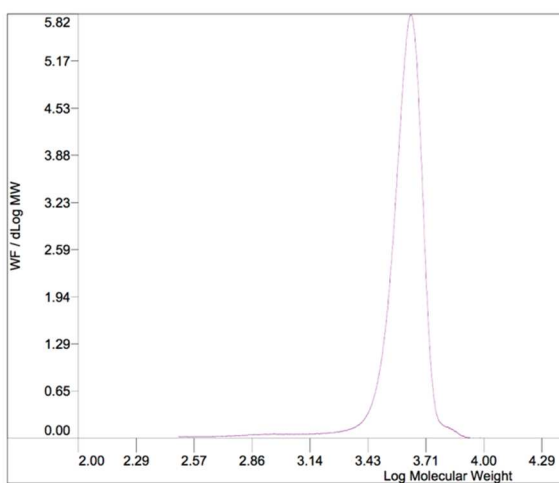


Figure S2.10: ^1H NMR (calibrated at 7.26 ppm) of **2**.

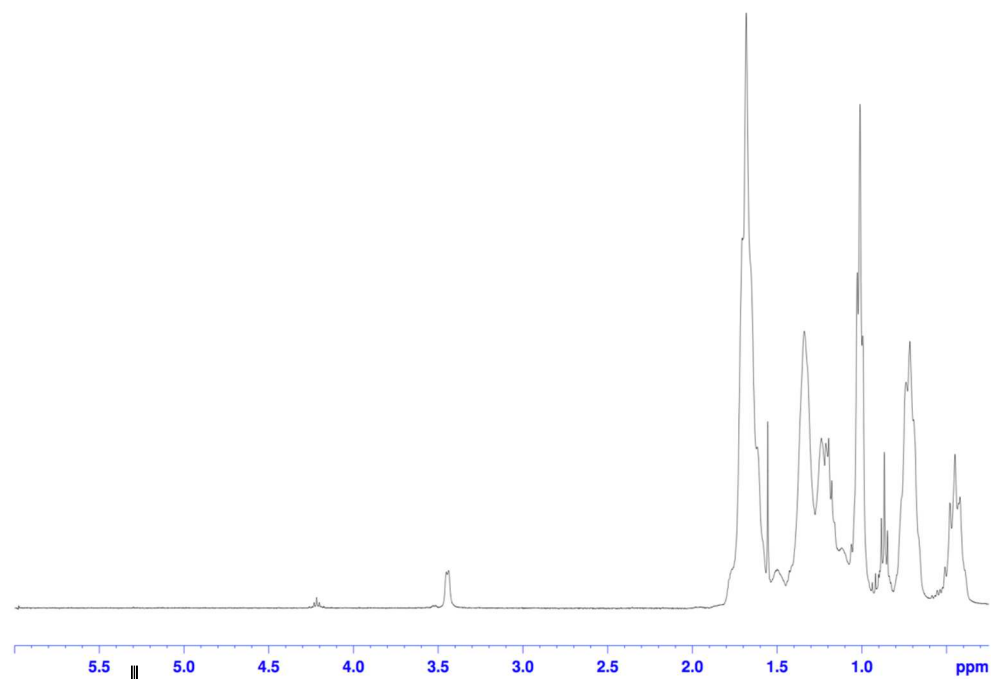


Figure S2.11: ^{13}C NMR (calibrated at 77.23 ppm) of **2**

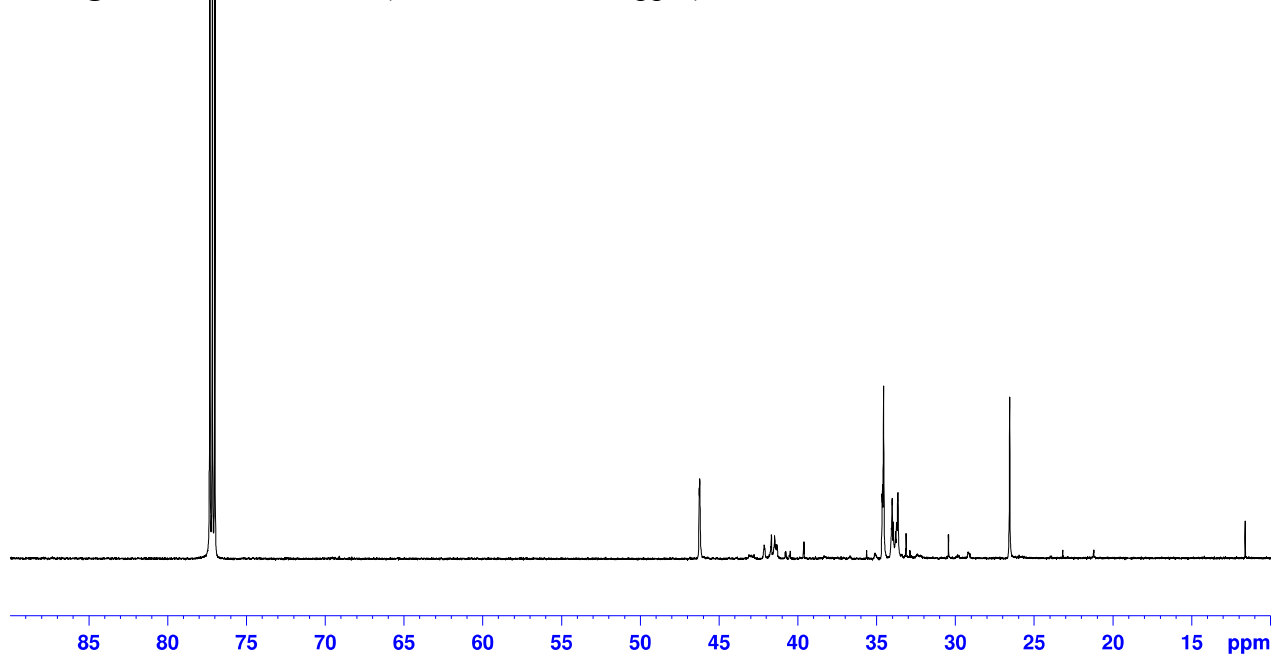


Figure S2.12: ^1H NMR (calibrated at 7.26 ppm) of **5**

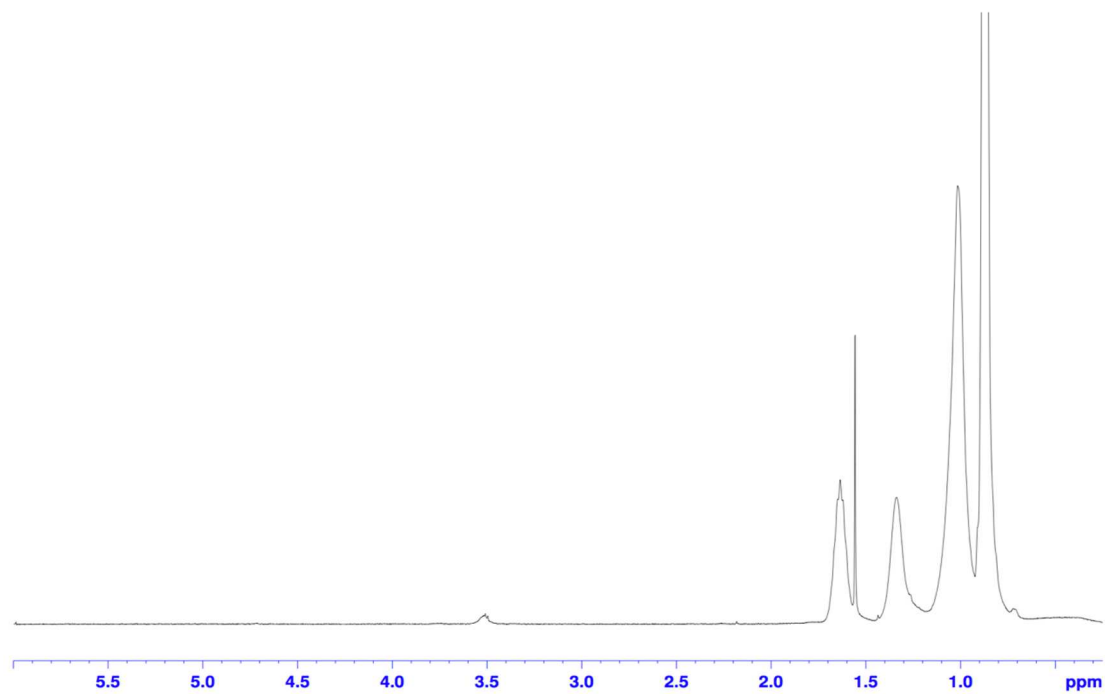


Figure S2.13: ^{13}C NMR (calibrated at 77.23 ppm) of **4**

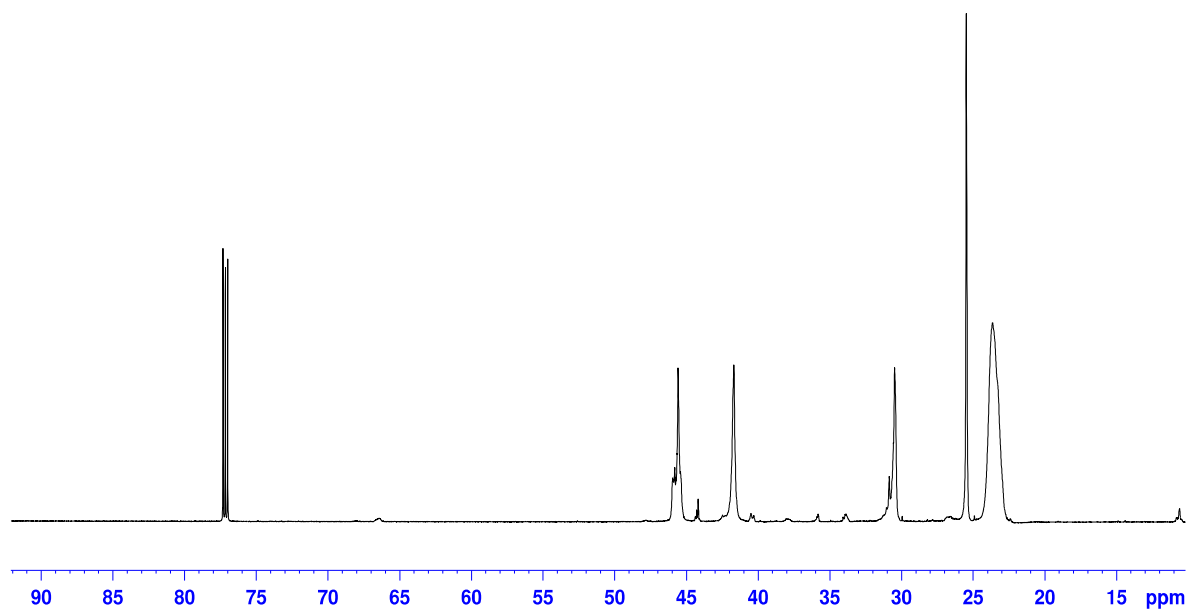


Figure S2.14: ^1H NMR (calibrated at 7.26 ppm) of **4**

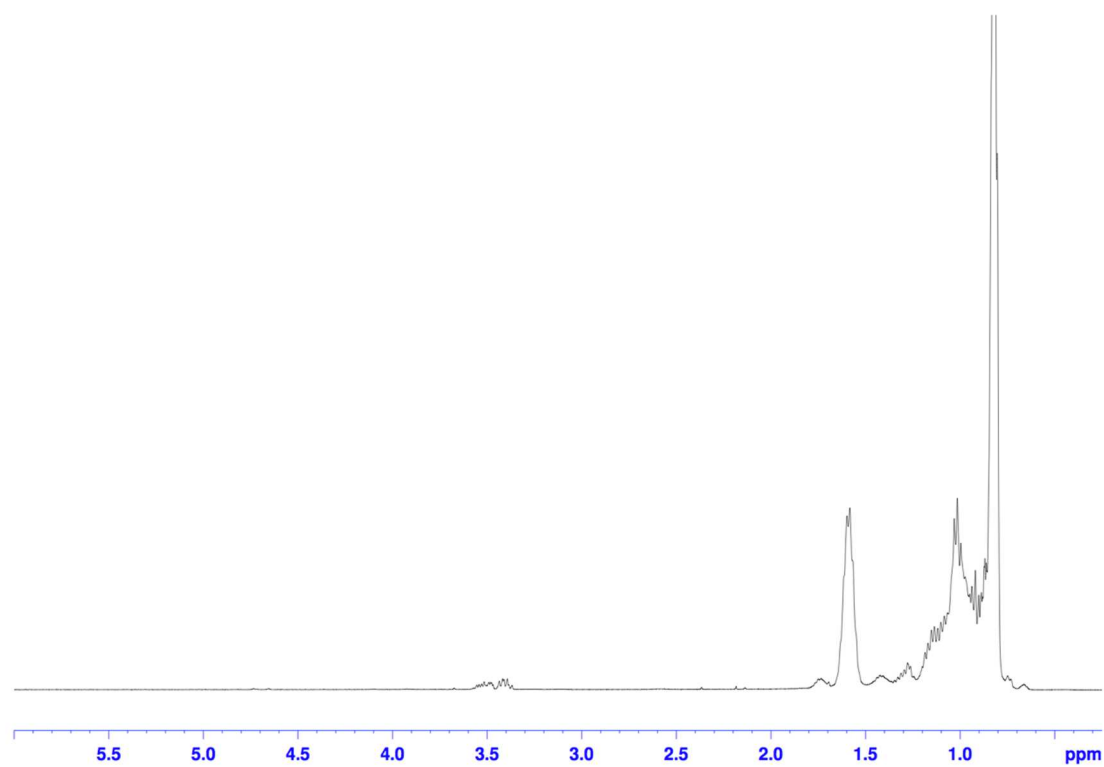


Figure S2.15: ^{13}C NMR (calibrated at 77.23 ppm) of **4**

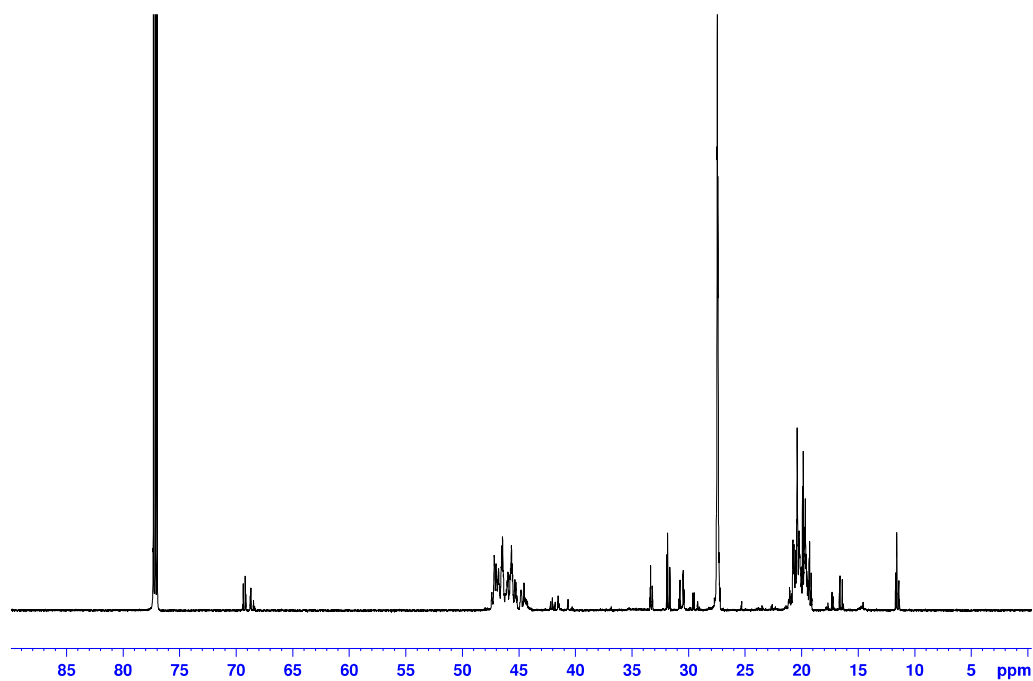


Figure S2.16: ^1H NMR (calibrated at 7.26 ppm) of **6**. Corresponding assignments were made for **7-9**

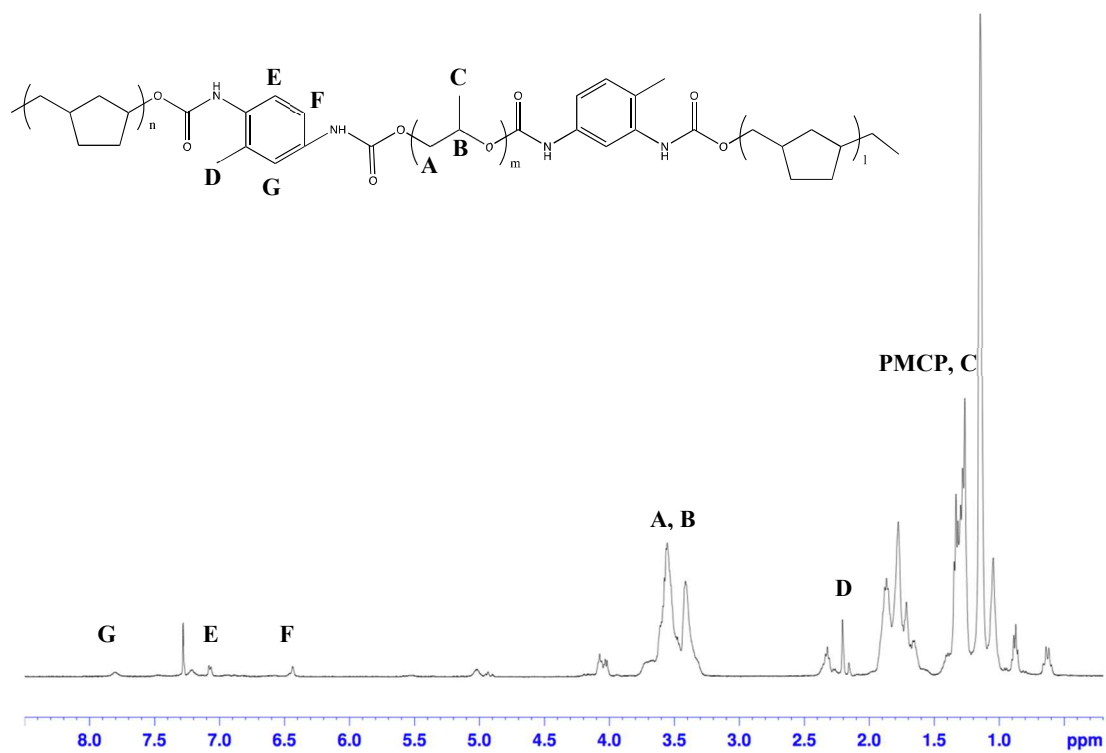


Figure S2.19: ^1H NMR (calibrated at 7.26 ppm) of **8**

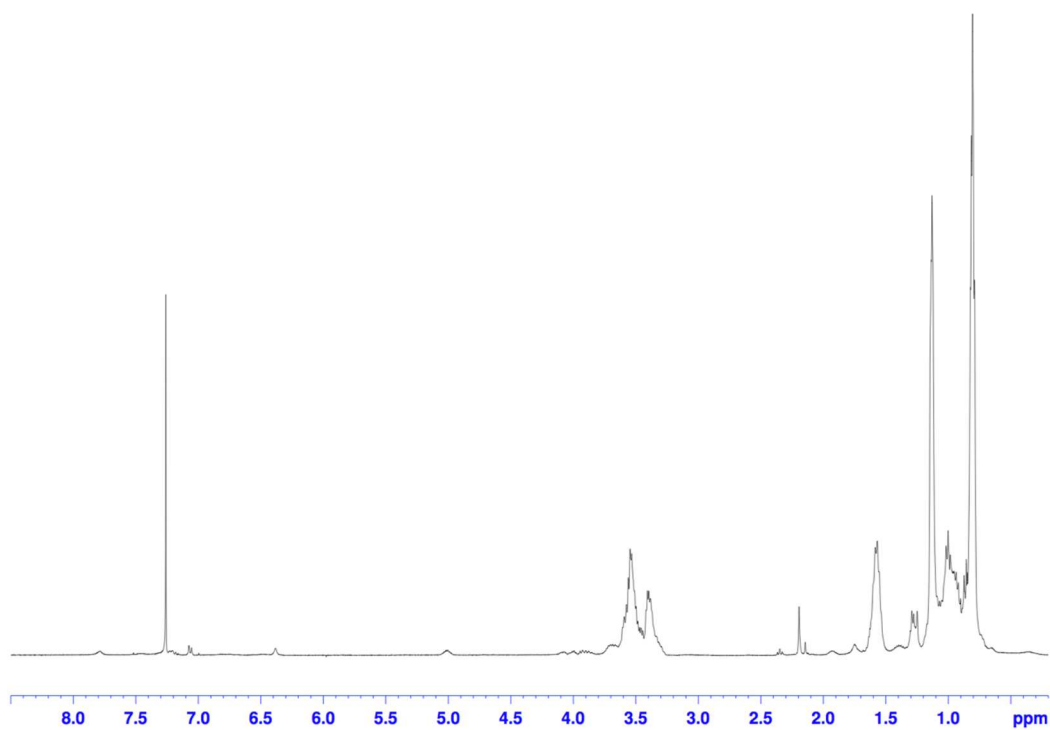


Figure S2.20: ^{13}C NMR (calibrated at 77.23 ppm) of **6**

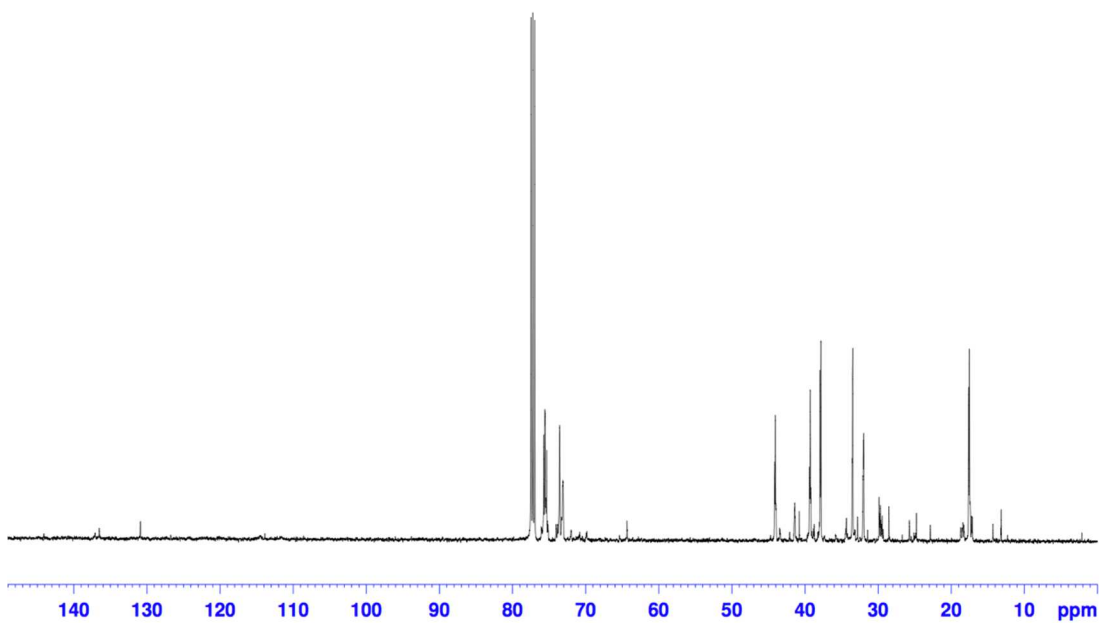


Figure S2.21: DSC of **1**. Heat/cool/heat 10 °C/min.

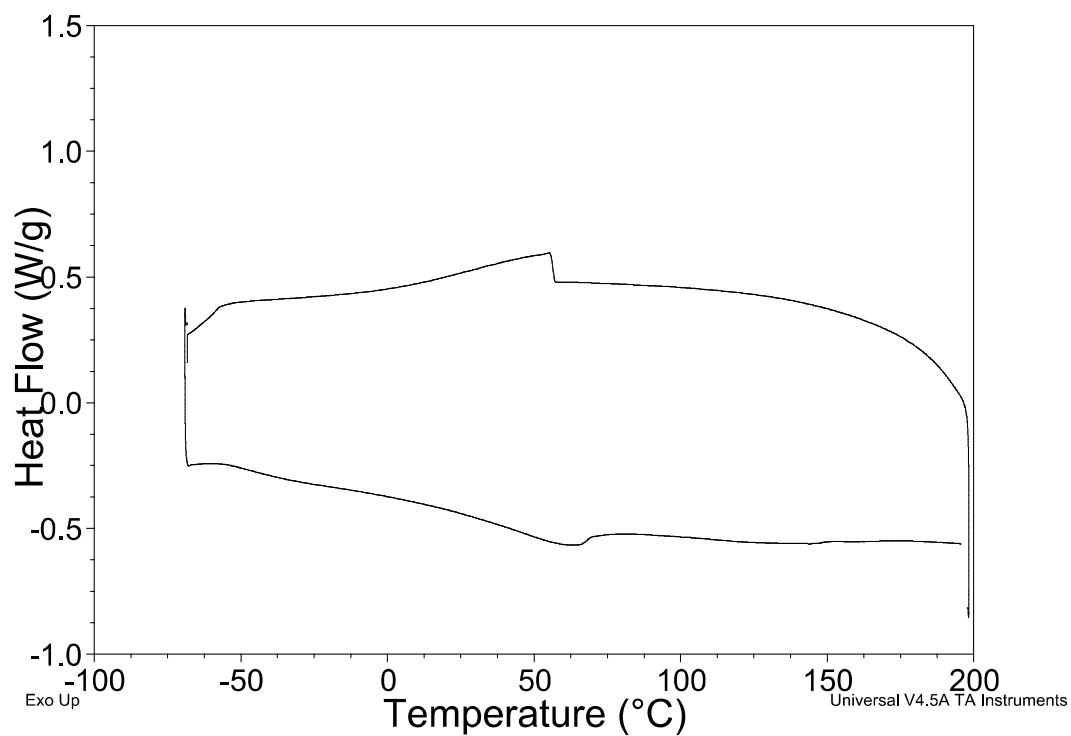


Figure S2.22: DSC of **2**. Heat/cool/heat 10 °C/min.

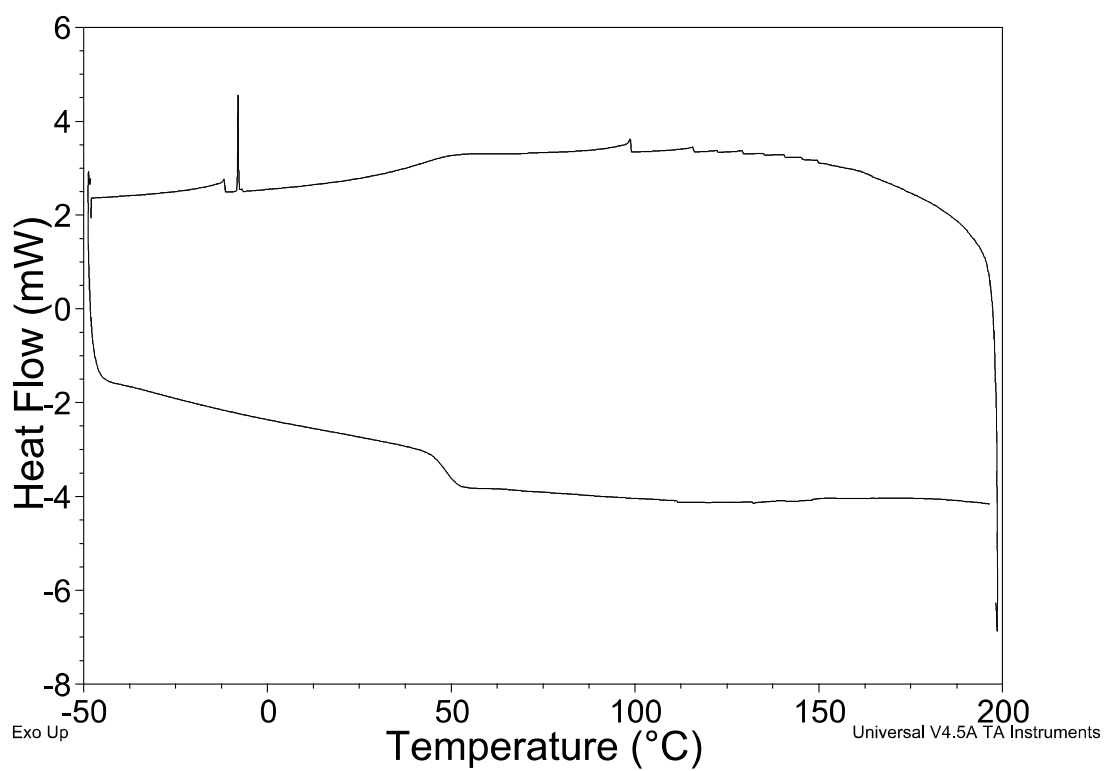


Figure S2.23: DSC of **5**. Heat/cool/heat 10 °C/min

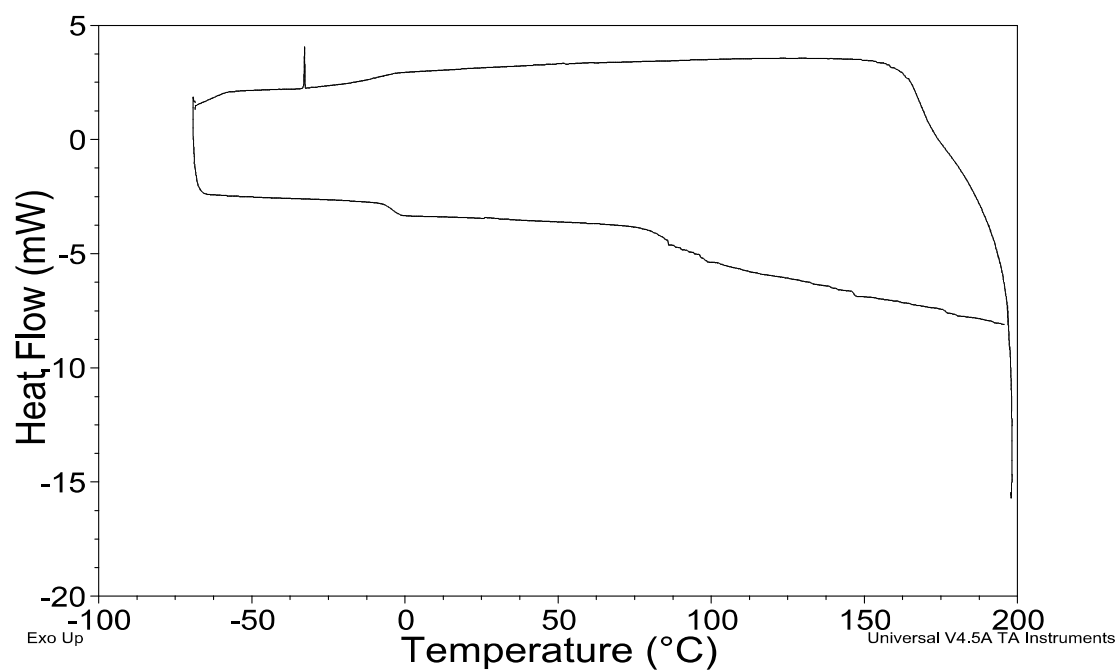


Figure S2.24: DSC of **6**. Heat/cool/heat 10 °C/min.

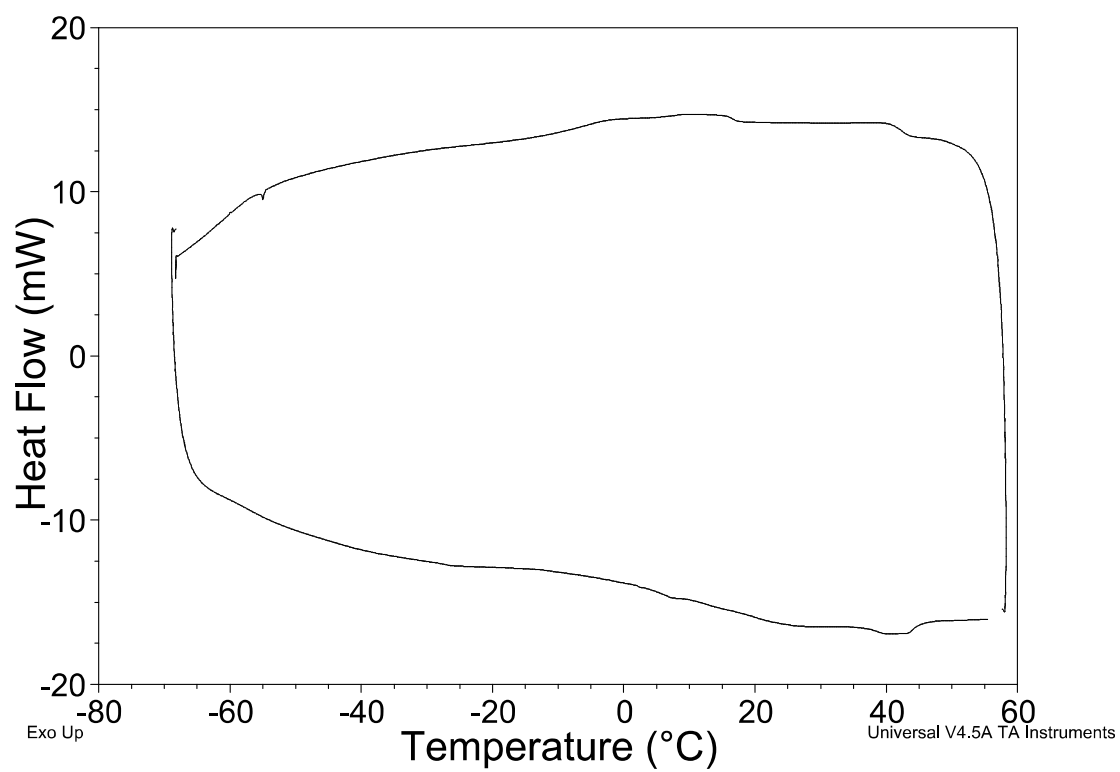


Figure S2.25: DSC of 7. Heat/cool/heat 10 °C/min.

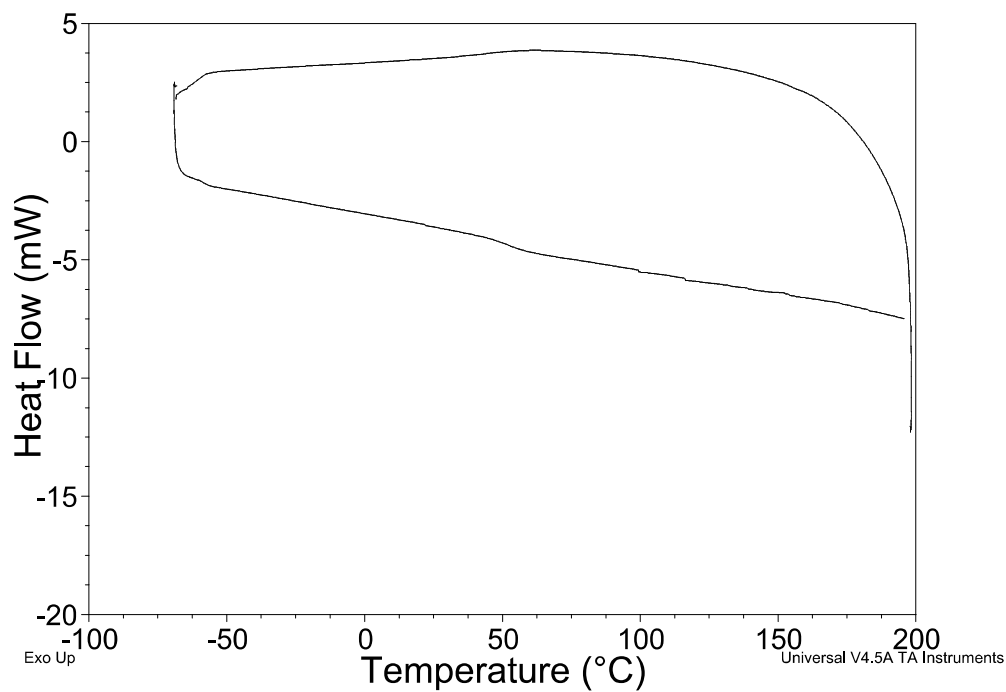


Figure S2.26: DSC of 9. Heat/cool/heat 10 °C/min.

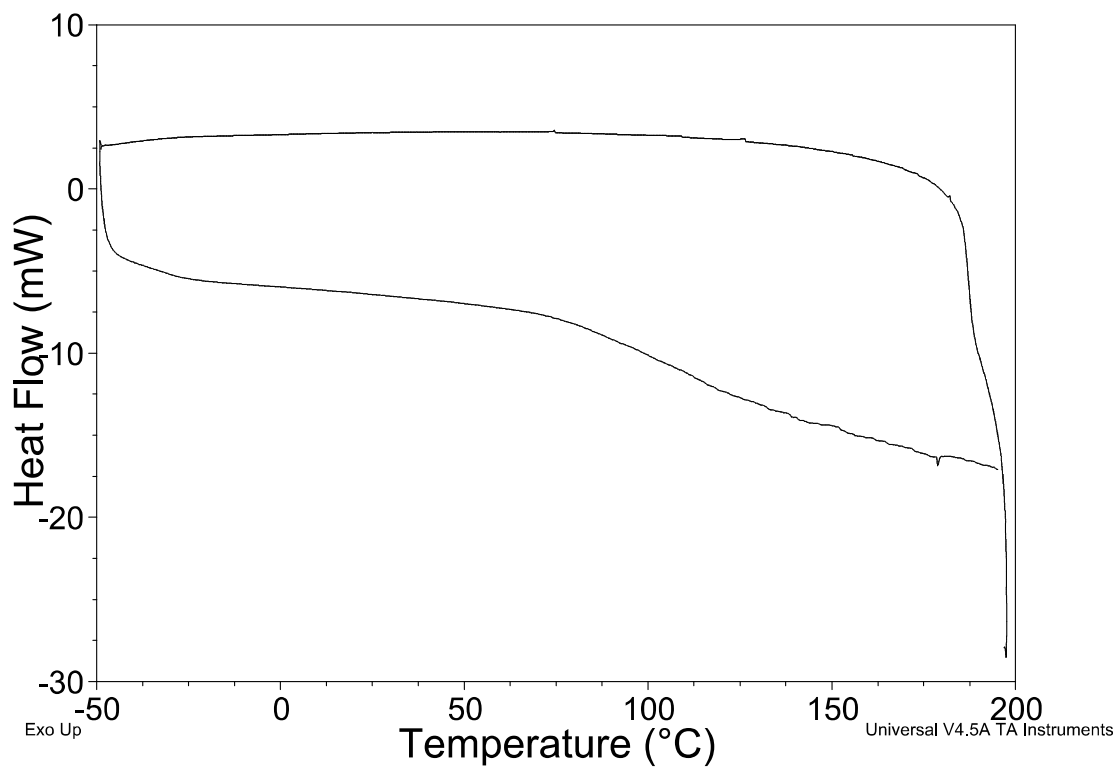


Figure S2.27: DSC of **8**. Heat/cool/heat 10 °C/min.

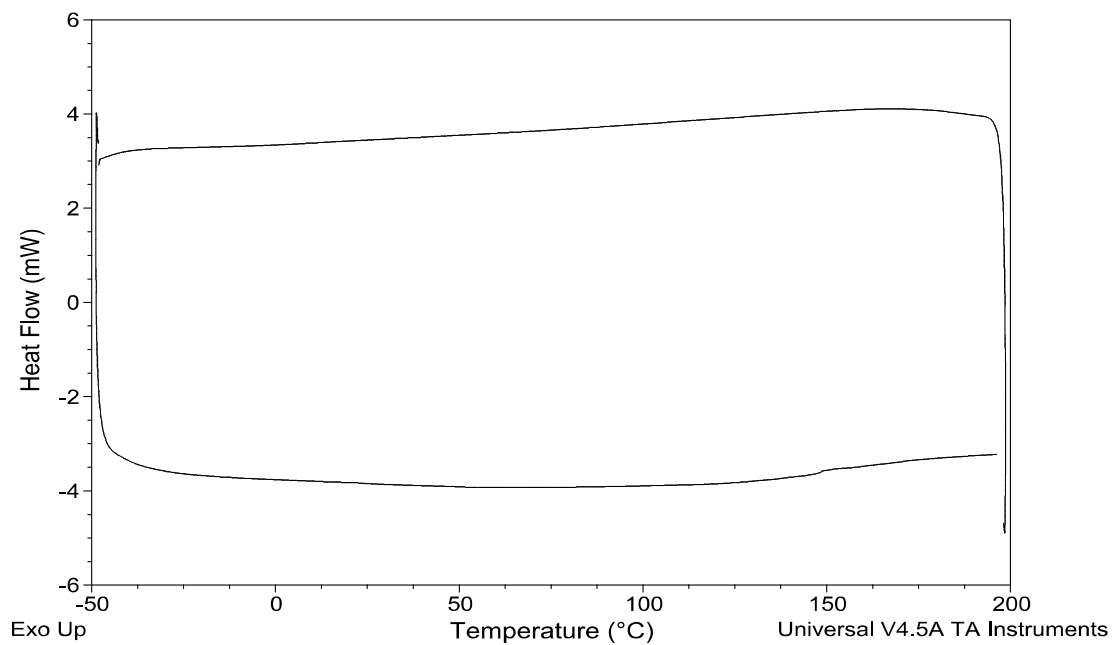


Figure S2.28: DSC of **3**. Heat/cool/heat 10 °C/min.

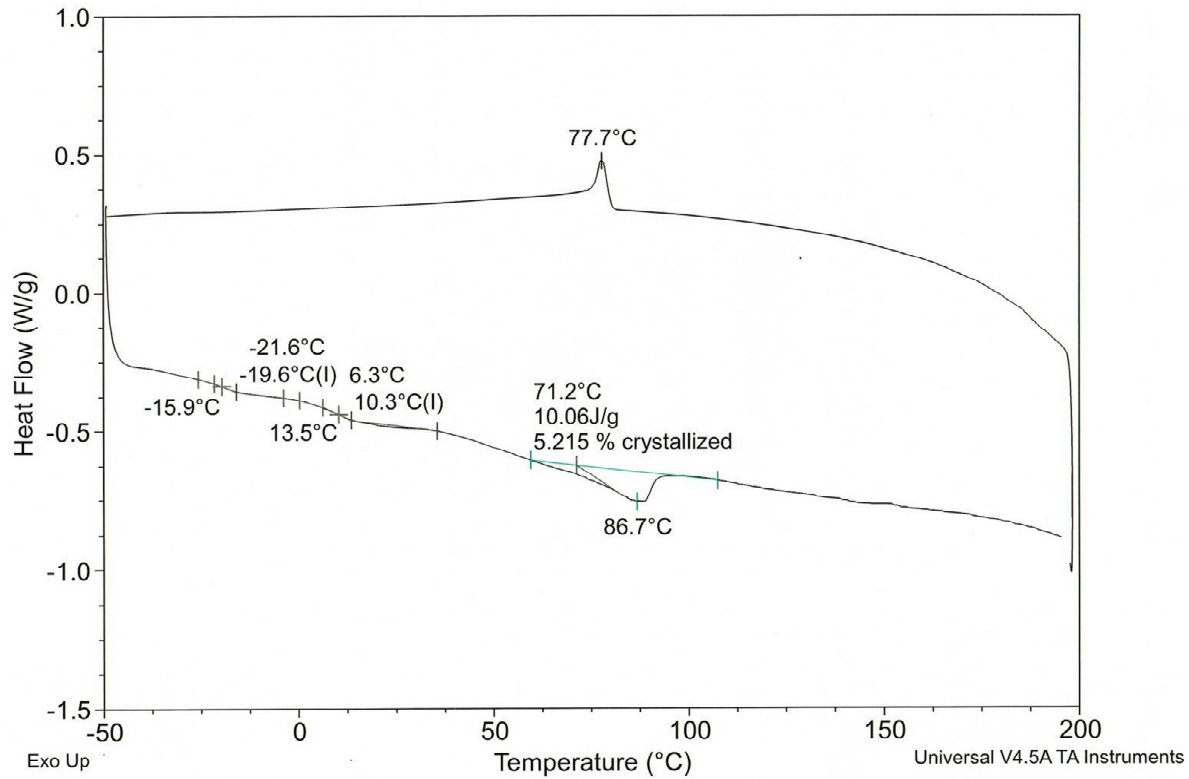


Figure S2.29: 1D WAXS plot of **6**

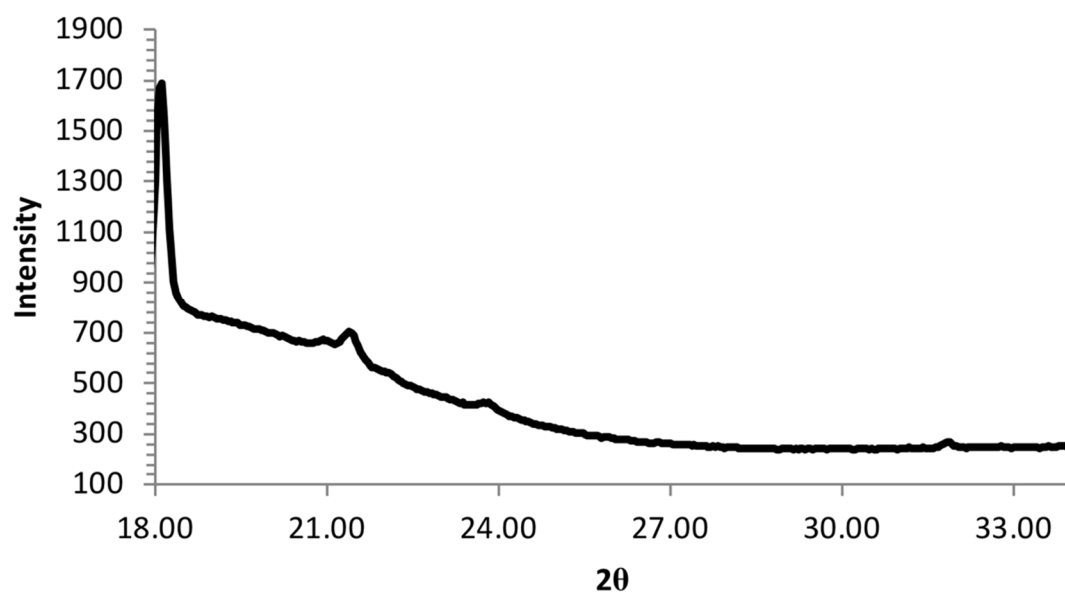


Figure S2.30: 1D SAXS plot of **9**

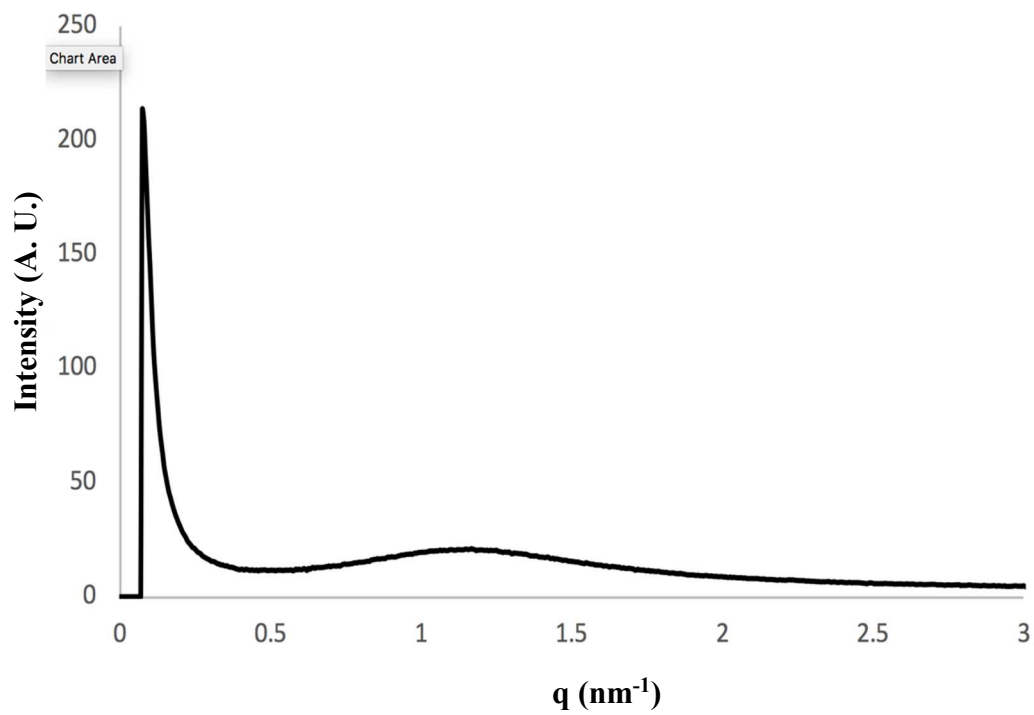


Figure S3.1: GPC trace of 10

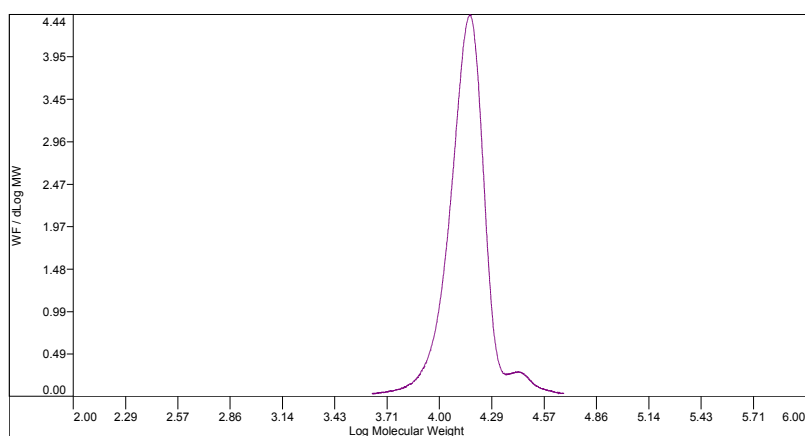


Figure S3.2: GPC trace of 11

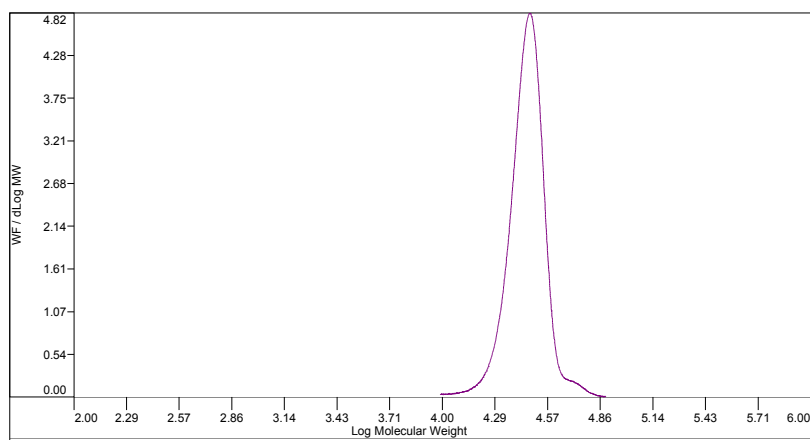


Figure S3.3: GPC trace of 12

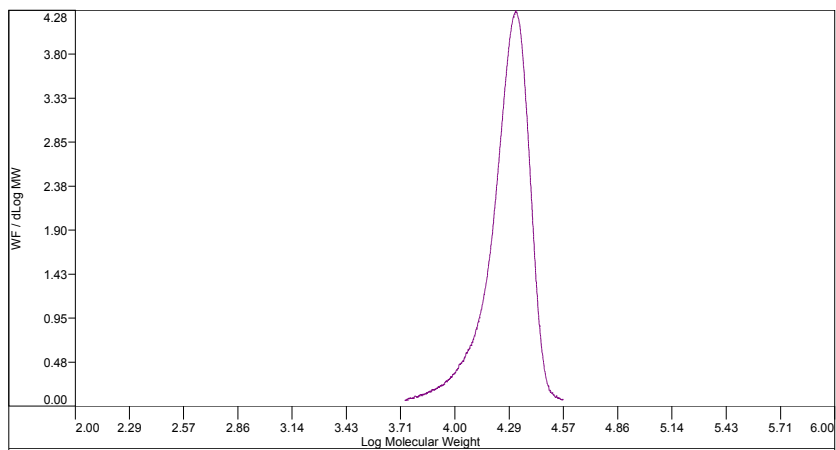


Figure S3.4: GPC trace of 13

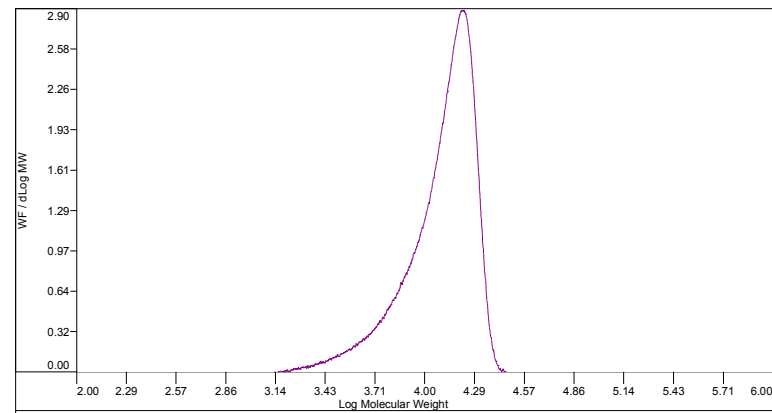


Figure S3.5: GPC trace of 14

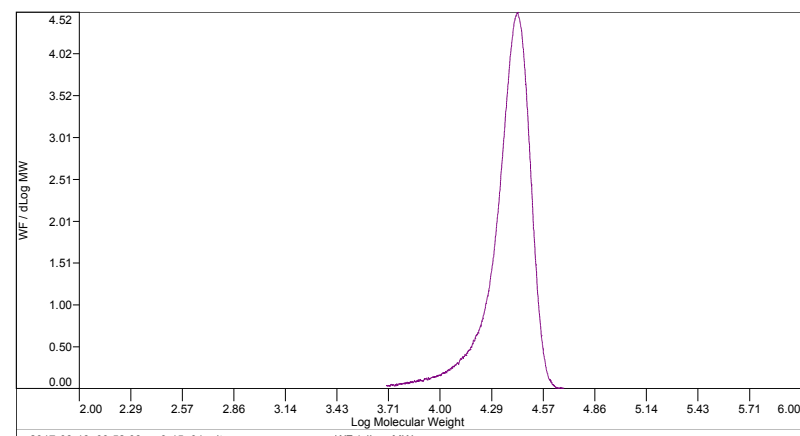


Figure S3.6: GPC trace of 16

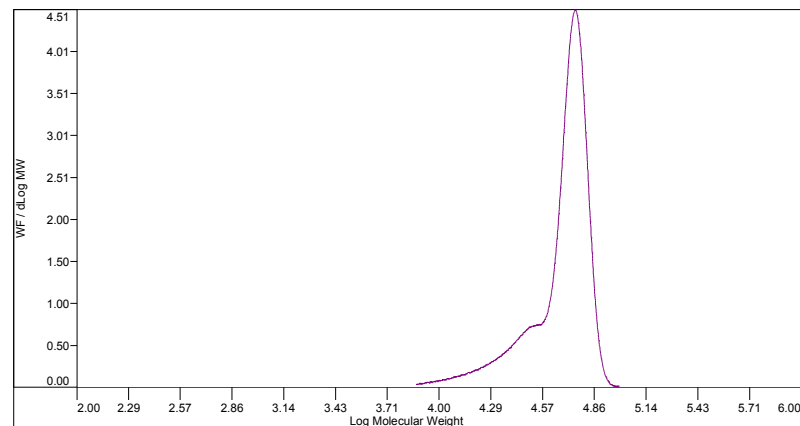


Figure S3.7: GPC trace of 17

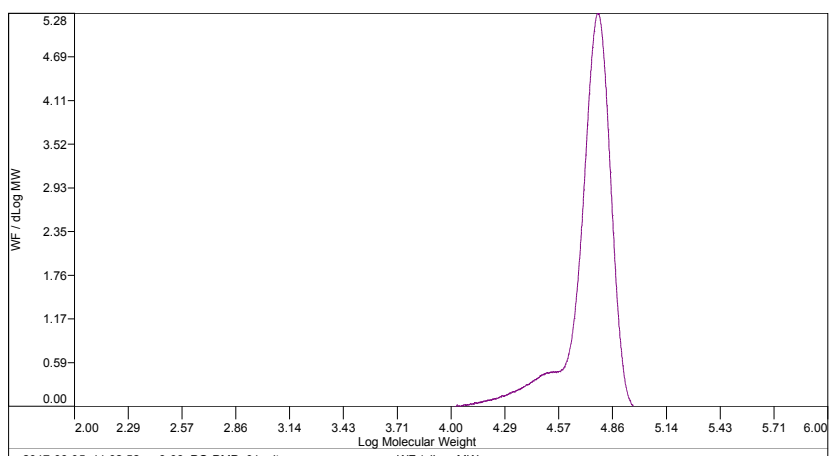


Figure S3.8: GPC trace of 18

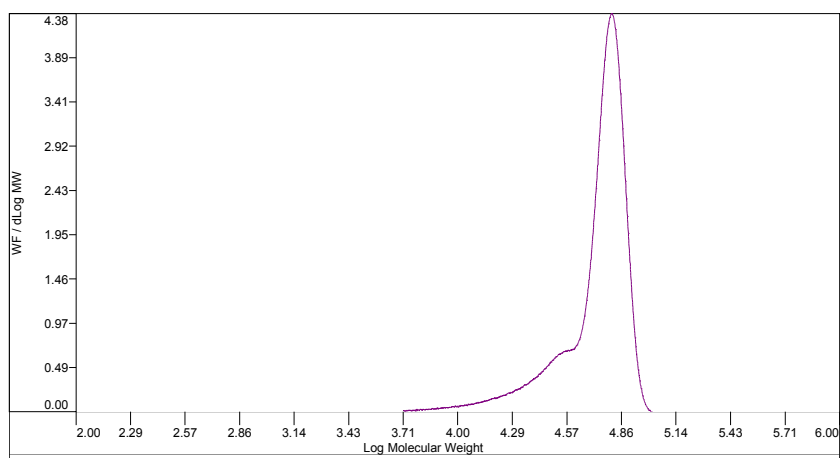


Figure S3.9: GPC trace of 19

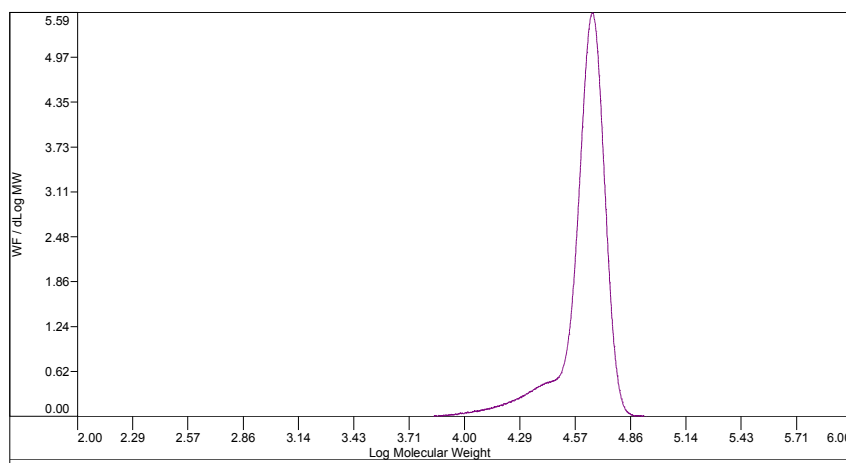


Figure S3.10: GPC trace of **20**

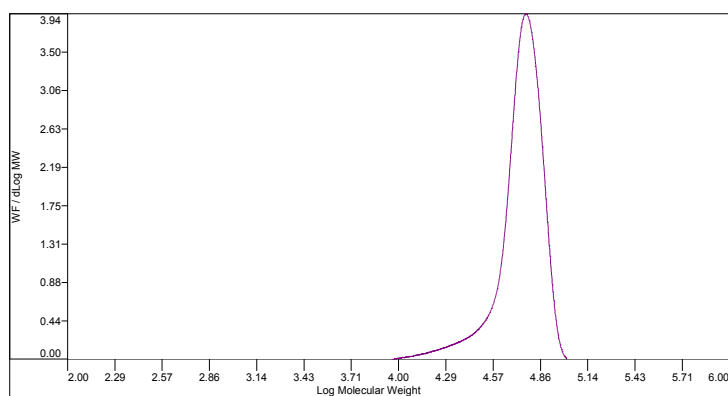


Figure S3.11: GPC trace of **21**

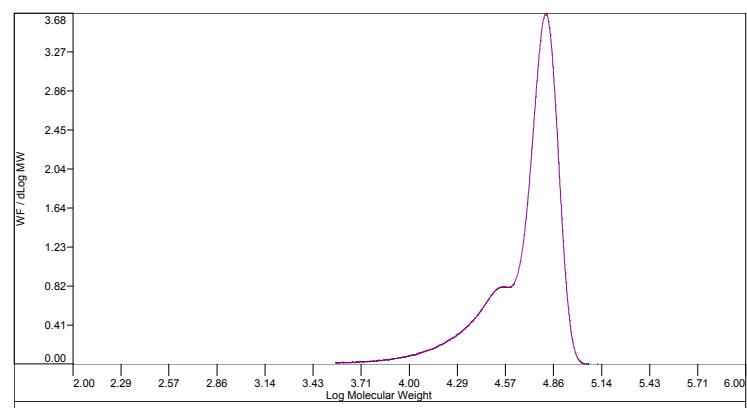


Figure S3.12: GPC trace of **22**

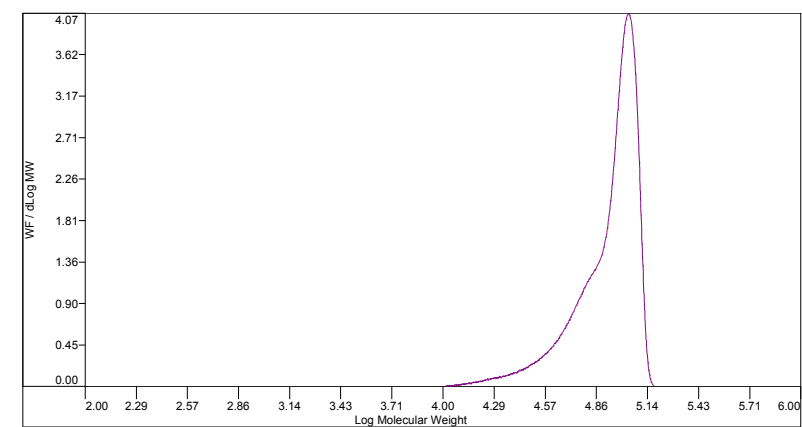


Figure S3.13: GPC trace of 23

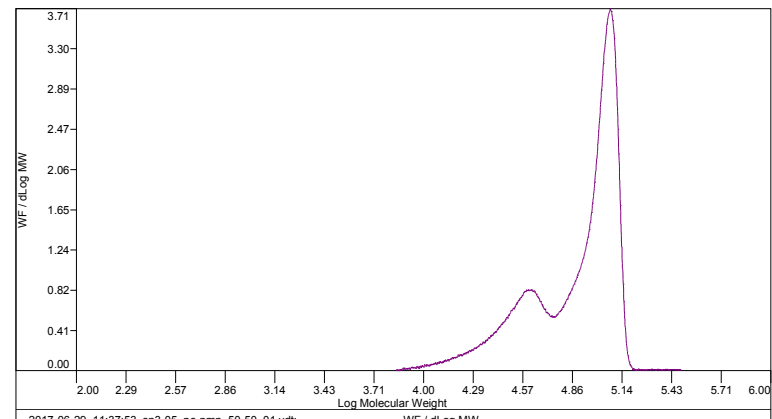


Figure S3.14: GPC trace of 24

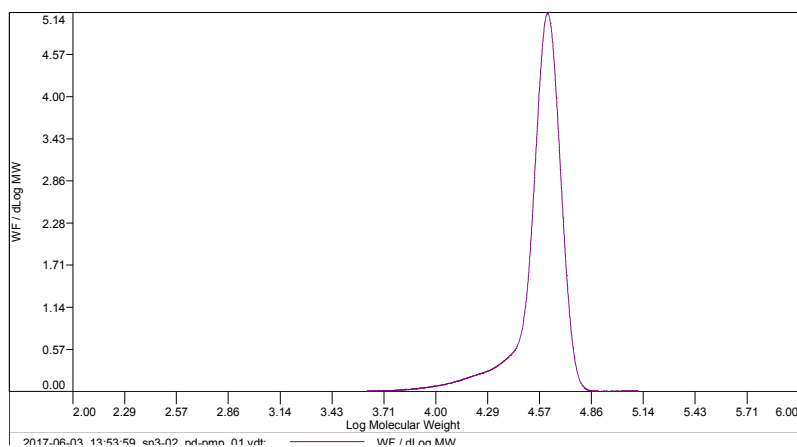


Figure S3.15: GPC trace of 25

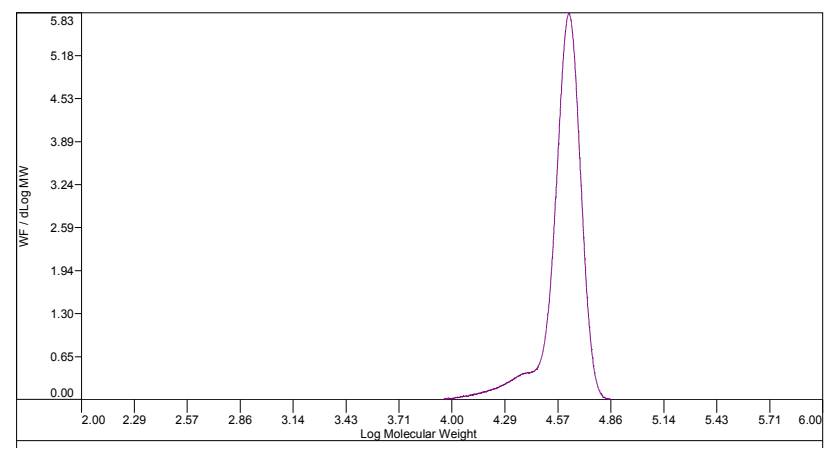


Figure S3.16: GPC trace of **27**

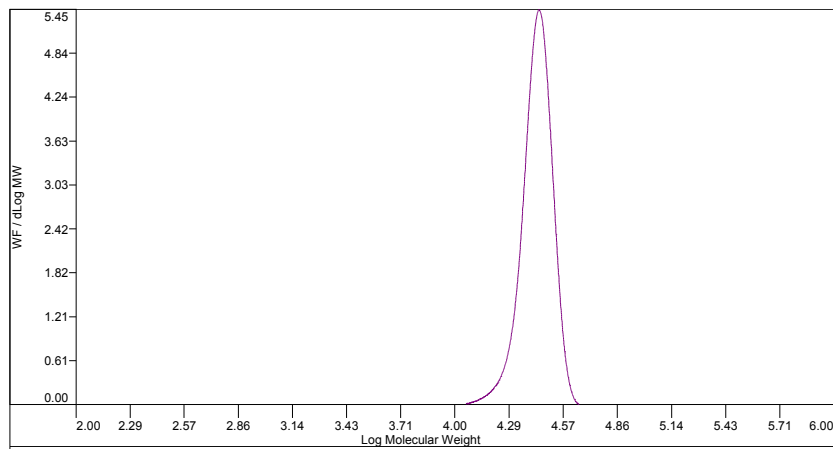


Figure S3.17: GPC trace of **26**

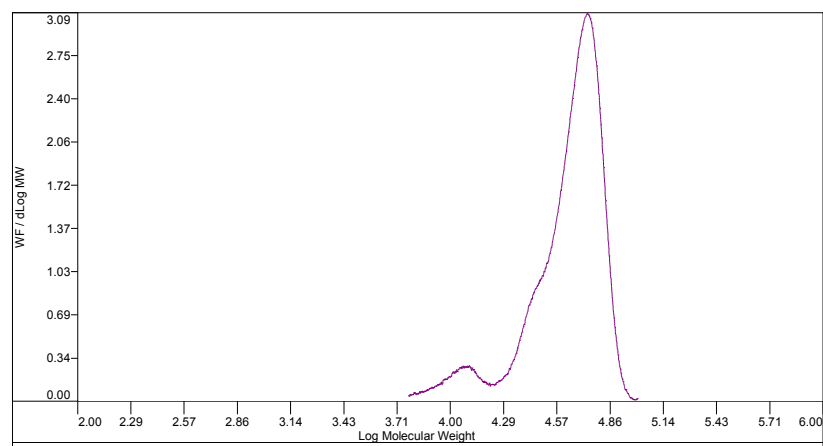


Figure S3.18: GPC trace of **28**

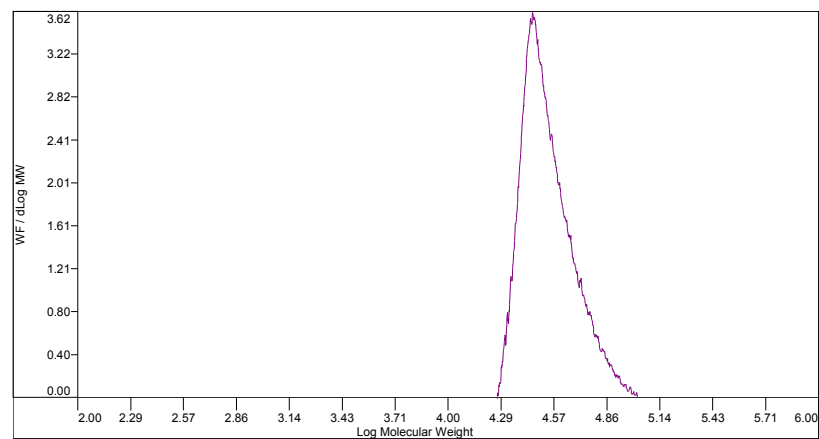


Figure S3.19: GPC trace of **29**

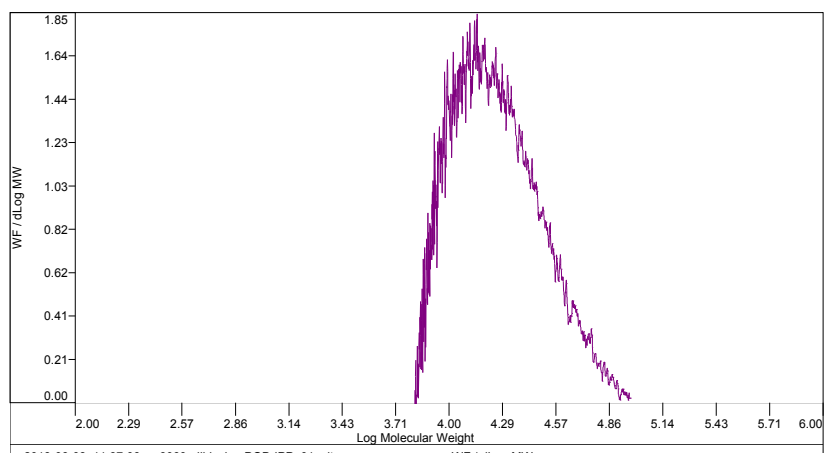


Figure S3.20: GPC trace of **30**

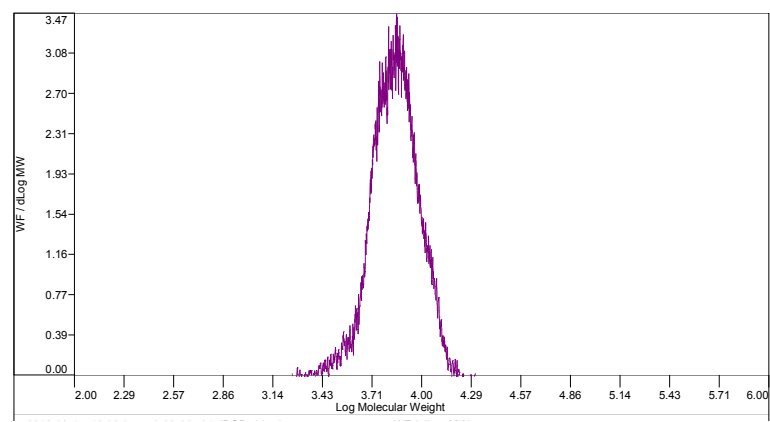


Figure S3.21: ^1H -NMR of **10**

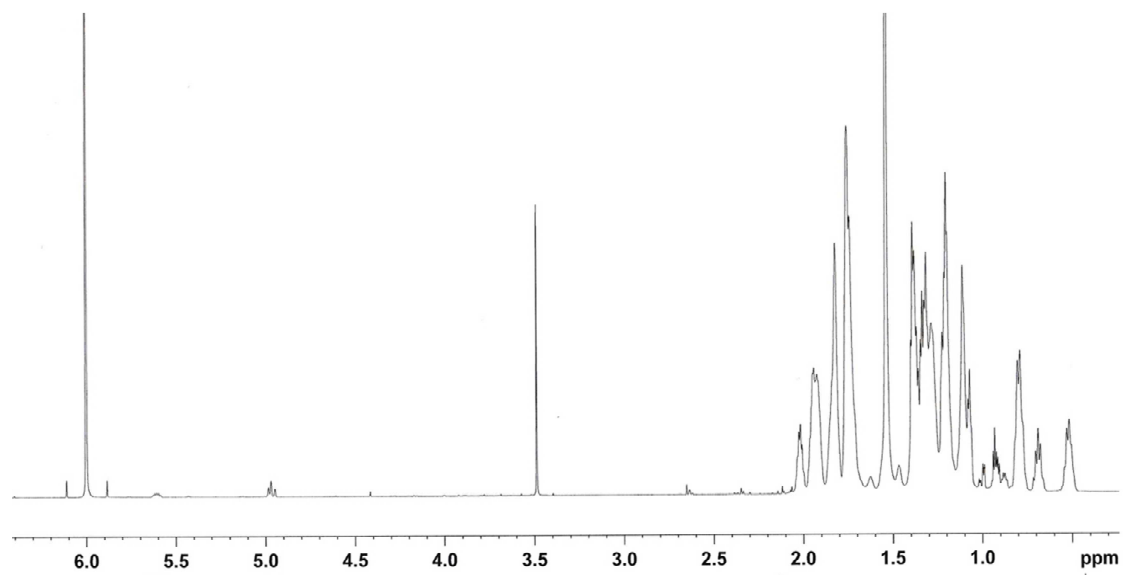


Figure S3.22: ^{13}C -NMR of **10**

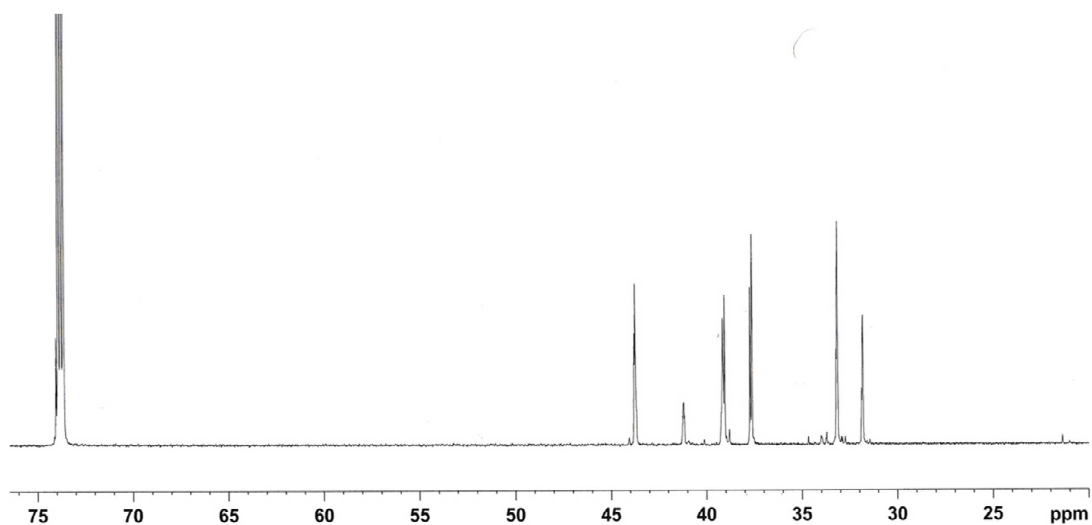


Figure S3.23: Representative ^1H -NMR of **11-14** (800 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 90 °C). The shift at 3.5 ppm represents methanol.

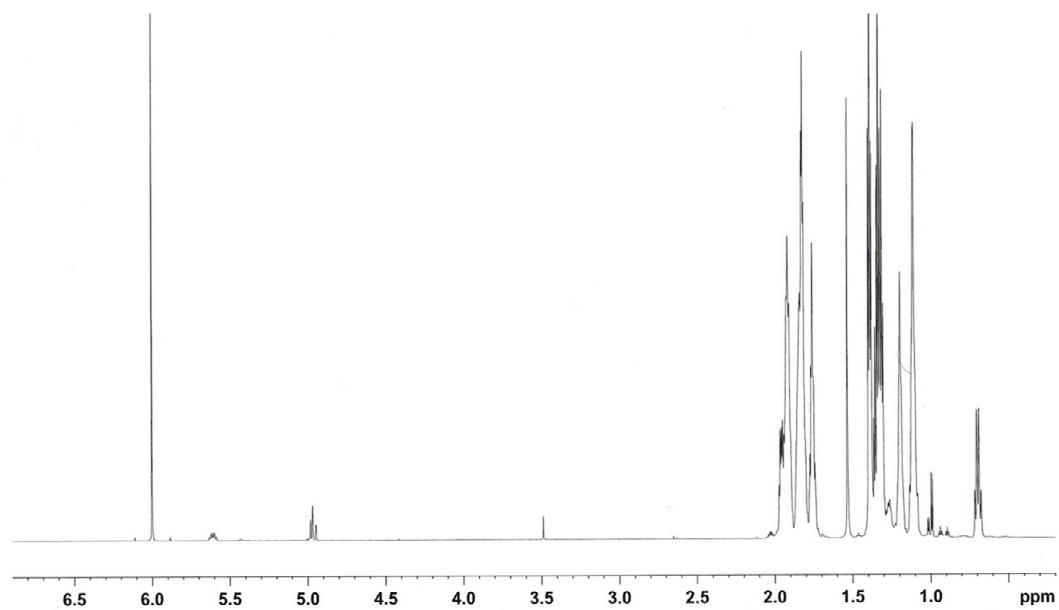


Figure S3.24: Representative inverse-gated proton decoupled ^{13}C -NMR of **11-14** (200 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 90 °C). Shifts marked with a plus (+) represent PMCH and shifts marked with an asterisk (*) represent PMCP

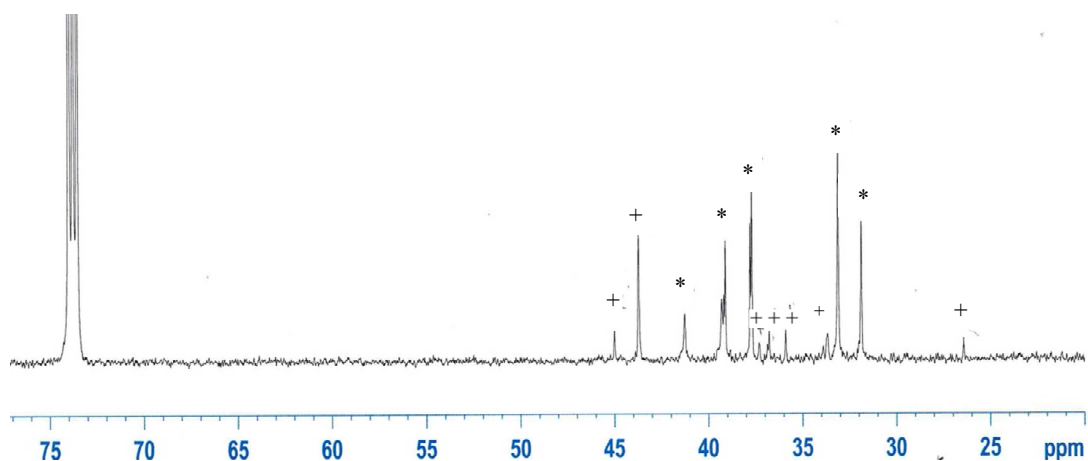


Figure S3.25: Representative ^1H -NMR of **16-17**. The shift at 3.5 ppm represents methanol.

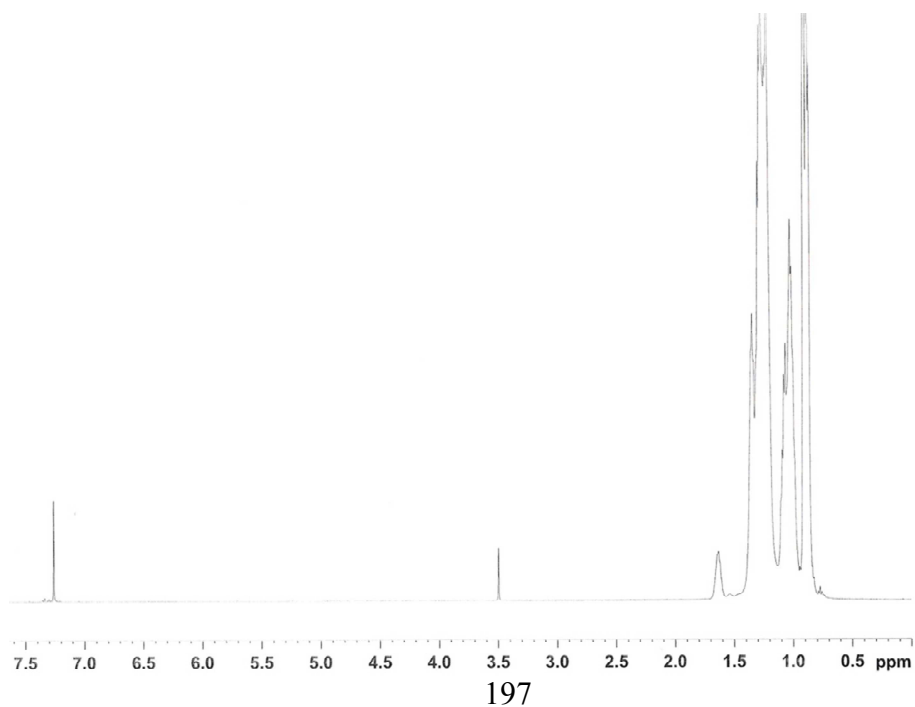


Figure S3.26: Representative partial inverse-gated proton decoupled ^{13}C -NMR of **16-17** (200 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 90 °C). Shifts marked with a plus (+) represent PH and shifts marked with an asterisk (*) represent PMP

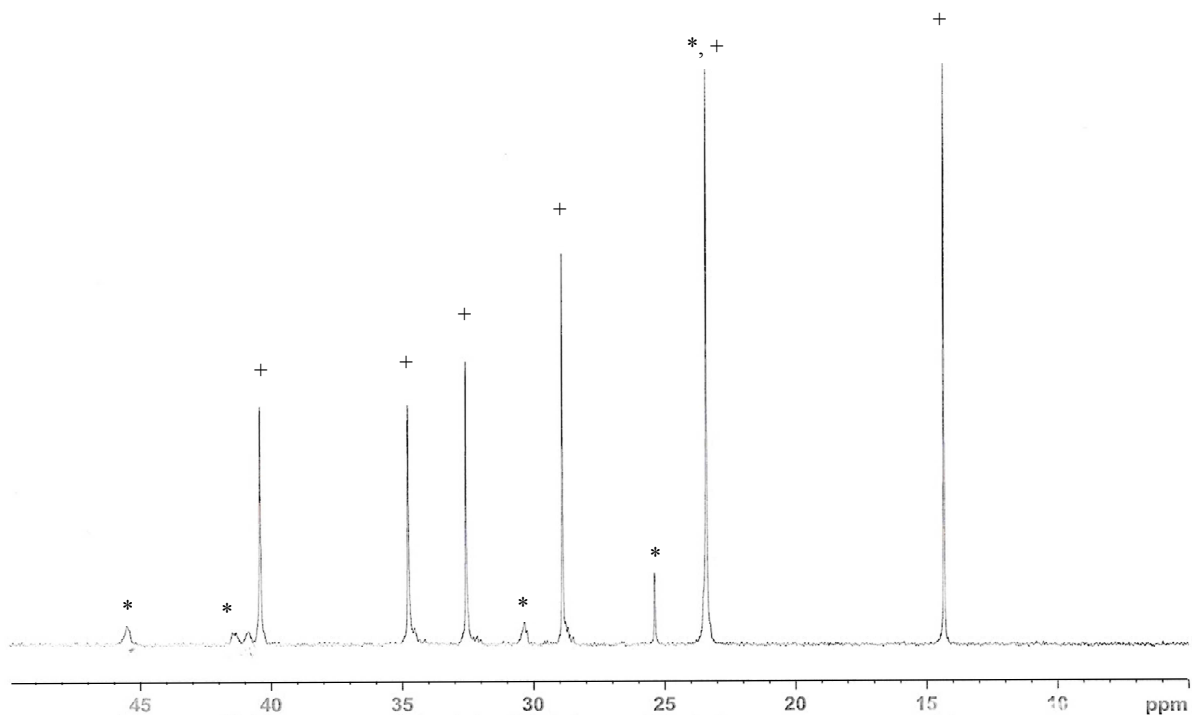


Figure S3.27: Representative ^1H -NMR of **18-23** (800 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 90 °C)

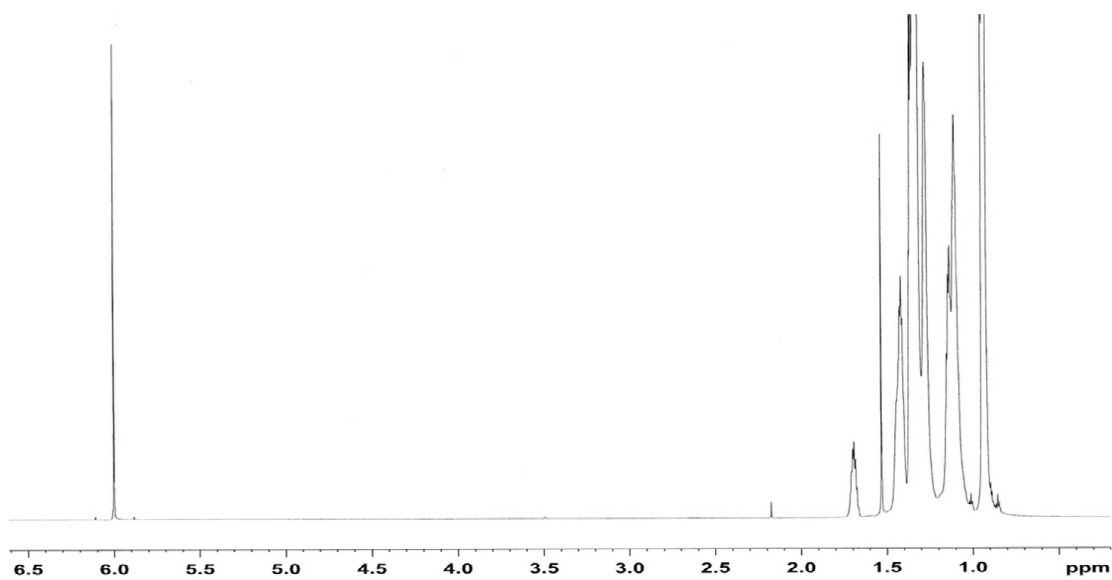


Figure S3.28: Representative partial inverse-gated proton decoupled ^{13}C -NMR of **18-23** (200 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 90 °C). Shifts marked with a plus (+) represent PO and shifts marked with an asterisk (*) represent PMP

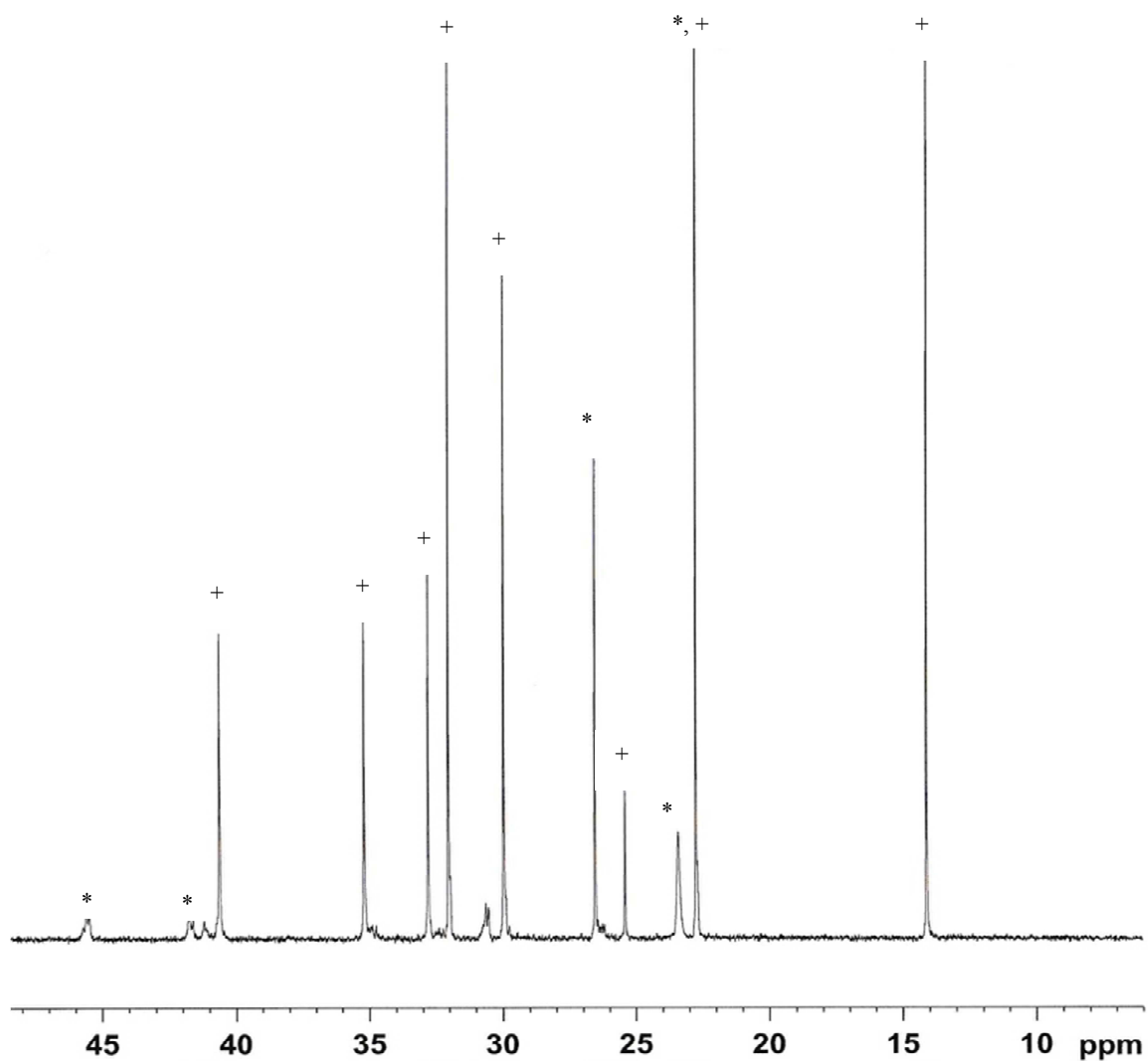


Figure S3.29: Representative ^1H -NMR of **24-25** (800 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 90 °C)

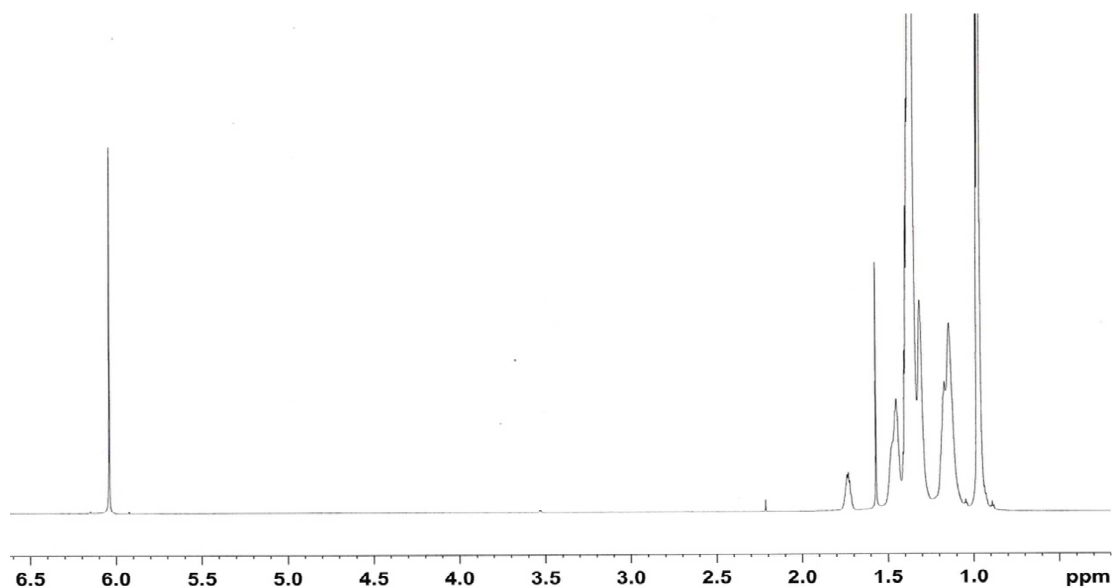


Figure S3.30: Representative partial inverse-gated proton decoupled ^{13}C -NMR of **24-25** (200 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 90 °C). Shifts marked with a plus (+) represent PD and shifts marked with an asterisk (*) represent PMP

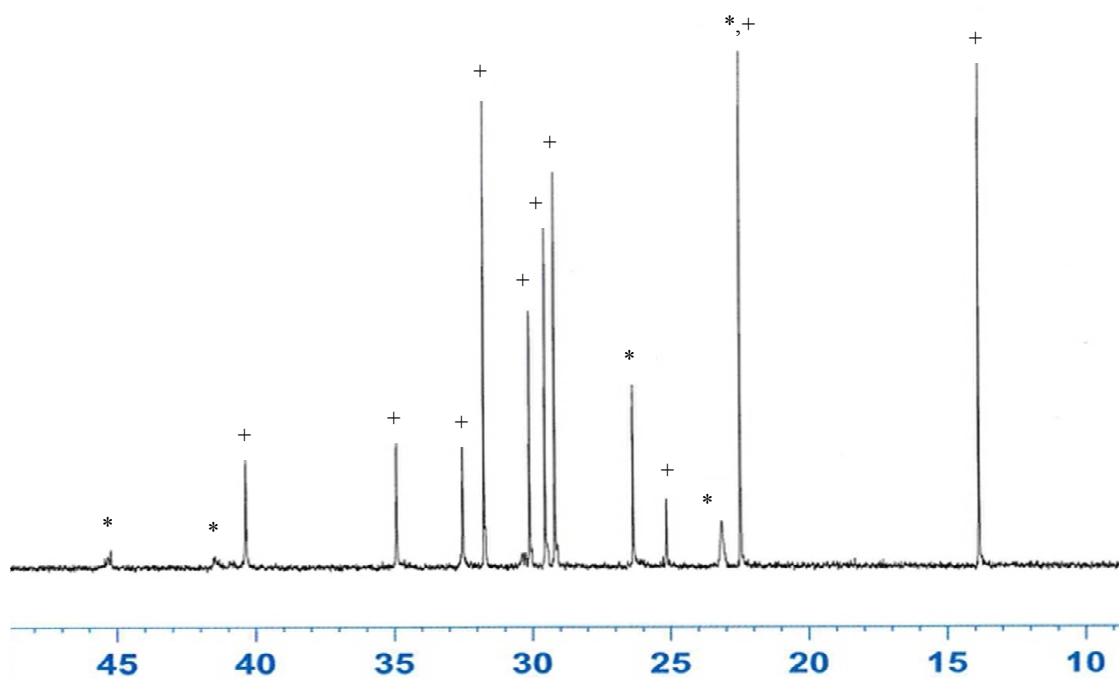


Figure S3.31: ^1H -NMR of **26-27**

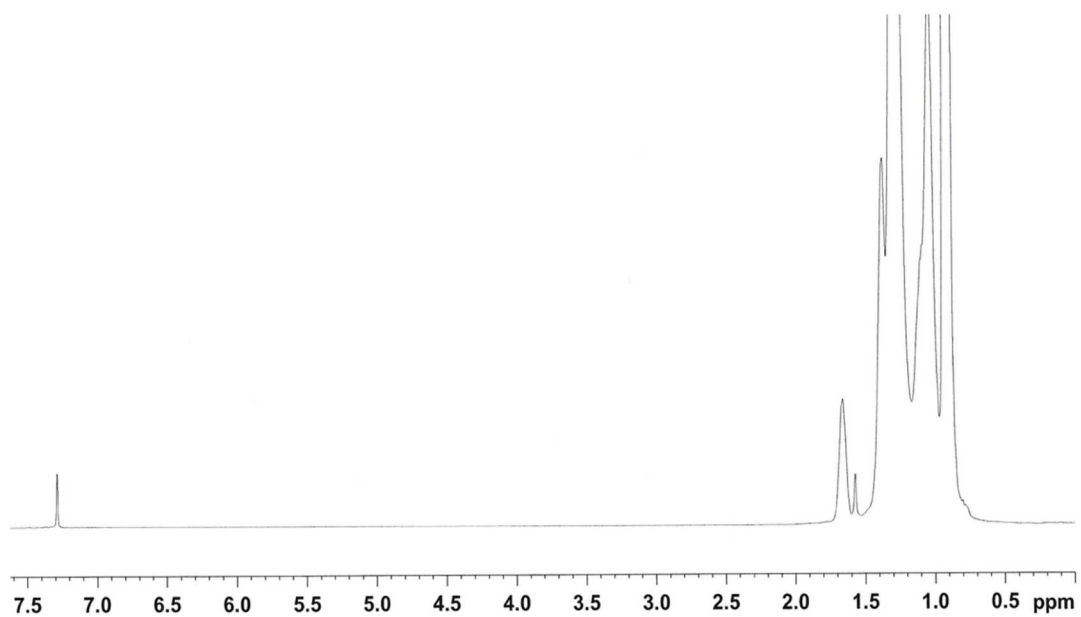


Figure S3.32: Representative partial inverse-gated proton decoupled ^{13}C -NMR of **26-27** (200 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 90 $^\circ\text{C}$). Shifts marked with a plus (+) represent PH and shifts marked with an asterisk (*) represent PMP

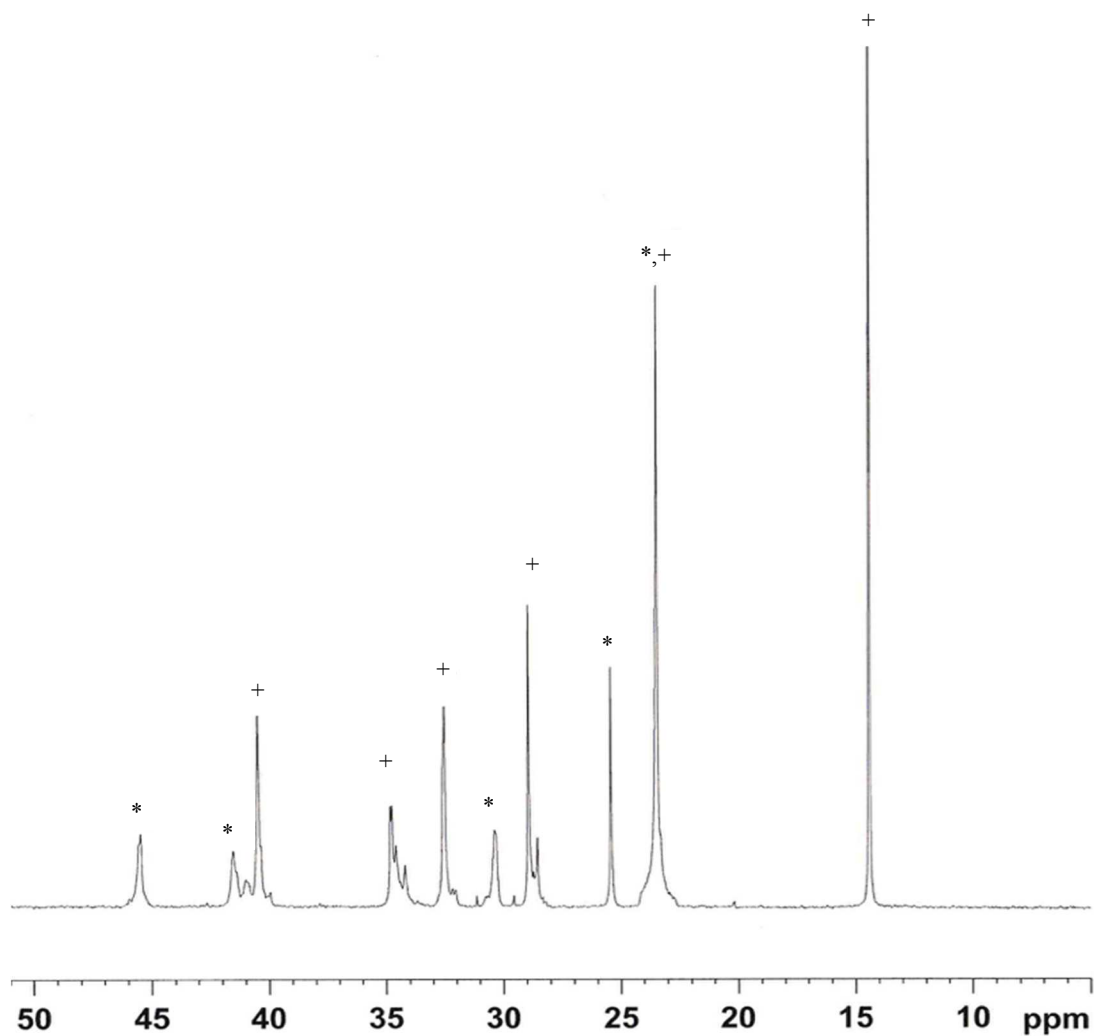


Figure S3.32: DSC trace of 10

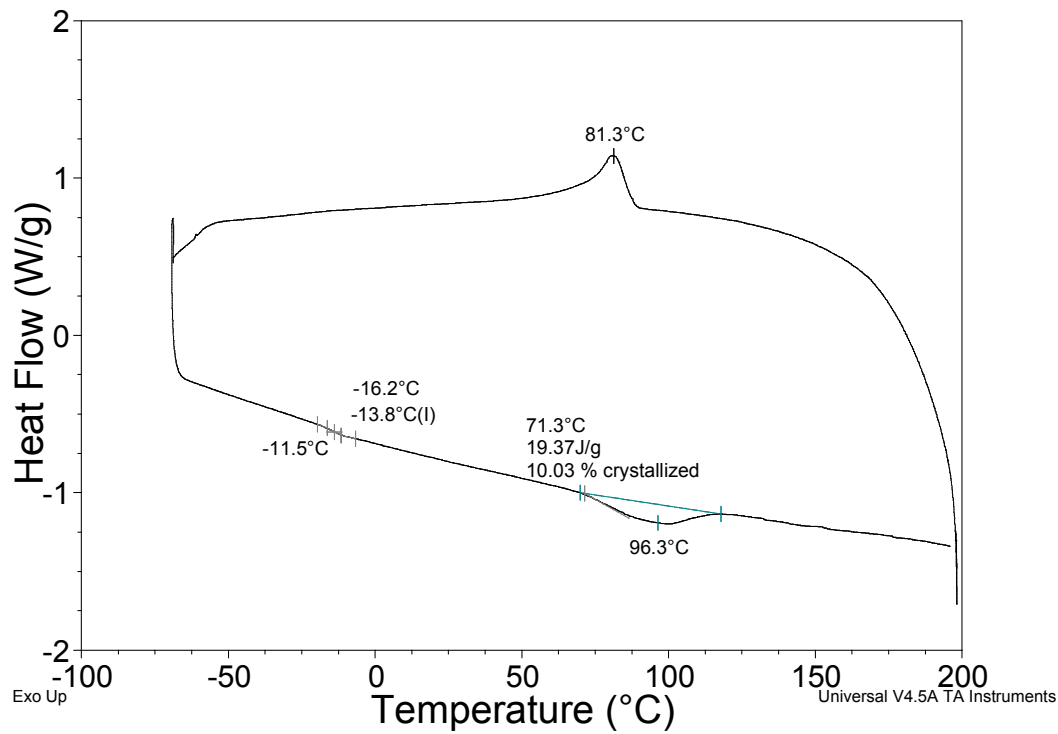


Figure S3.33: DSC trace of 11

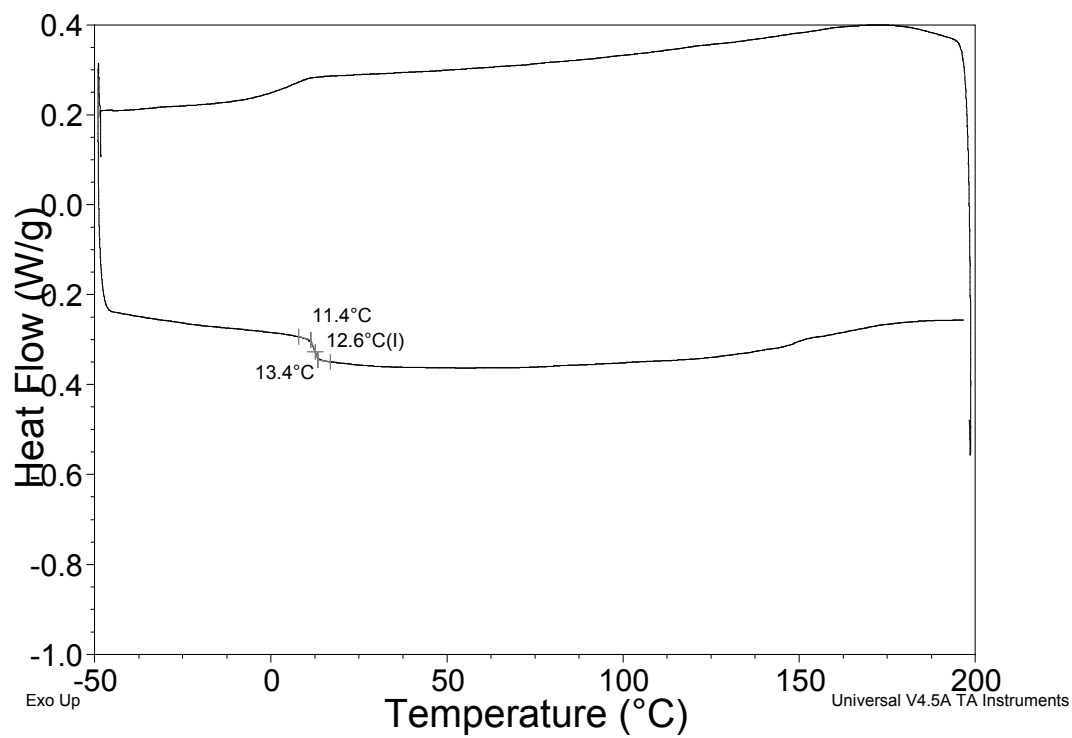


Figure S3.34: DSC race of 12

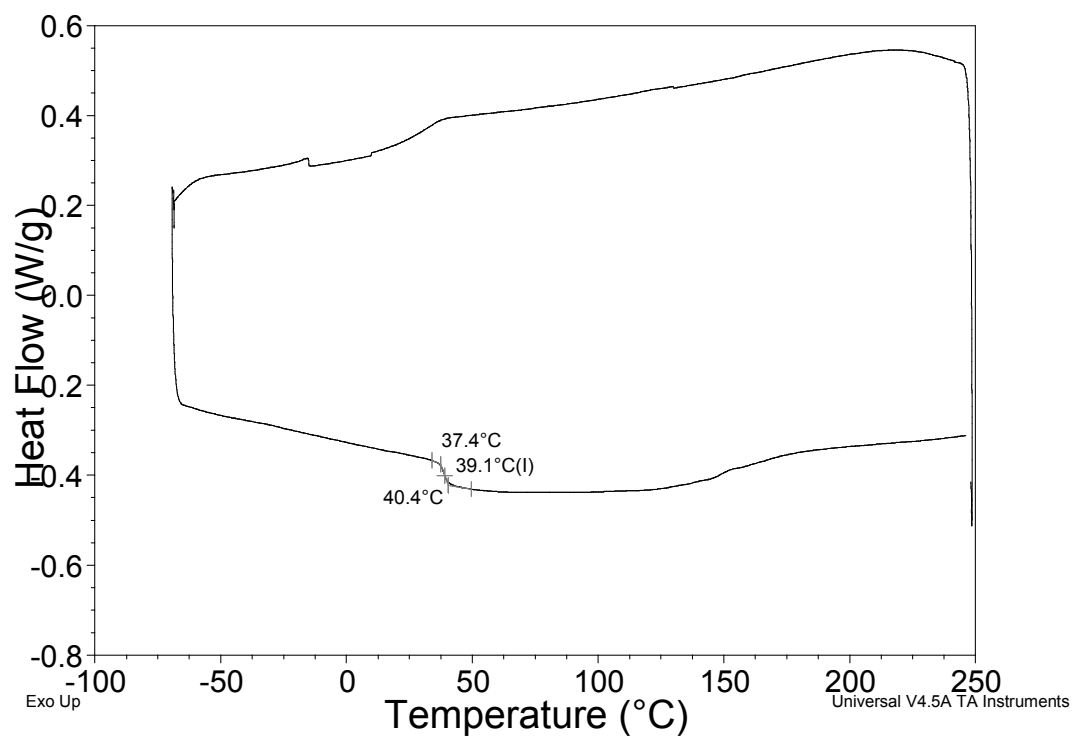


Figure S3.35: DSC trace of 13

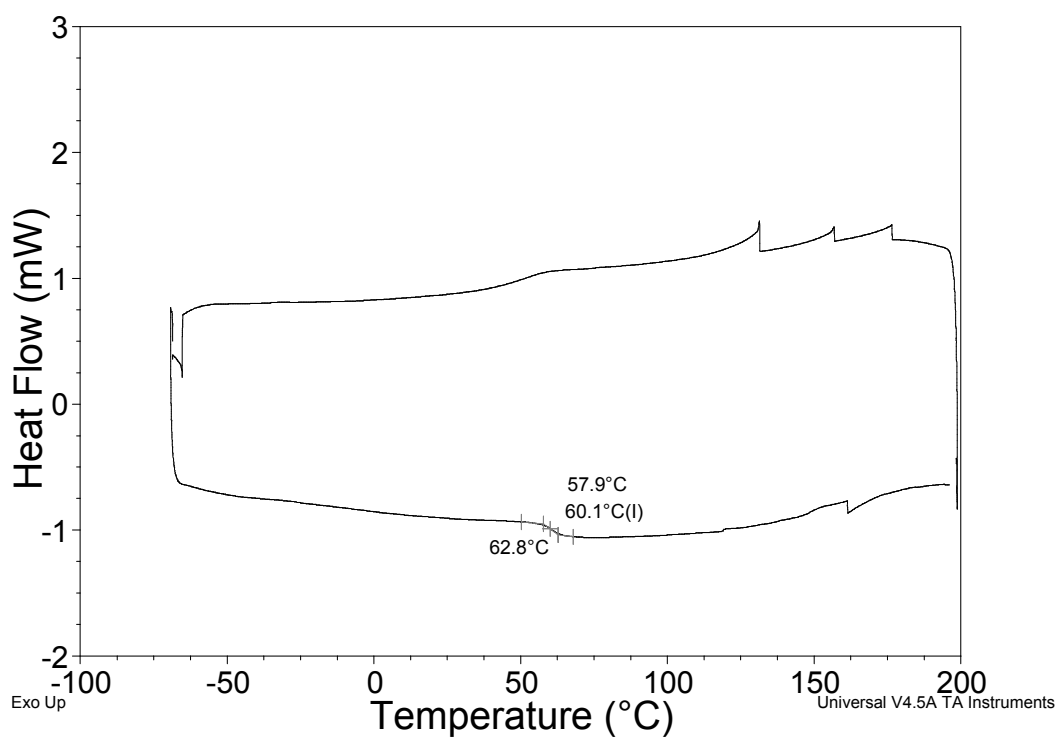


Figure S3.36: DSC trace of 14

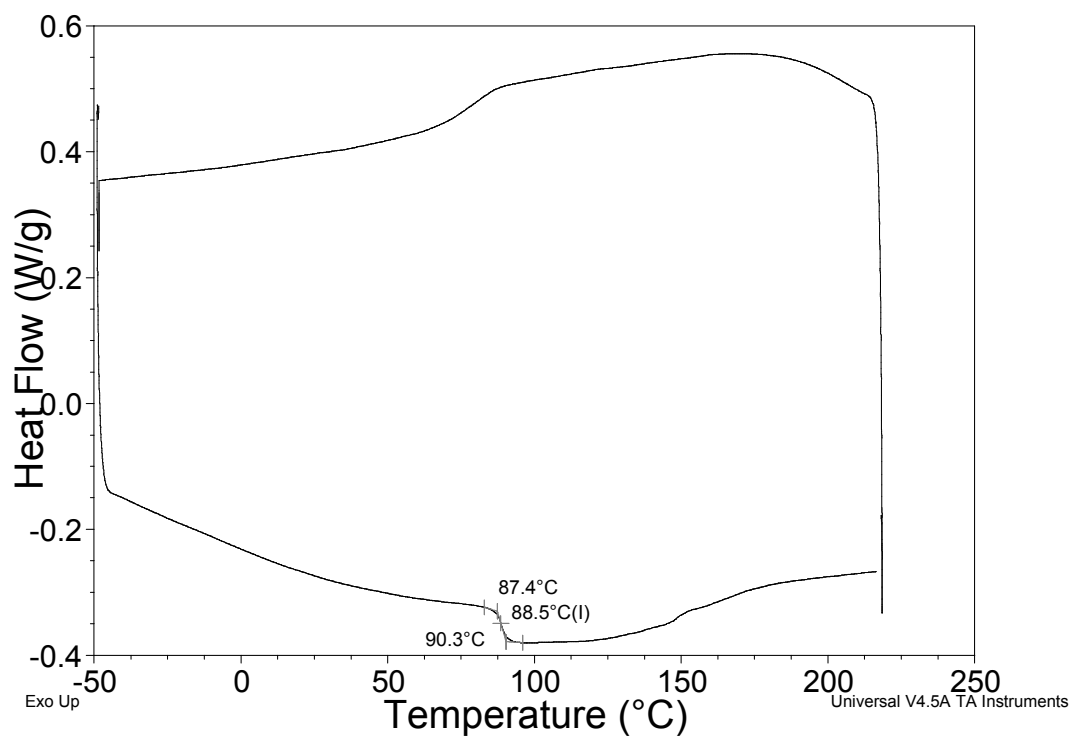


Figure S3.37: DSC trace of 16

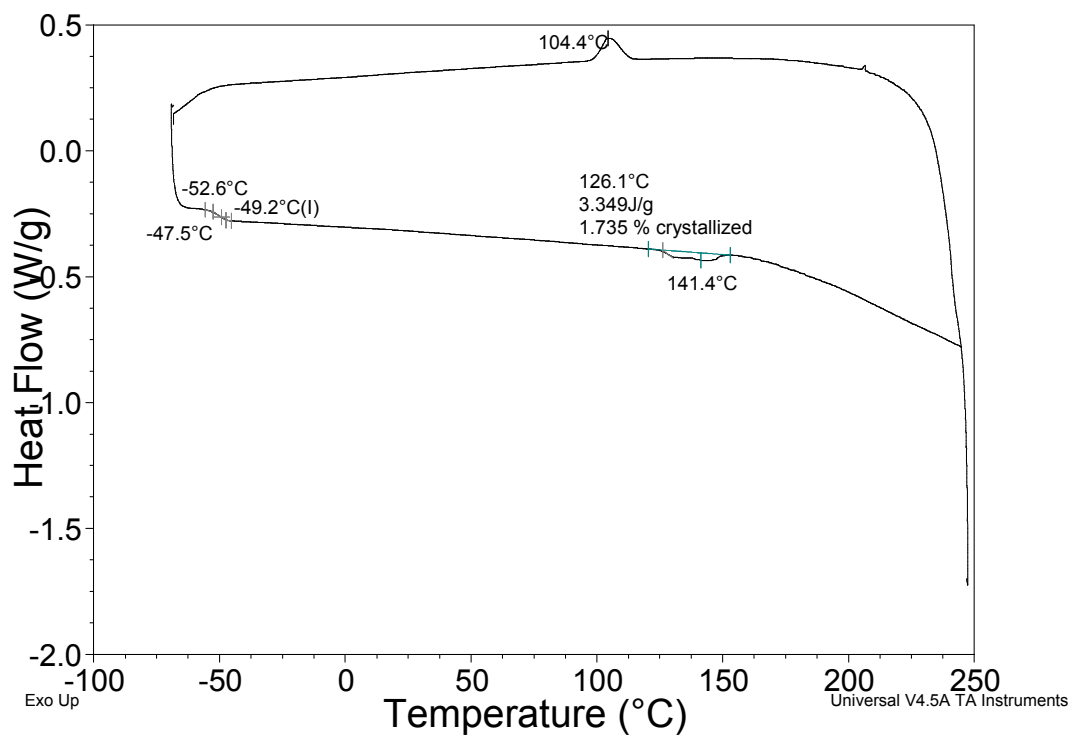


Figure S3.38: DSC trace of **17**

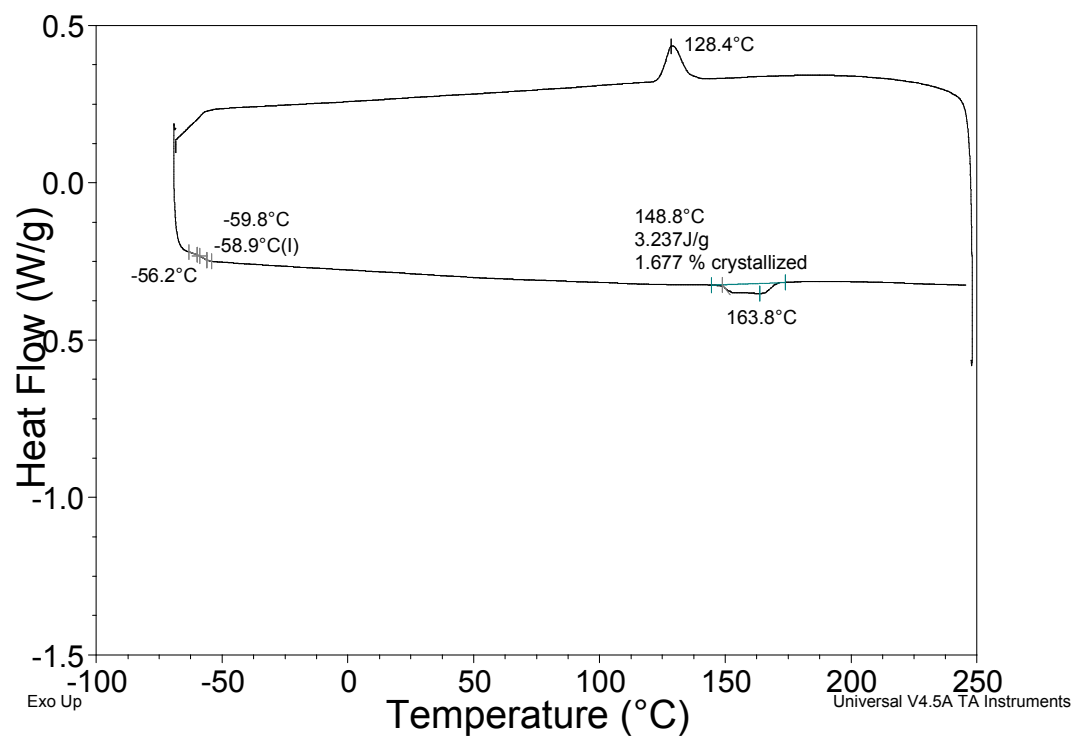


Figure S3.39: DSC trace of **18**

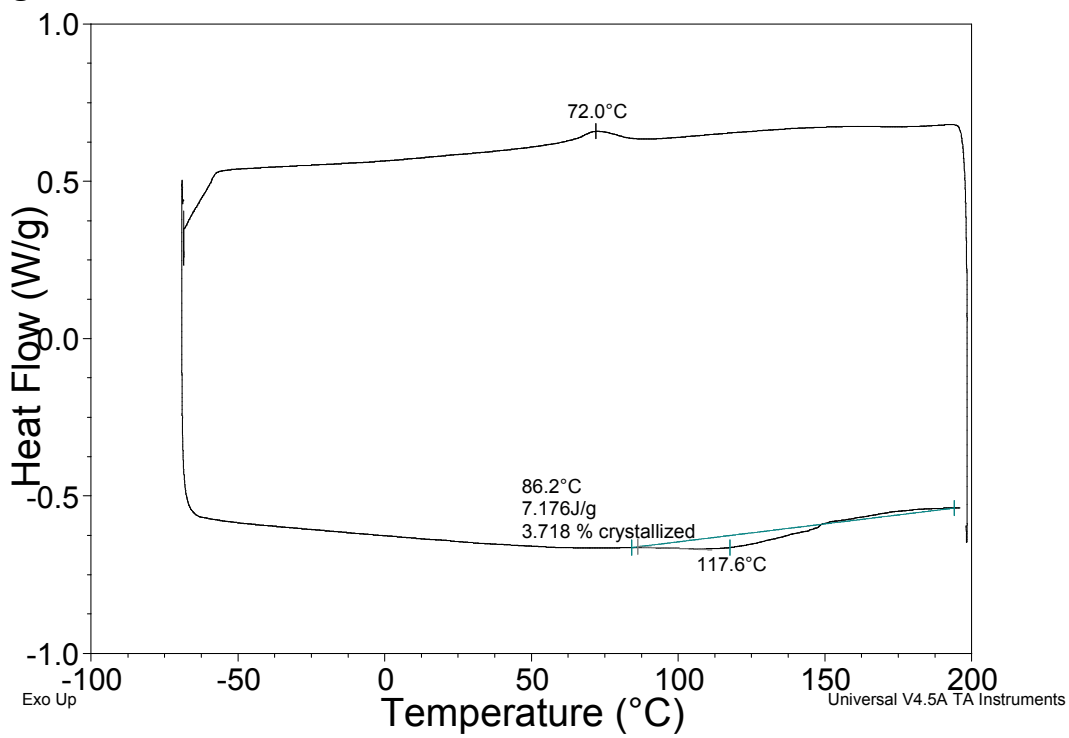


Figure S3.40: DSC trace of **19**

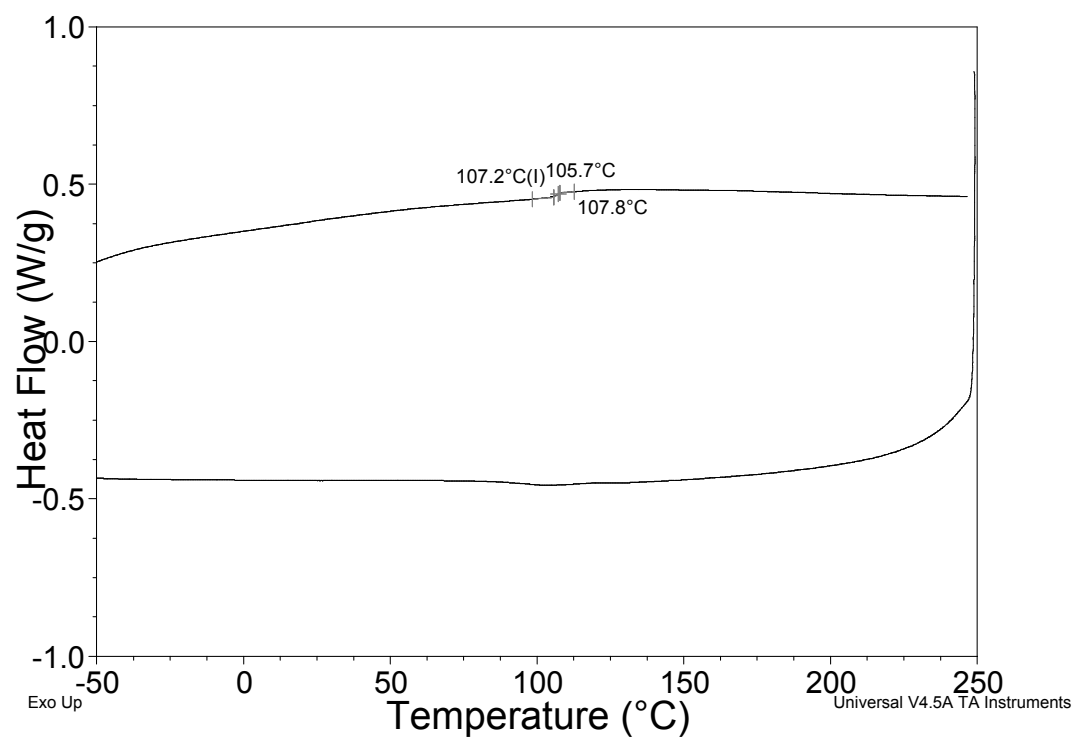


Figure S3.41: DSC trace of **20**

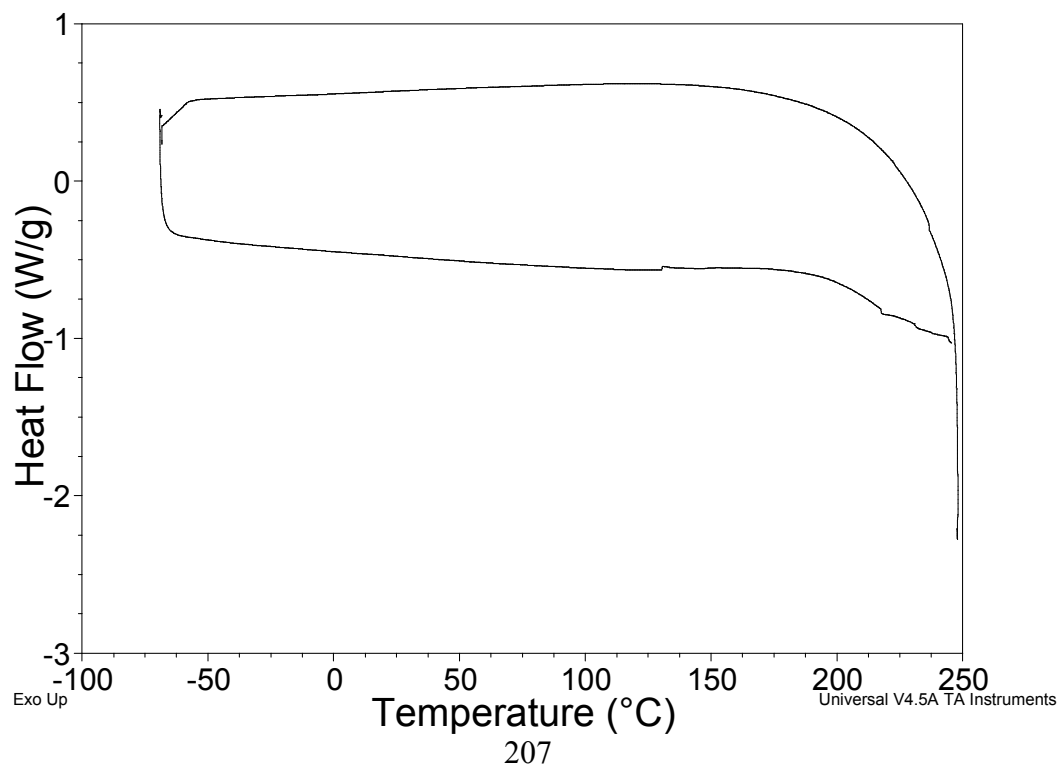


Figure S3.42: DSC trace of 21

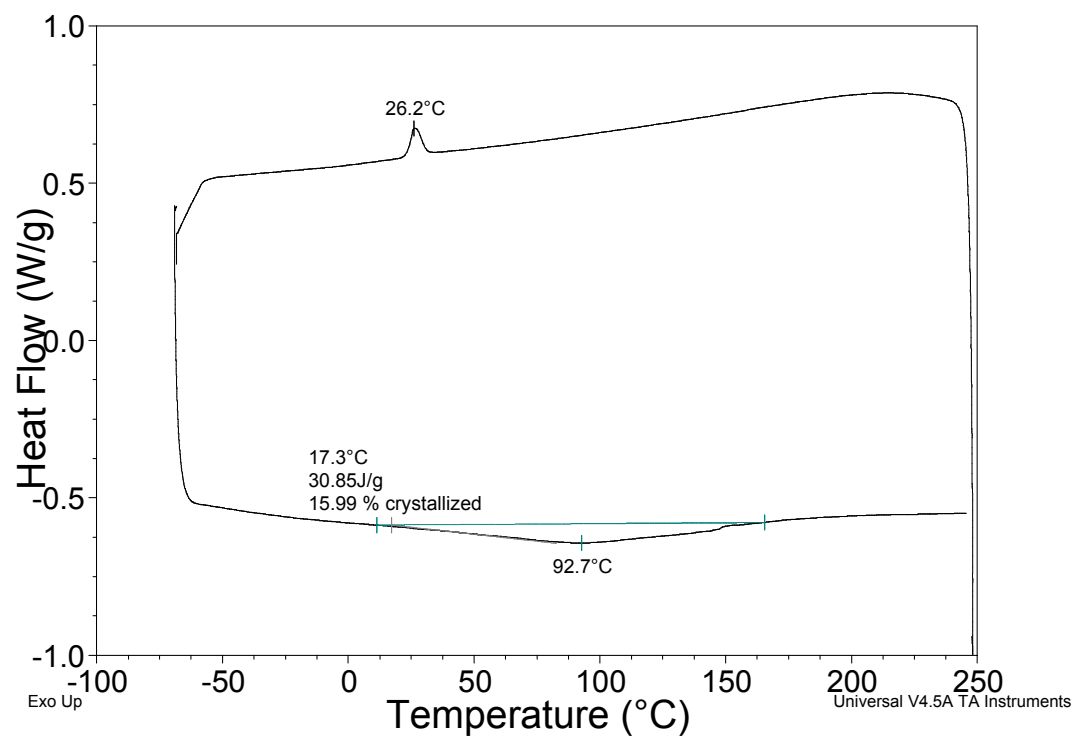


Figure S3.43: DSC trace of 22

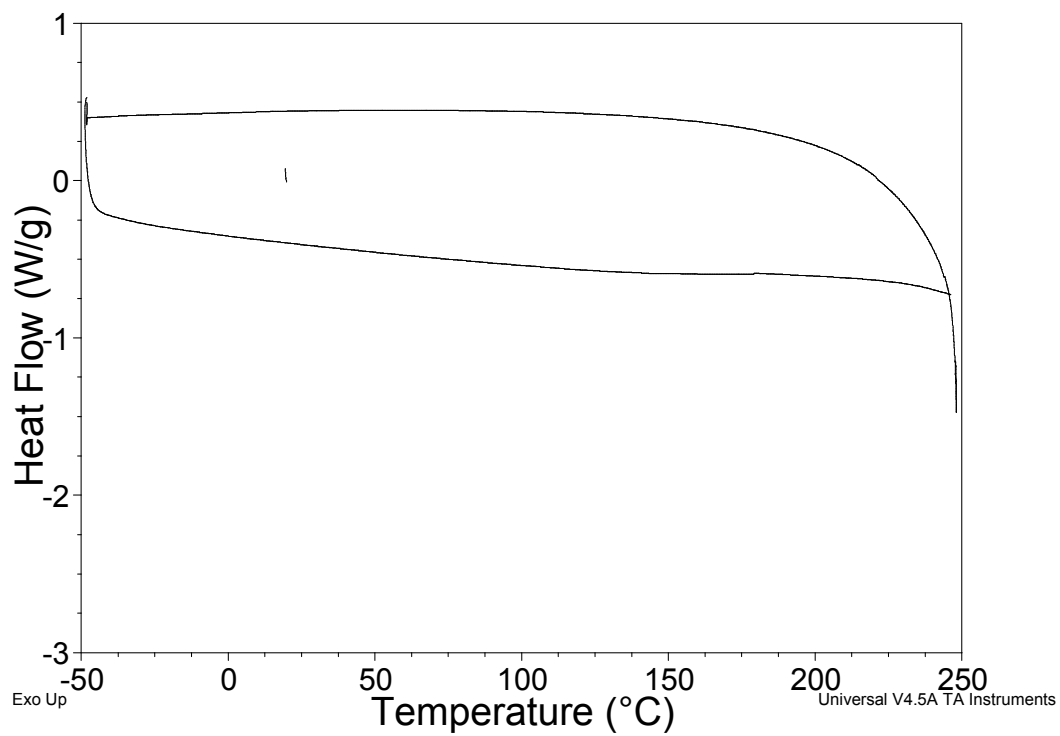


Figure S3.44: DSC trace of 23

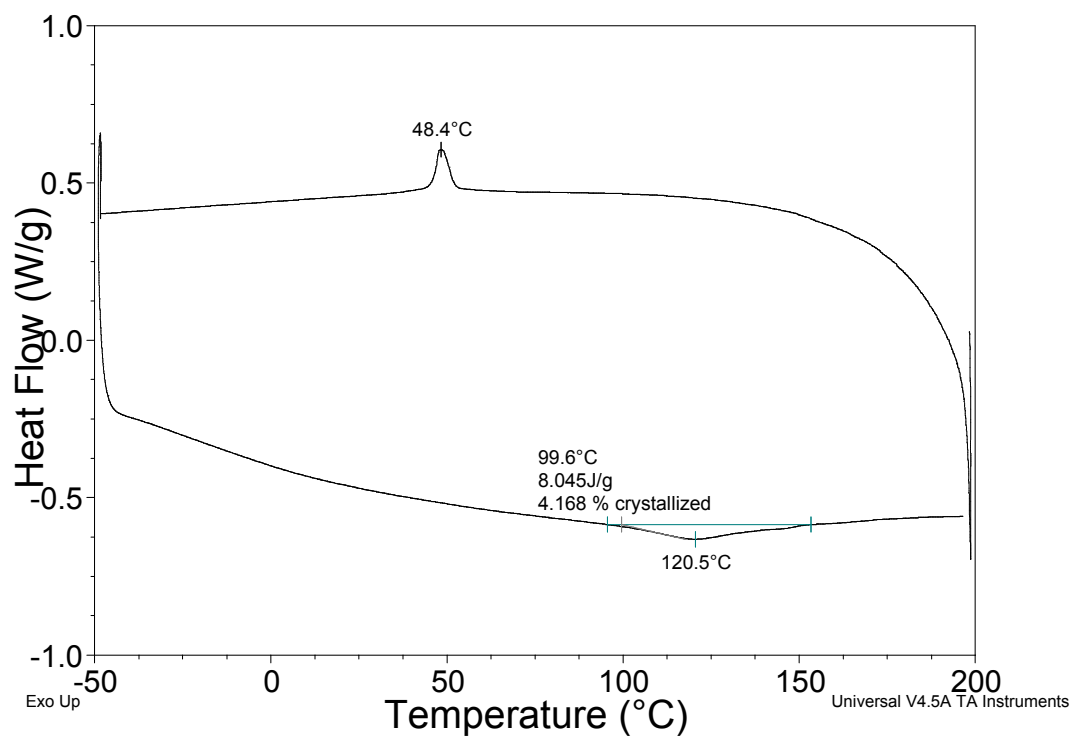


Figure S3.45: DSC trace of 24

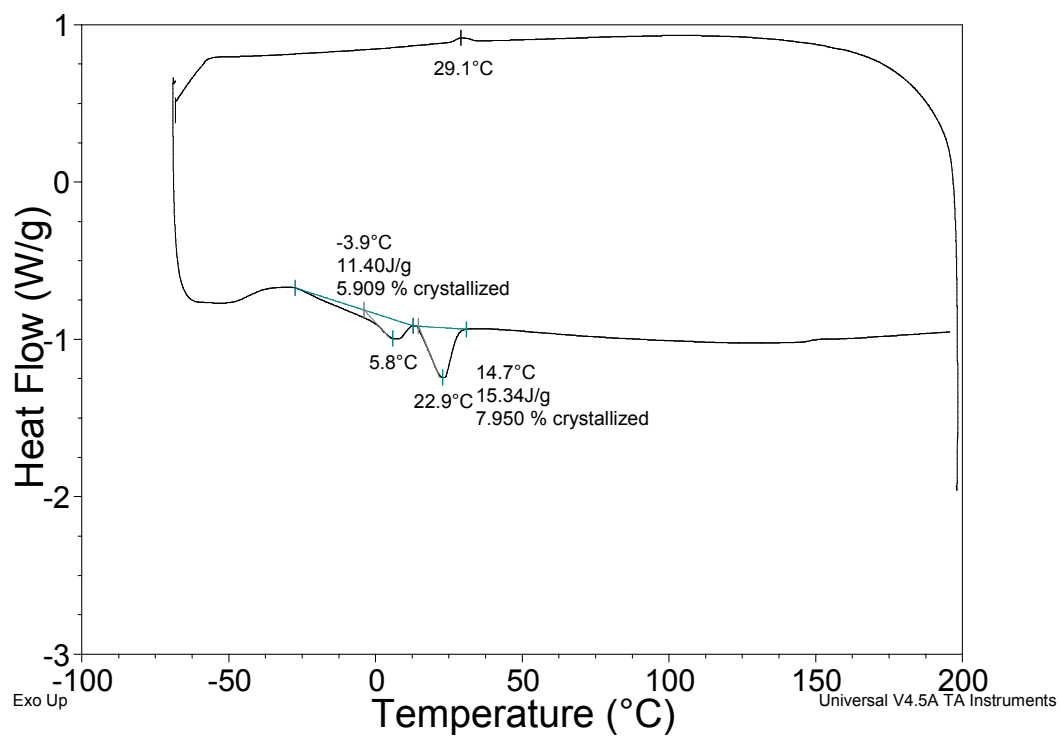


Figure S3.46: DSC trace of 25

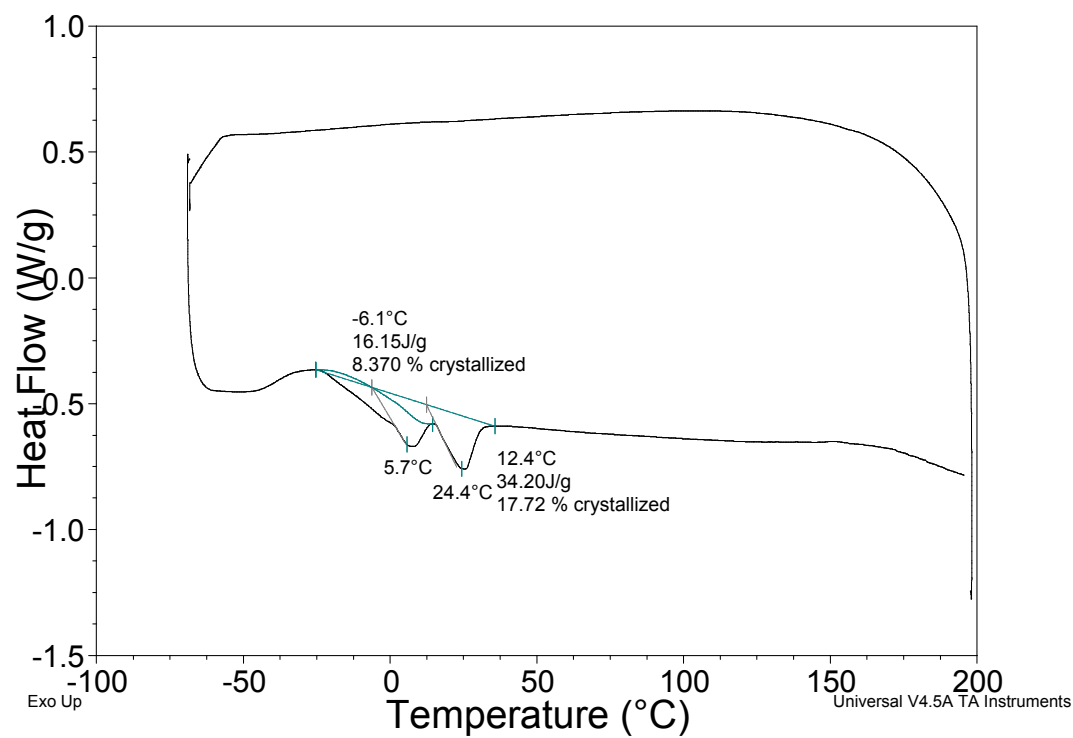


Figure S3.47: DSC trace of 27

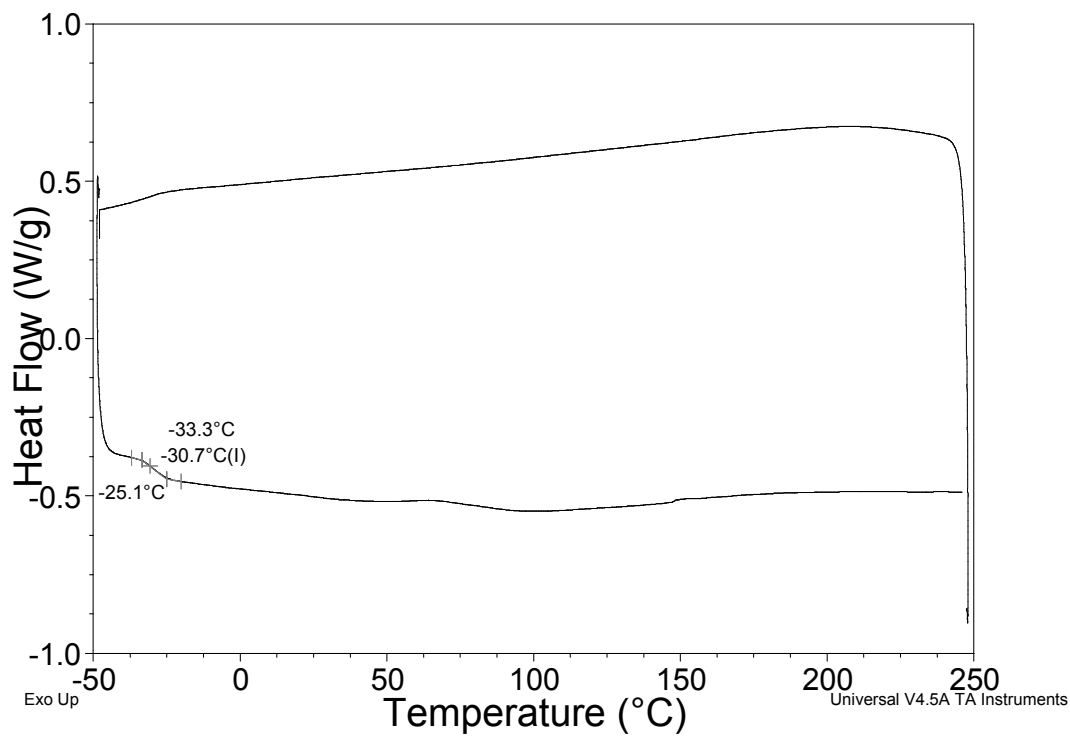


Figure S3.48: DSC trace of 26

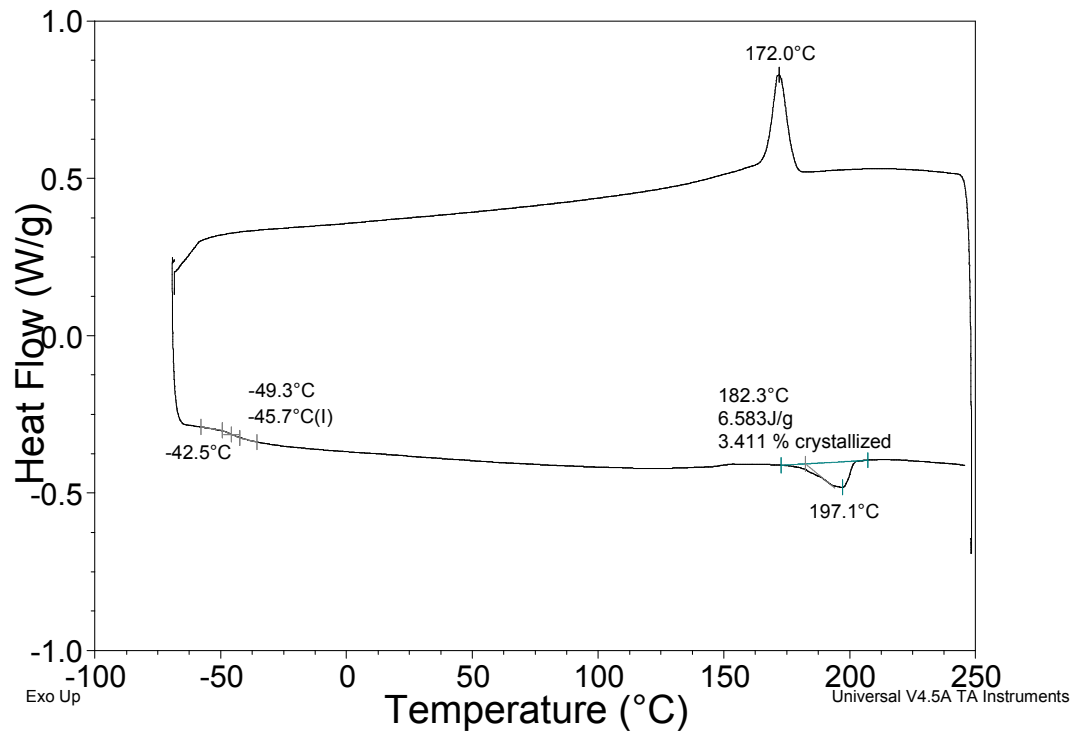


Figure S3.49: DSC trace of 28

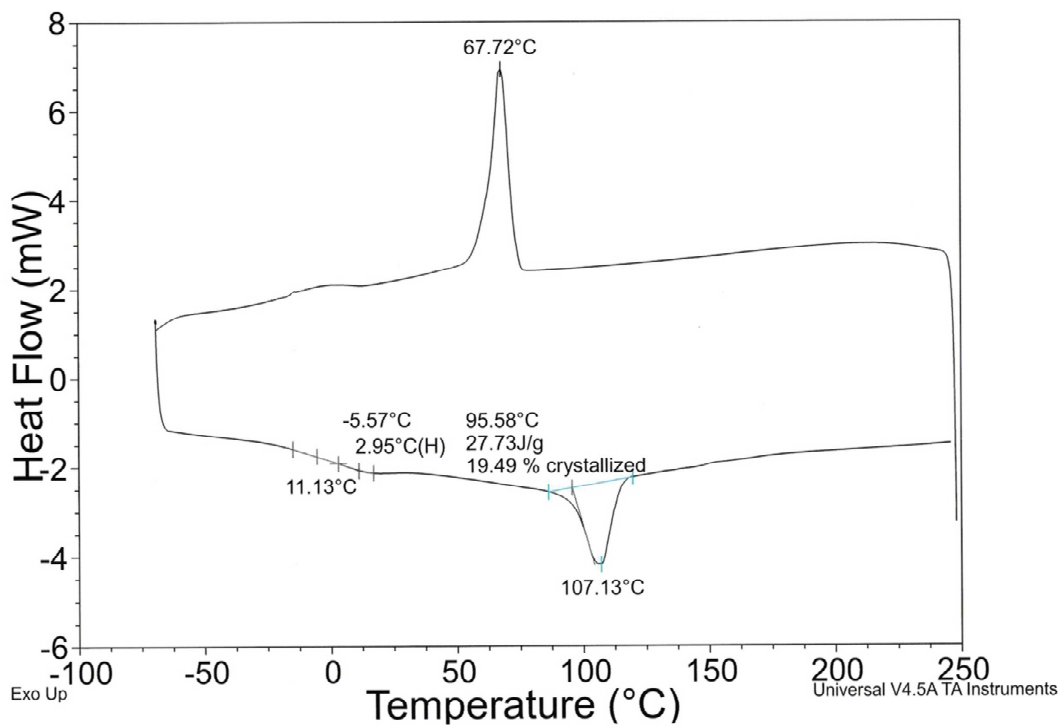


Figure S3.50: DSC trace of 29

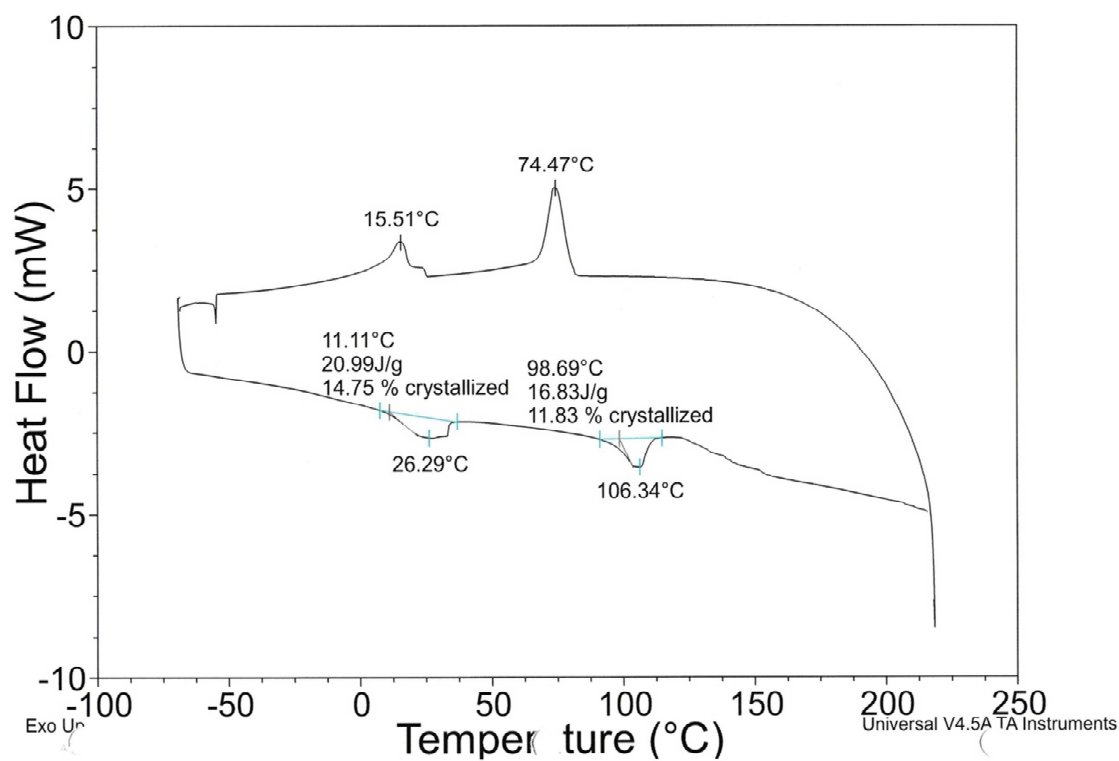


Figure S3.51: DSC trace of 30

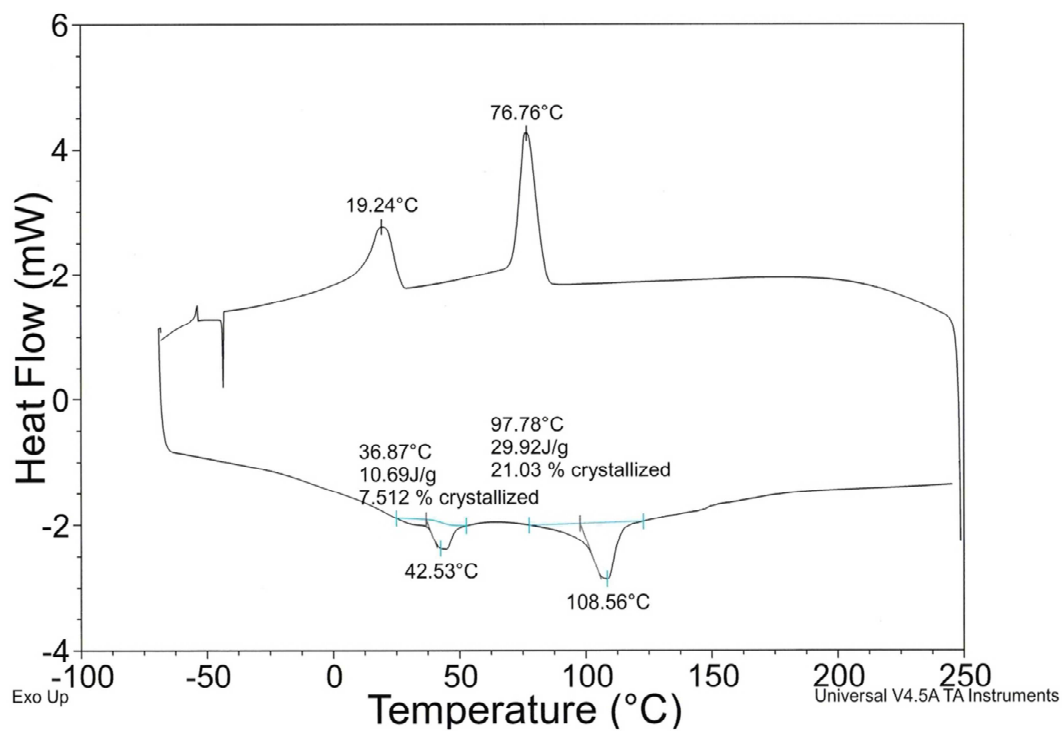


Figure S3.52: 1D SAXS (top) and WAXS (bottom) plots of **19** unannealed showing formation of PMP crystals

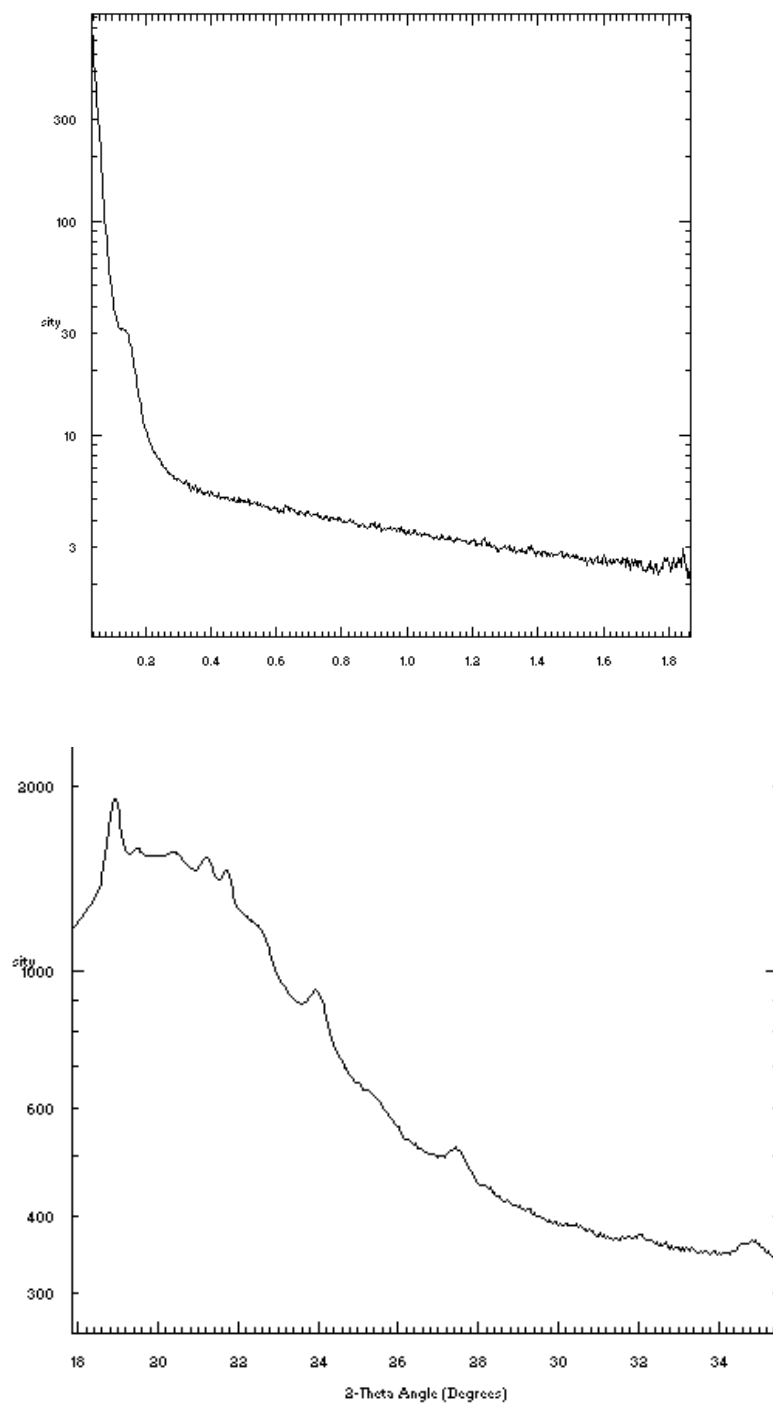


Figure S3.53: 1D SAXS (top) and WAXS (bottom) plots of **19** annealed *in vacuo* at 160 °C showing microphase-separation in the melt state (absence of crystals)

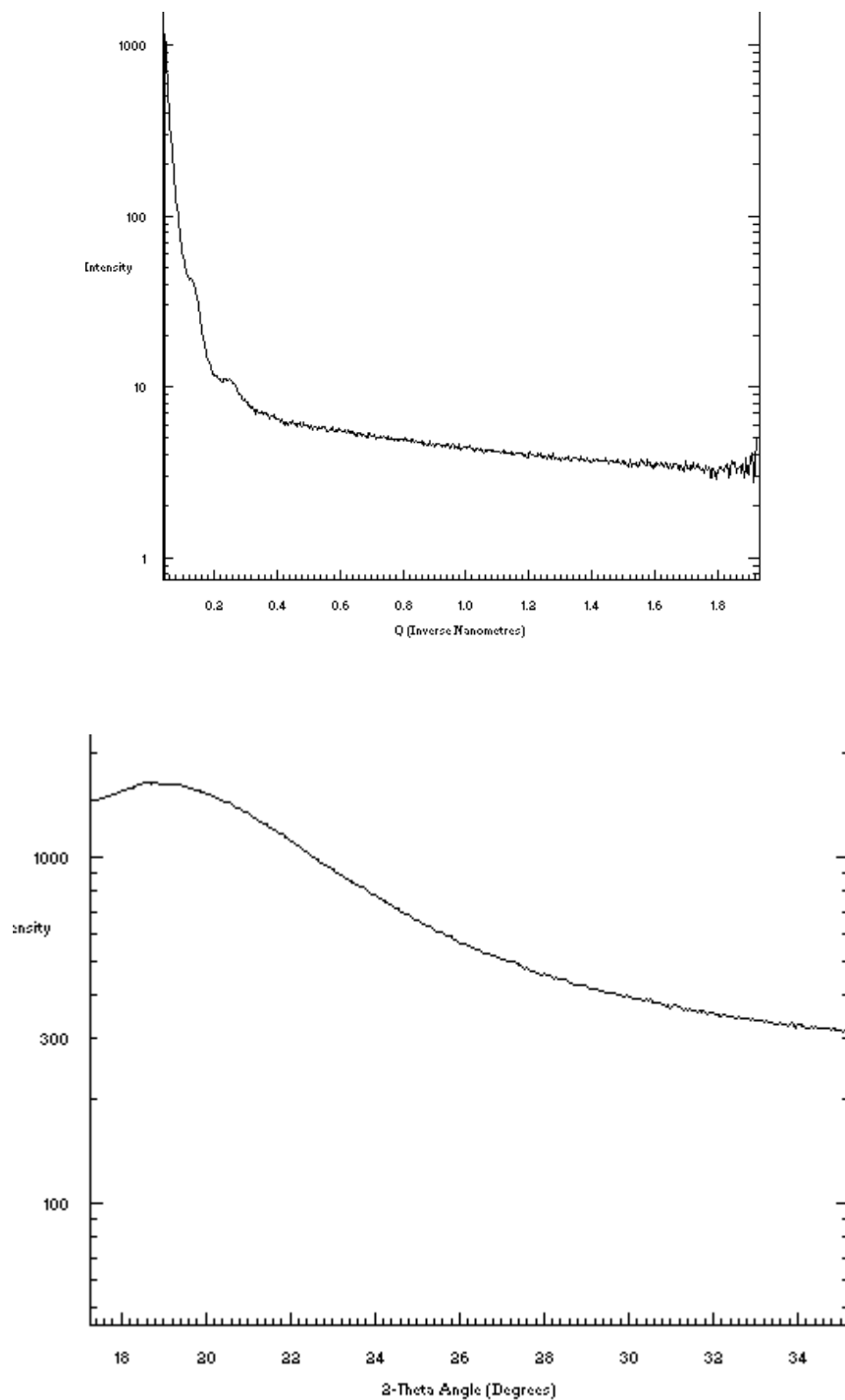


Figure S3.54: 1D SAXS plot of **26** annealed *in vacuo* at 210 °C showing no microphase-separation in the melt state

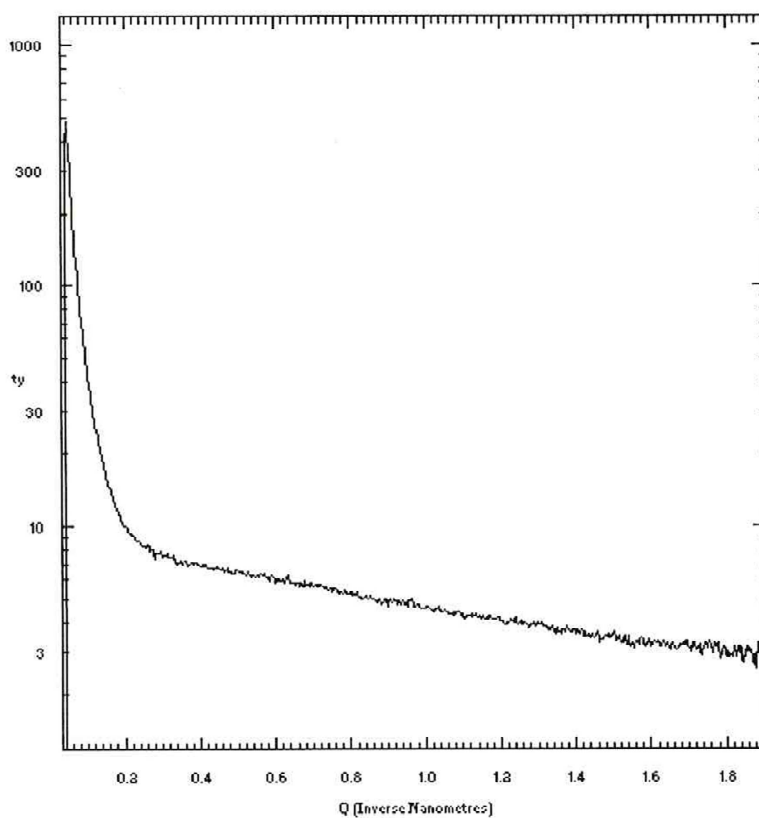


Figure S4.1. GPC Trace of aPP-N₃ (**32**). $M_n=1.3$ kDa, $M_w=1.4$ kDa, $M_w/M_n=1.09$.

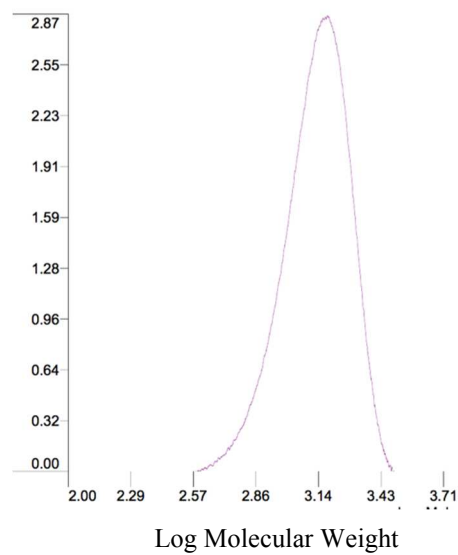


Figure S4.2. ¹H-NMR spectrum of aPP-I (**31**) (400 MHz, CDCl₃, RT, calibrated at 7.27 ppm)

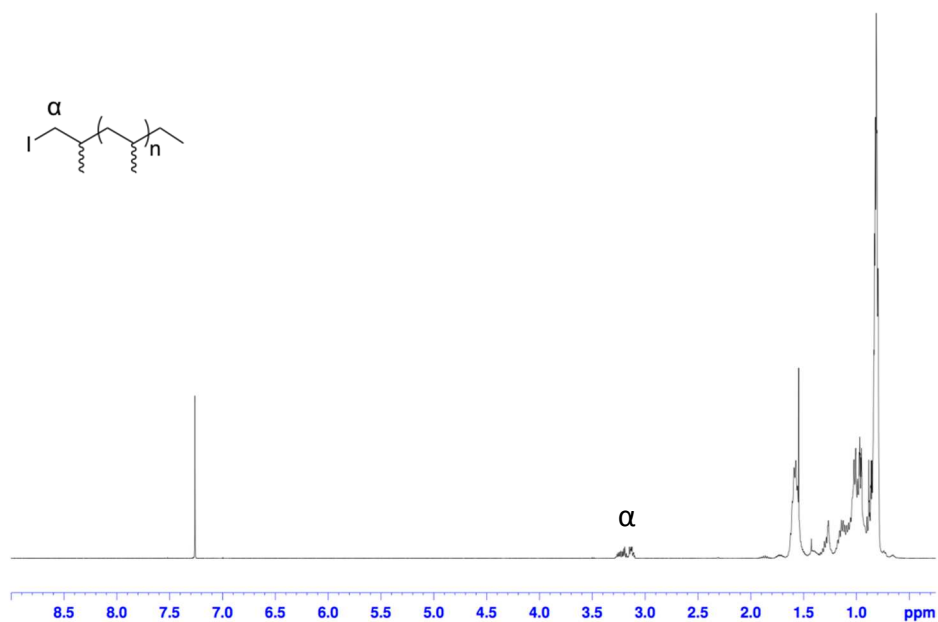


Figure S4.3: ^1H -NMR spectrum of aPP-N₃ (**32**) (400 MHz, CDCl₃, RT, calibrated at 7.27 ppm)

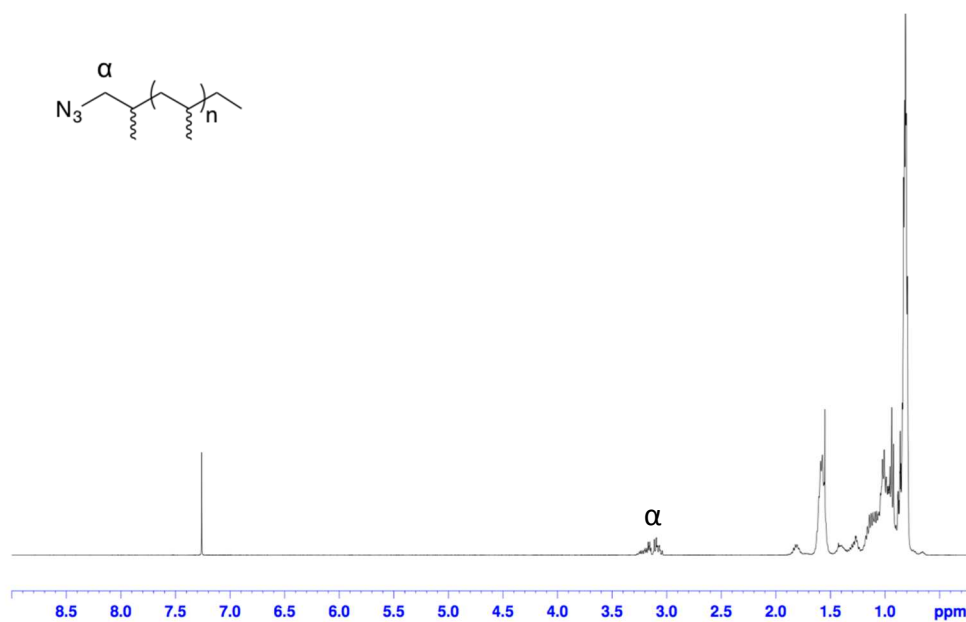


Figure S4.4: ^1H -NMR spectrum of AcN-propargyl cellobiose (**33**) (600 MHz, D₂O, RT, calibrated at 4.80 ppm)

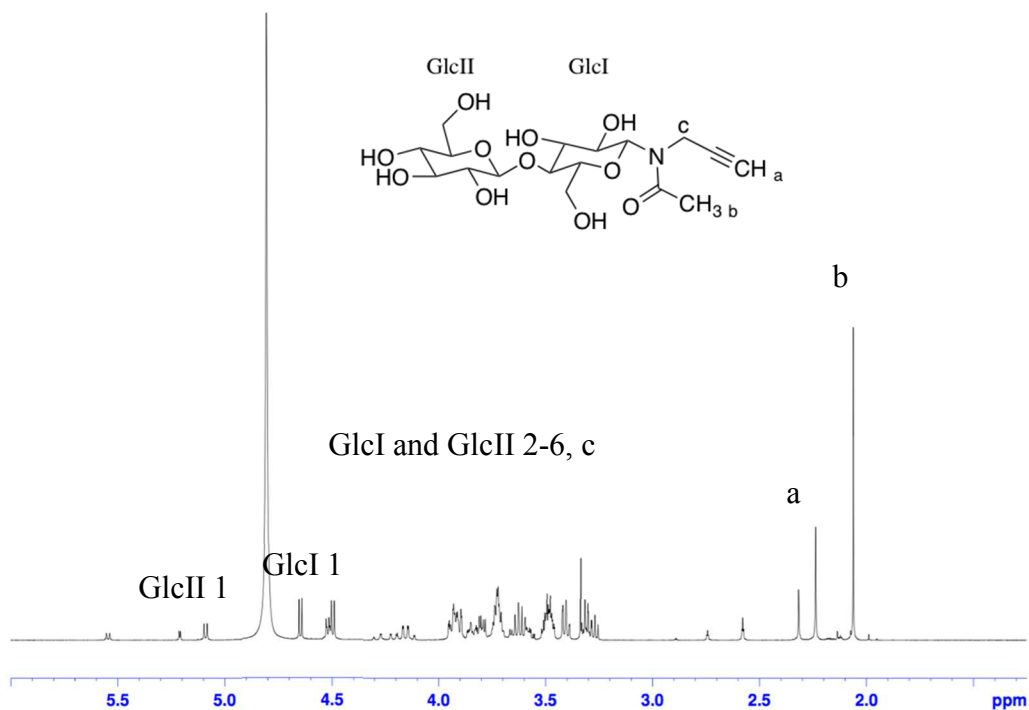


Figure S4.5: (top) ^1H -NMR spectrum (600 MHz, $\text{DMF-}d_7$, RT, calibrated at 8.01 (COH) ppm) and (bottom) ^{13}C -NMR spectrum (150 MHz, $\text{DMF-}d_7$, RT, calibrated at 163.15 ppm) of **34**. Peaks labeled with an asterisk represent DMF.

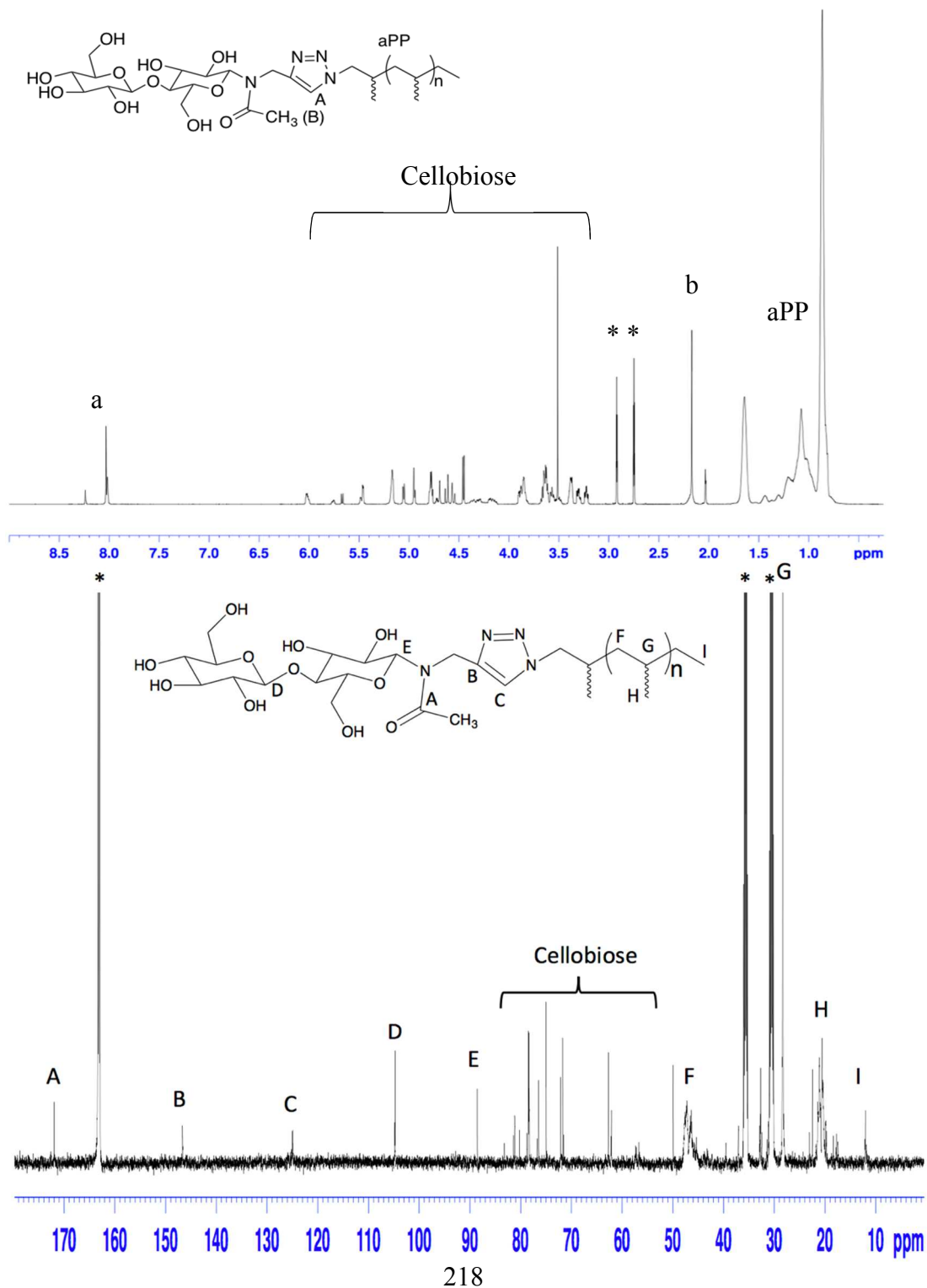


Figure S4.6: GISAXS of 1.0 wt% **34** equilibrated for 1 h at each temperature (Carbon coated Si (100) substrate, 600 s/frame, film=65 nm).

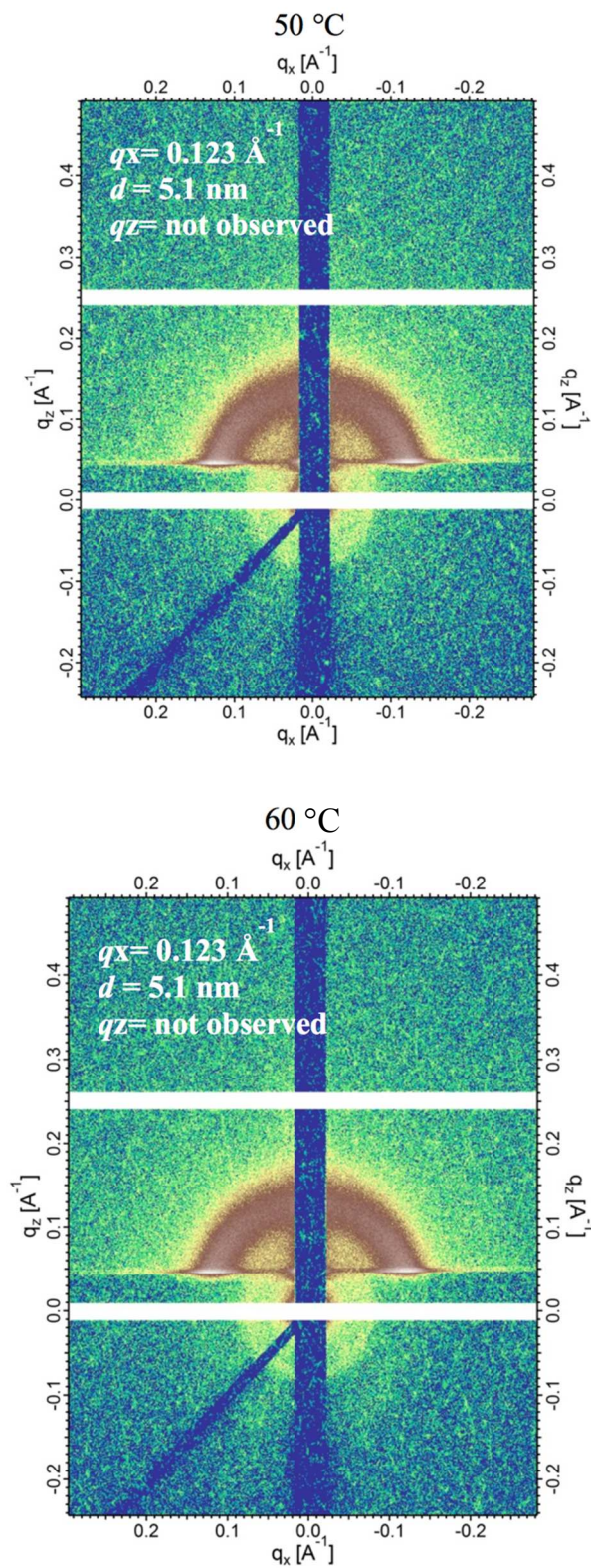


Figure S4.6: GISAXS of 1.0 wt% **34** equilibrated for 14 h at 50 °C in a vacuum oven (Carbon coated Si (100) substrate, 600 s/frame, film=65 nm).

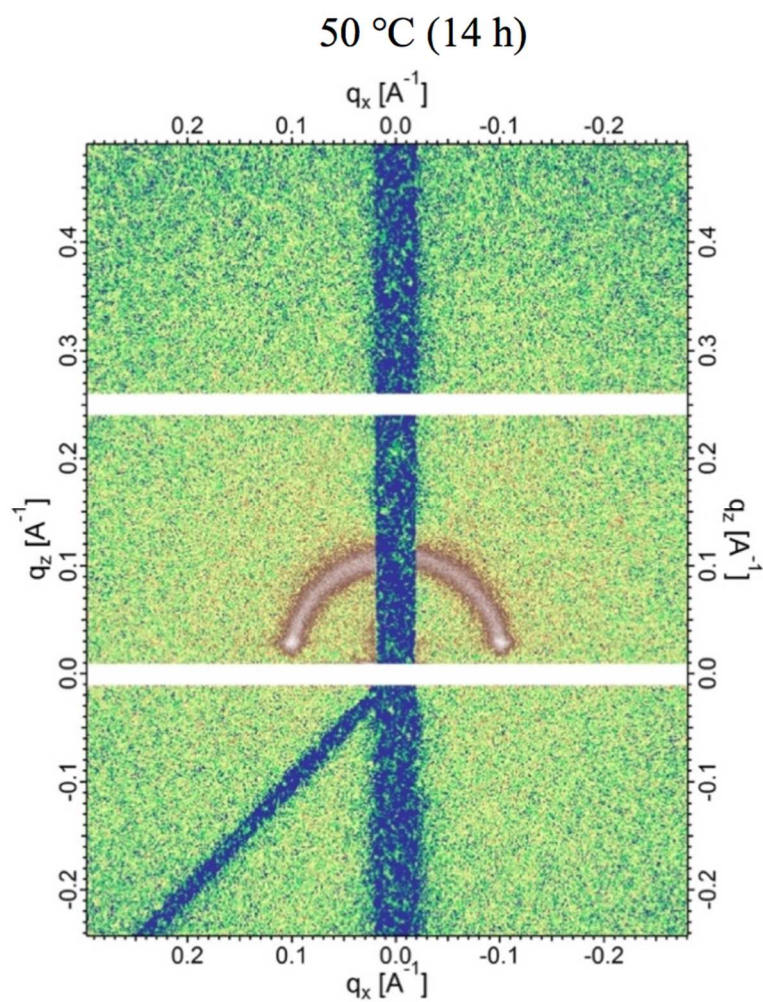


Figure S4.7: DSC curve of (D)-(+)-Cellobiose (Heat/cool/heat at 10 °C/min from -70 °C to 200 °C)

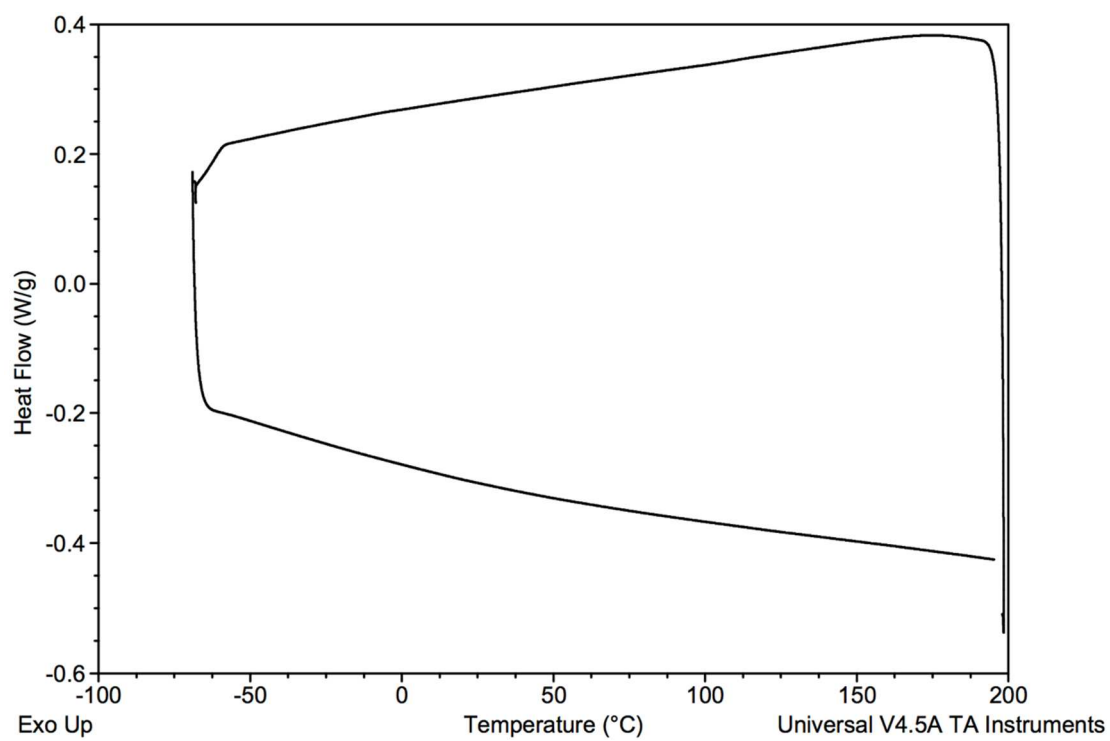
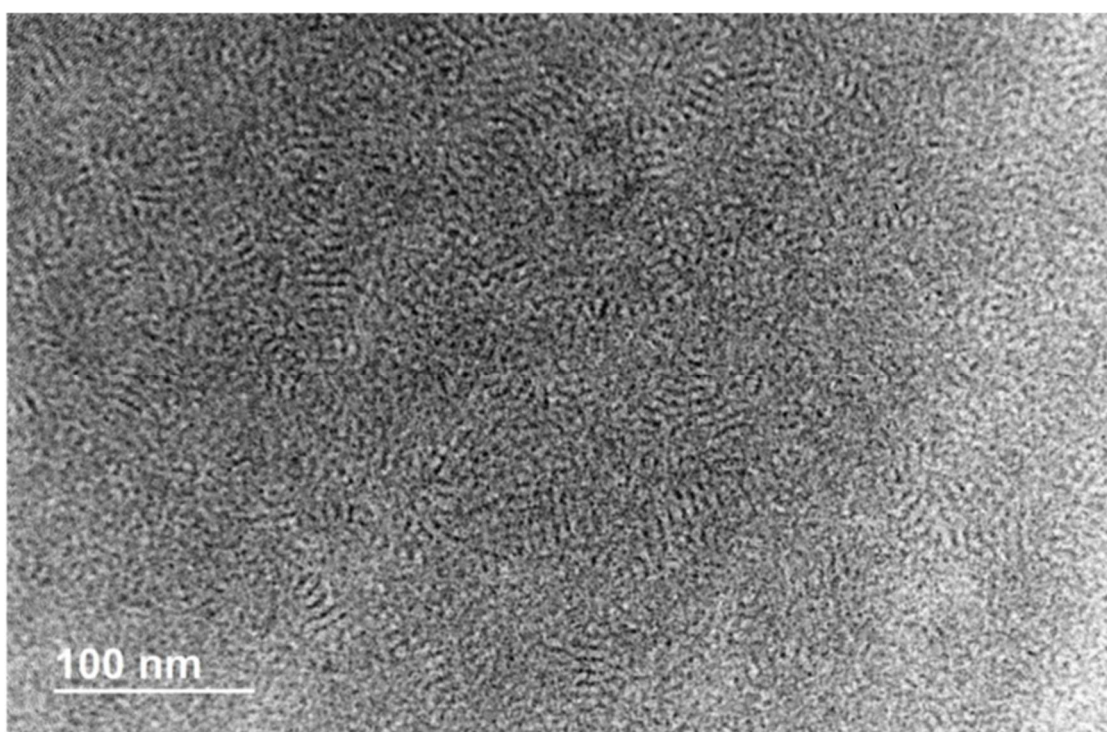
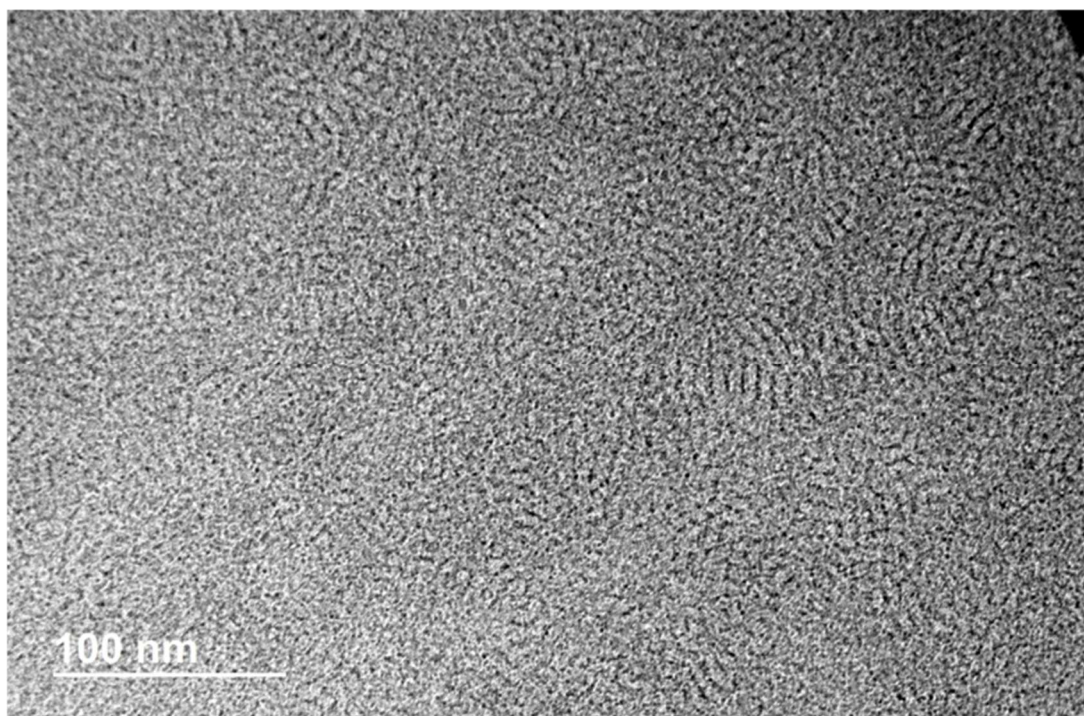


Figure S4.8: TEM images of **34** (0.3 wt% in 1:1 BuOH/Hexane, dip-coated on holey carbon grid, unannealed)



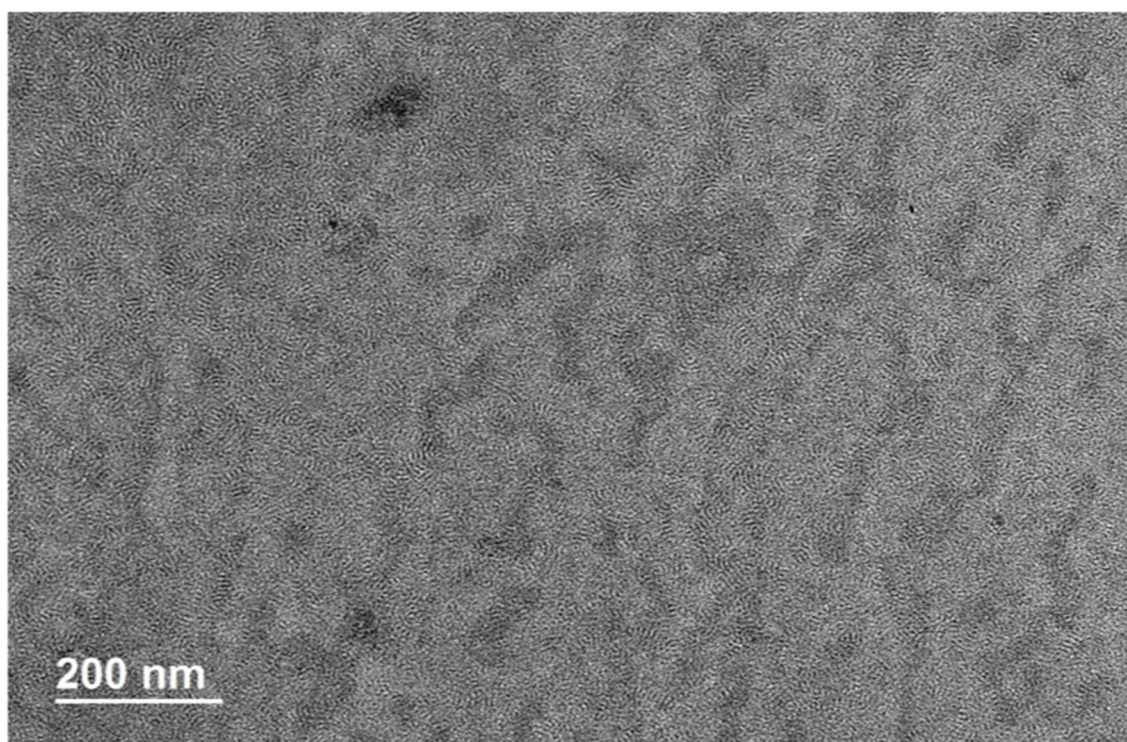
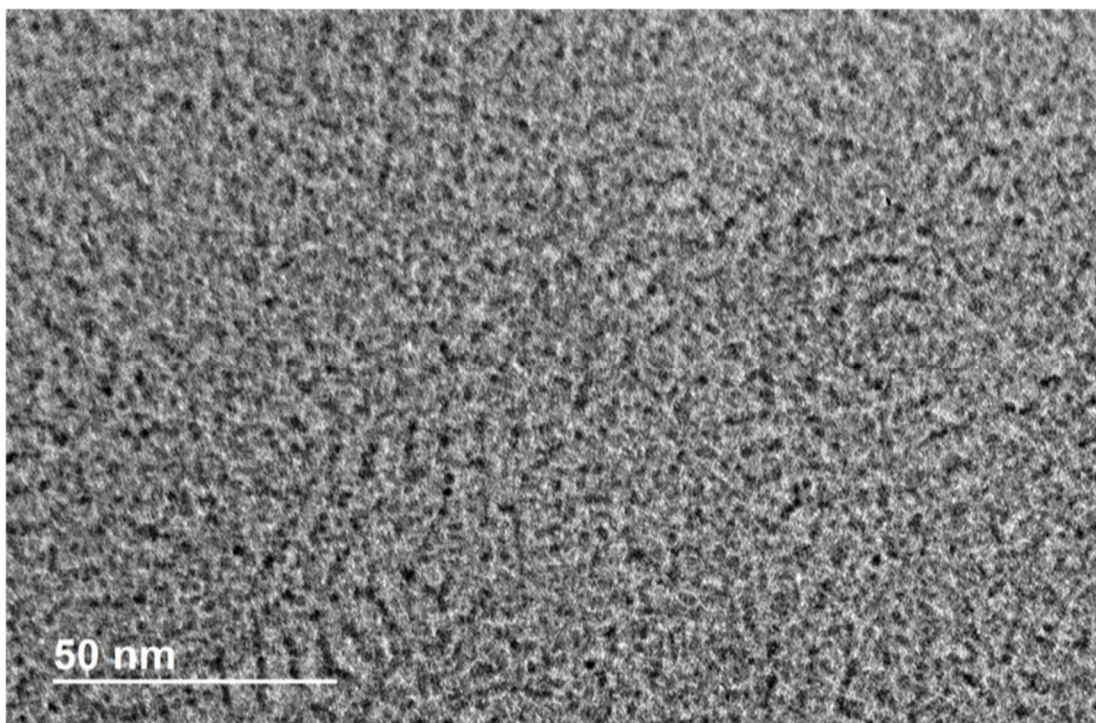
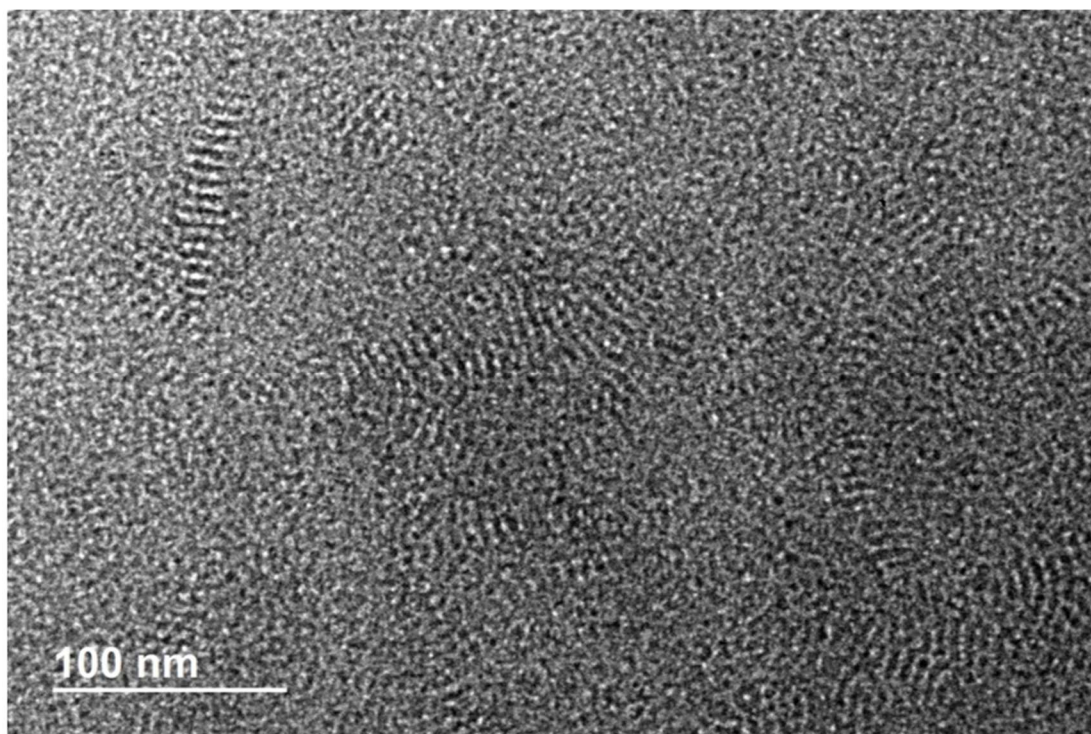
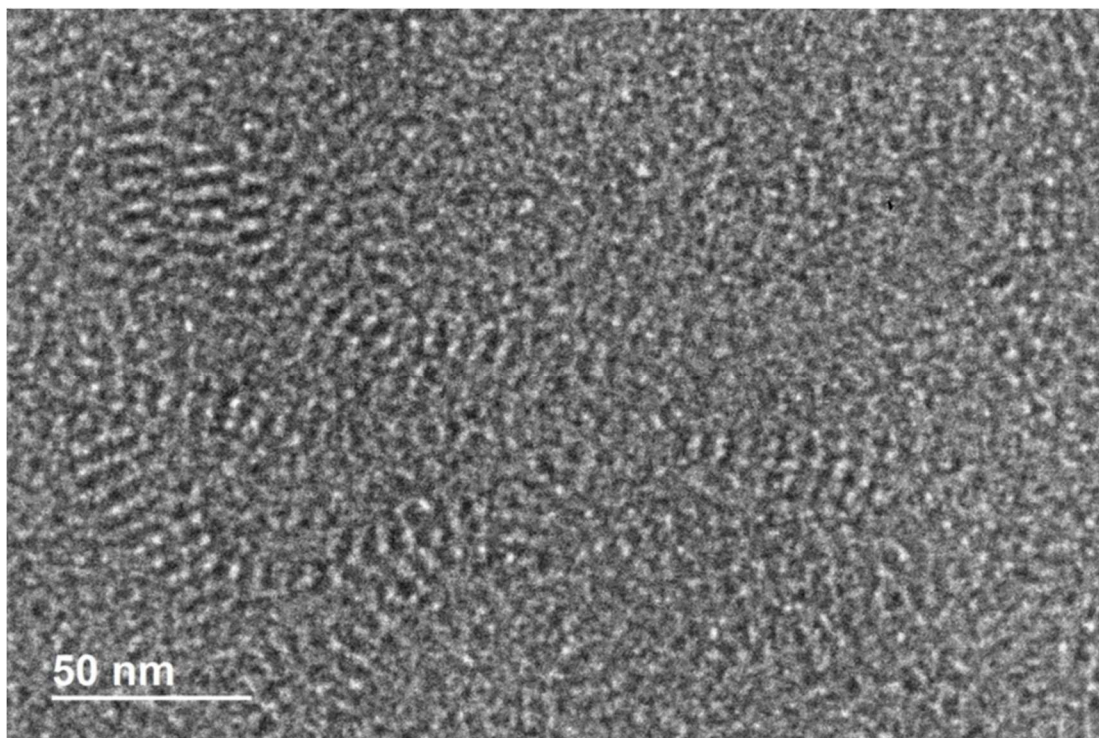


Figure S4.8: TEM images of **34** (0.3 wt% in 1:1 BuOH/Hexane, dip-coated on holey carbon grid) annealed at 60 °C for 14 h in a vacuum oven.



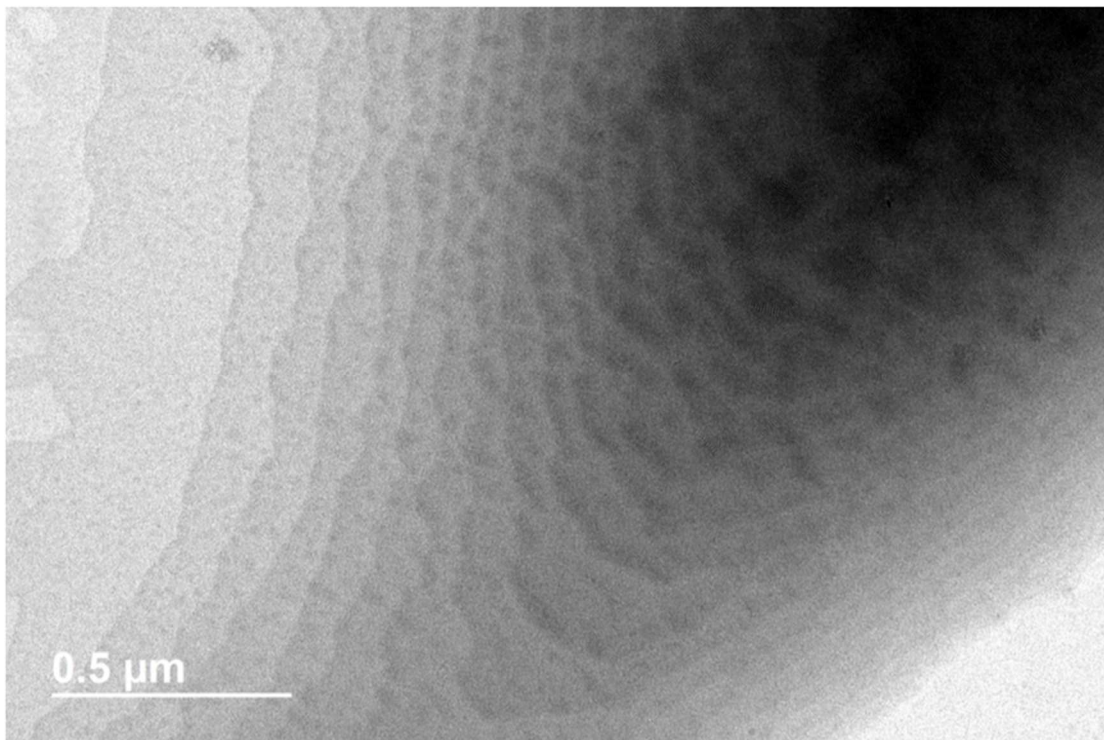
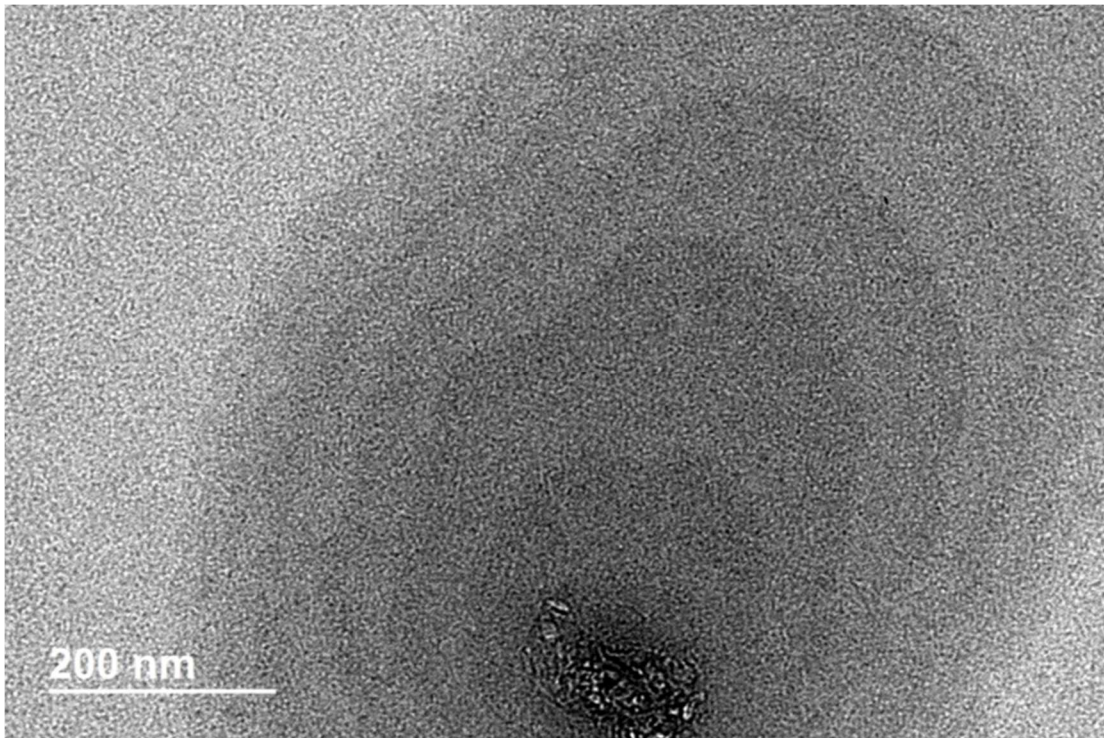


Figure S4.9: Cross-sectional analysis of AFM height image of **34** spun-cast from a 0.1% (w/v) solution in 1:1 butanol/hexane after thermal annealing at 60 °C for 24 h.

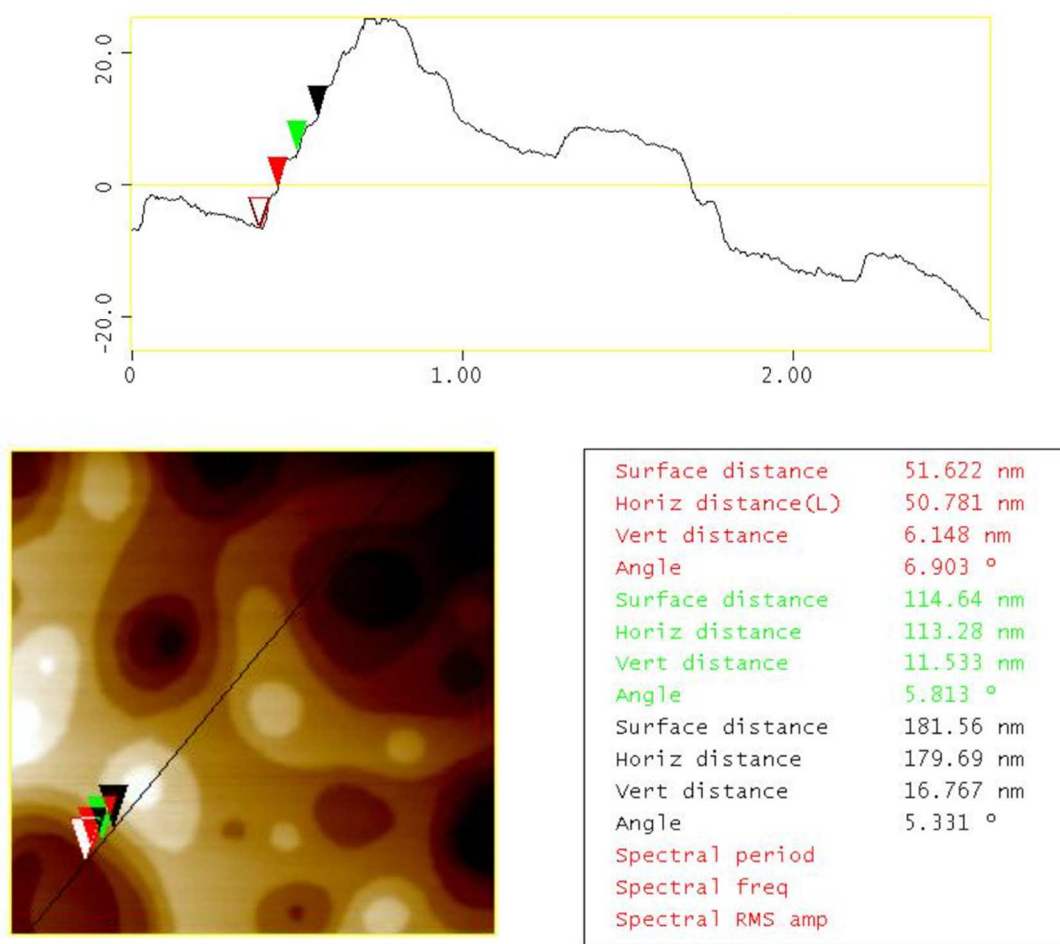


Figure S4.10: AFM phase images of **34** spun-cast from a 0.1 % (w/v) solution in 1:1 butanol/hexane after thermal annealing at 60 °C for 48 h.

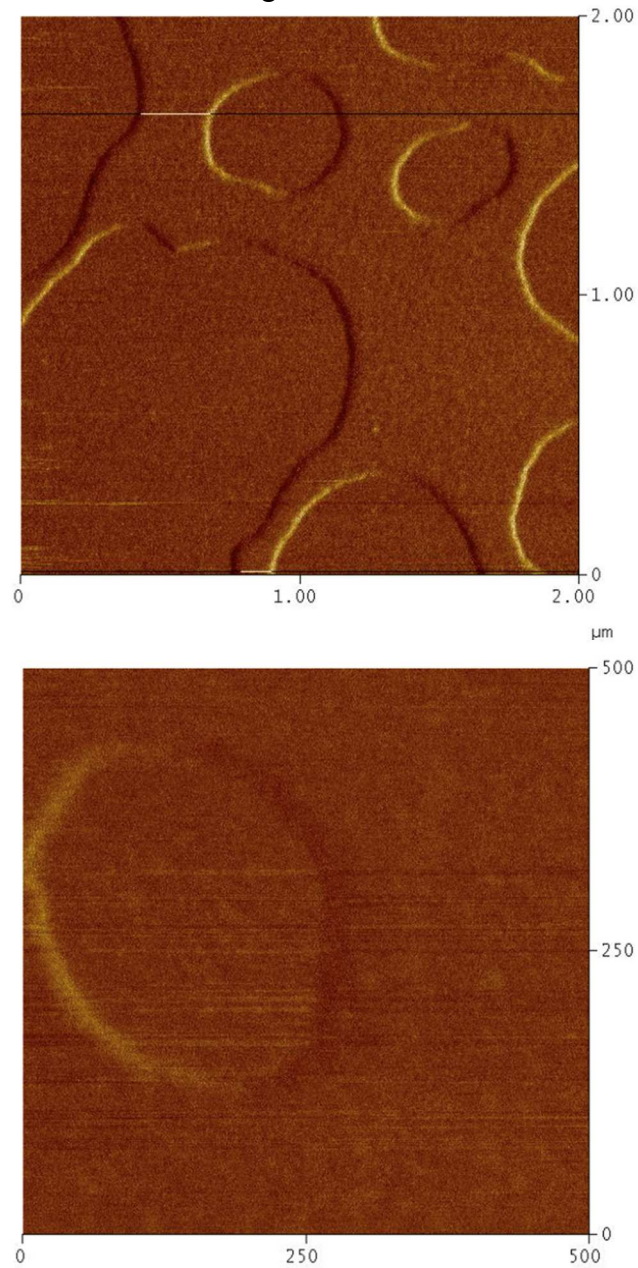


Figure S4.11: AFM phase images of **34** spun-cast from a 0.1 % (w/v) solution in 1:1 butanol/hexane after thermal annealing at 38 °C for 72 h.

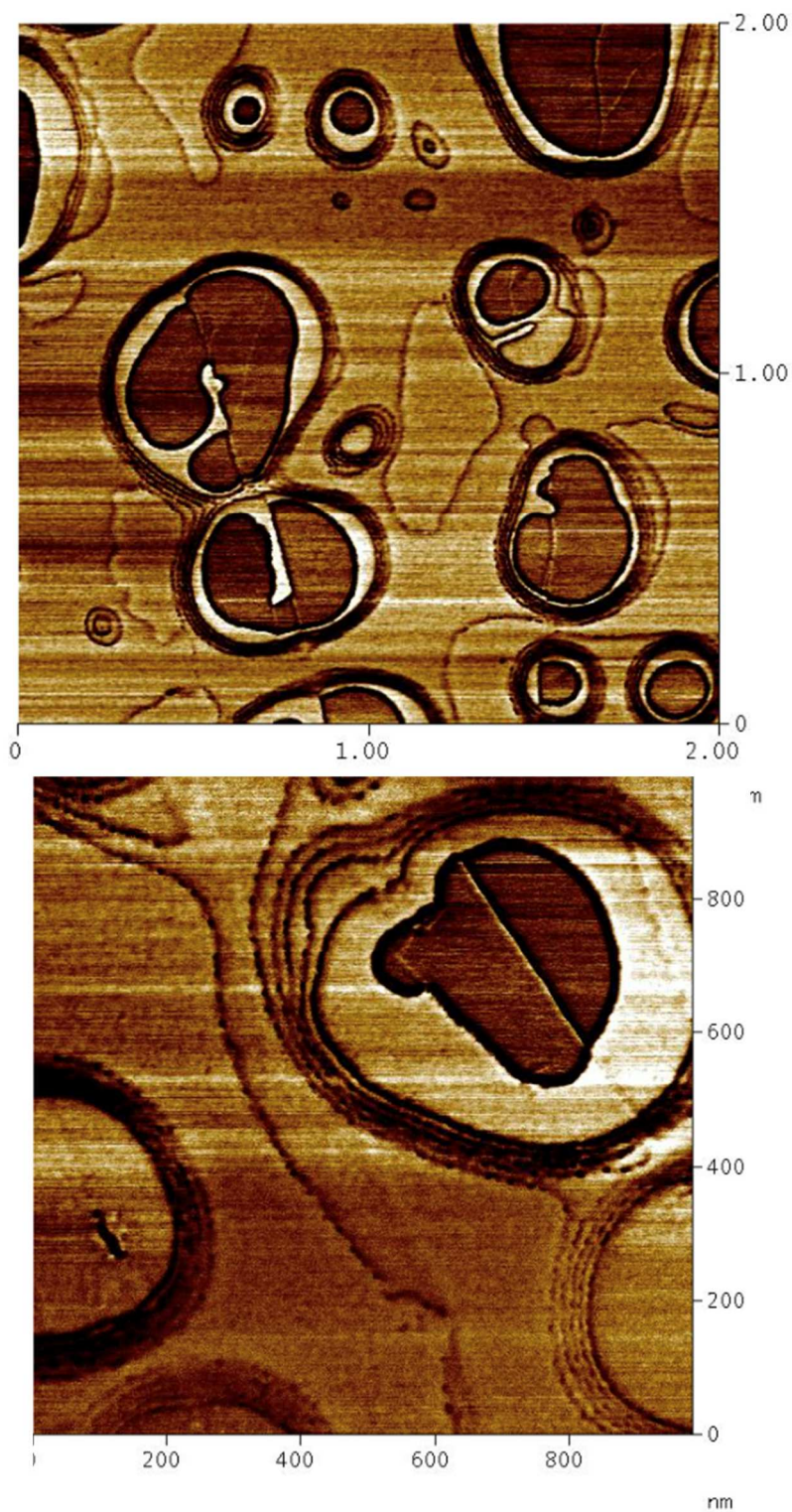


Figure S4.12: Cross-sectional analysis of an AFM height map of **34** spun-cast from a 0.1 % (w/v) solution in 1:1 butanol/hexane after thermal annealing at 38 °C for 72 h.

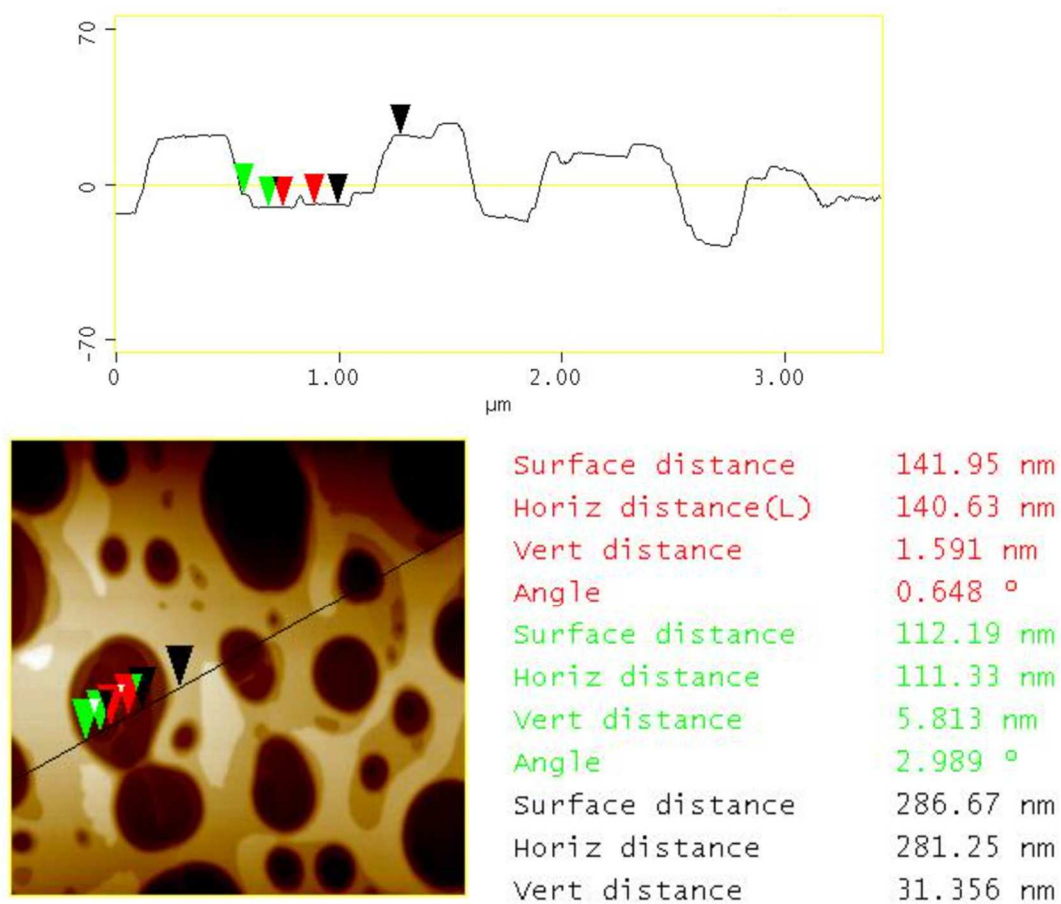


Figure S5.1: ^1H -NMR (600 MHz, $\text{DMF-}d_7$, RT, calibrated at 8.01 (COH) ppm) of **35**. Assignments were made based upon those made previously for **34**

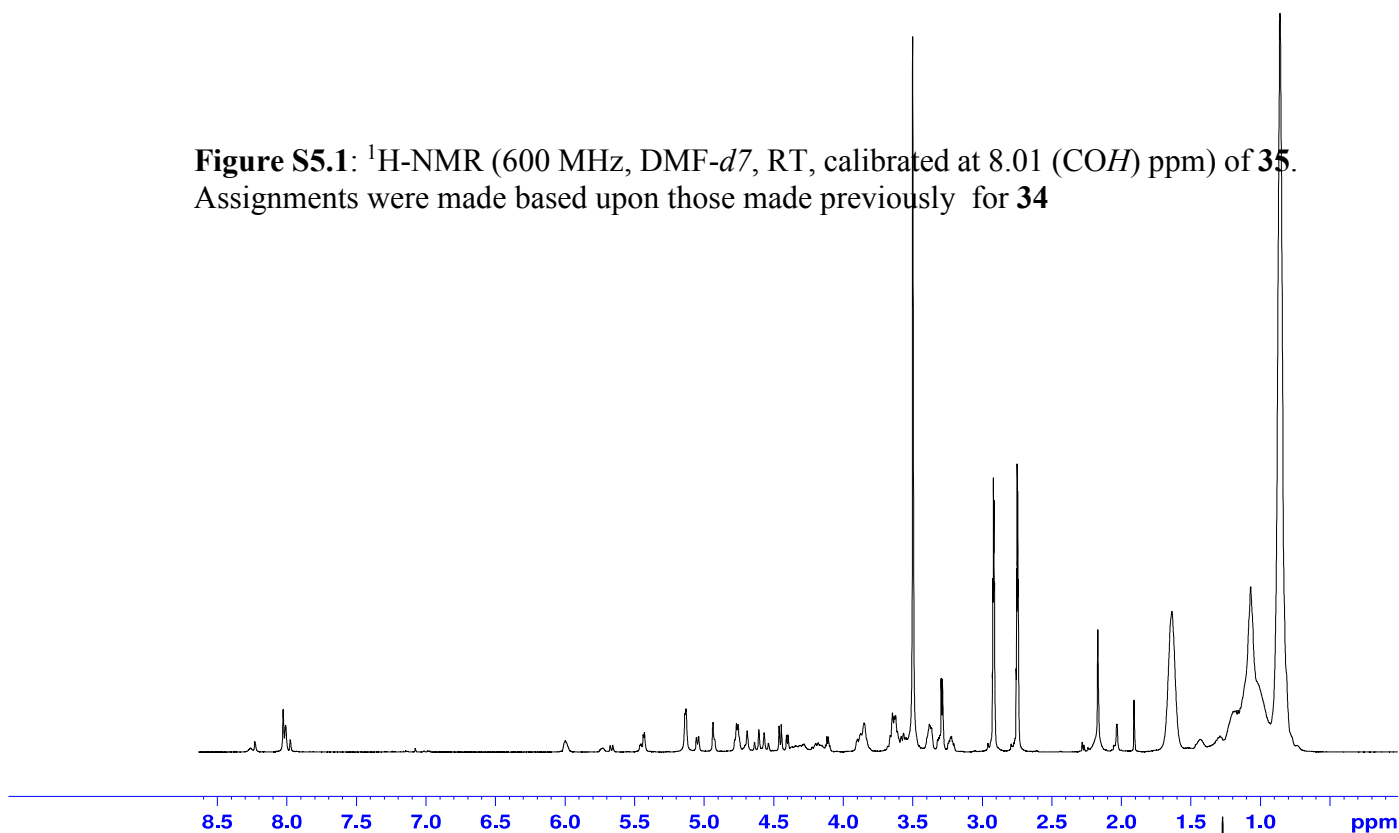


Figure S5.2: ^1H -NMR (600 MHz, $\text{DMF-}d_7$, RT, calibrated at 8.01 (COH) ppm) of **37**. Assignments were made based upon those made previously for **34**

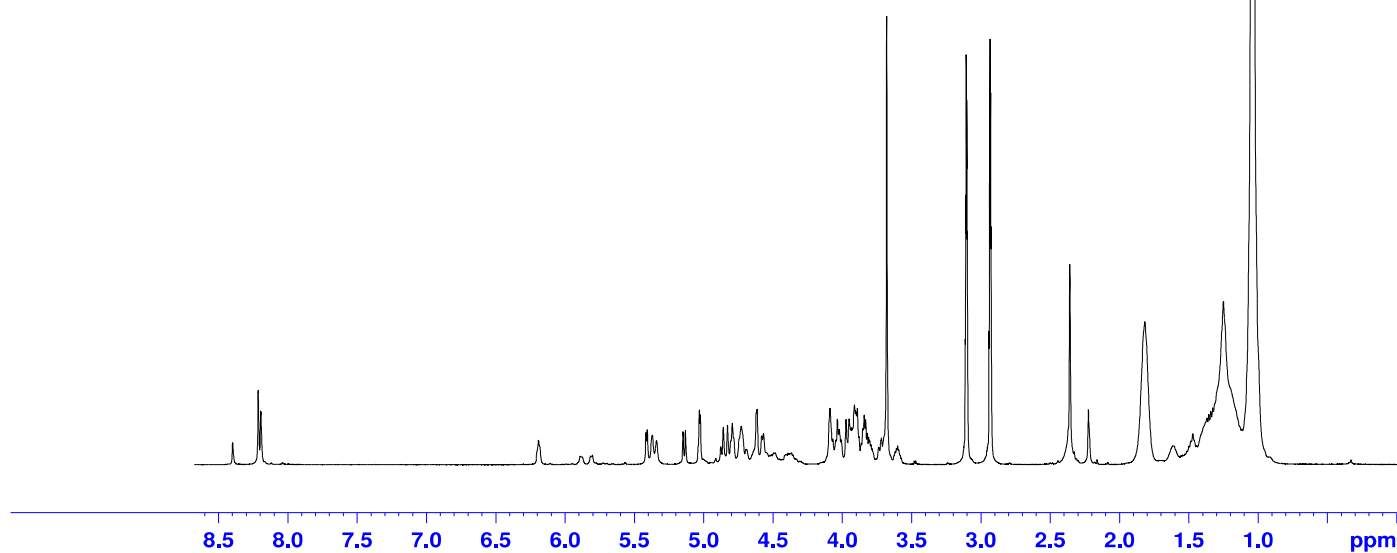


Figure S5.3: DSC curve of **35**

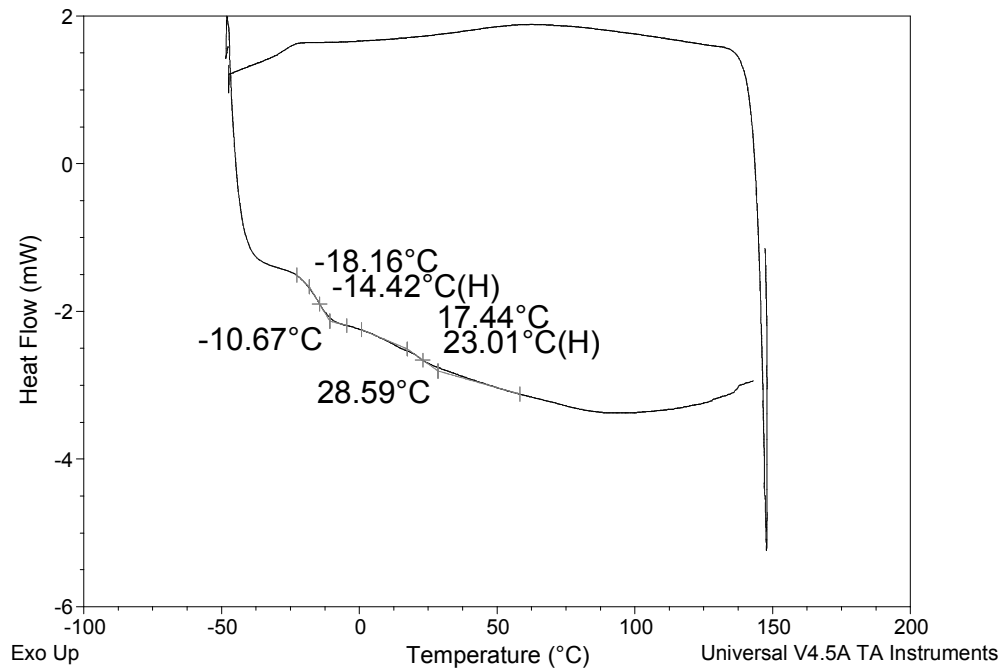


Figure S5.4: DSC curve of **36**

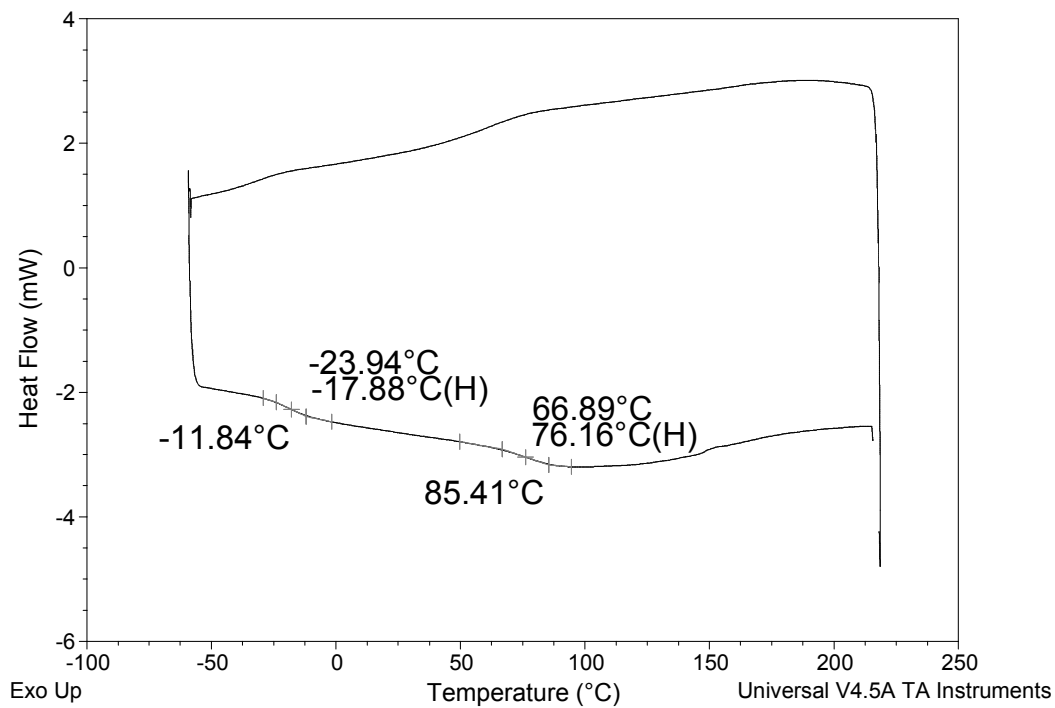


Figure S5.5: DSC curve of **37**

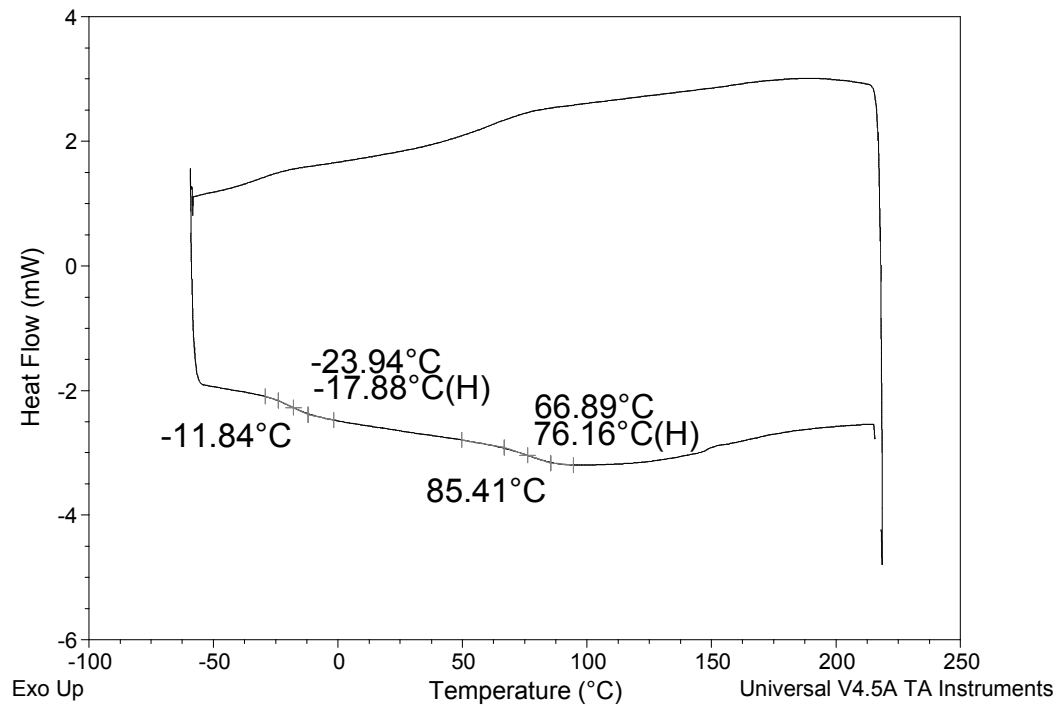


Figure S5.6: SAXS profiles of **35** during the LAM $\rightarrow$ HPL transition. Successive plots are shifted in intensity for clarity.

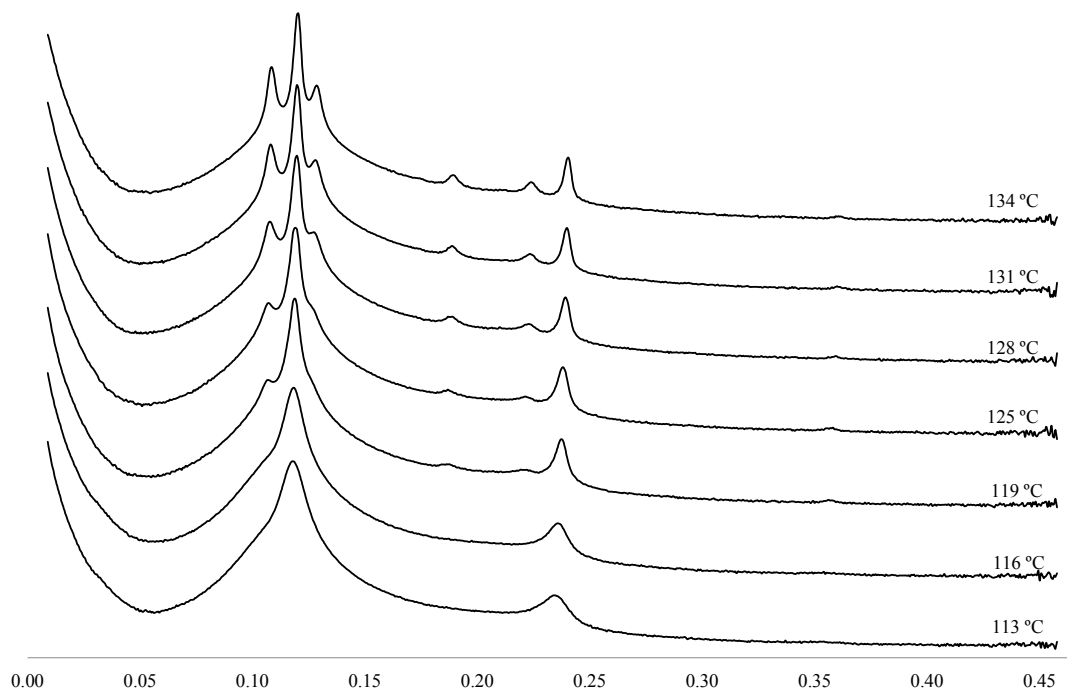


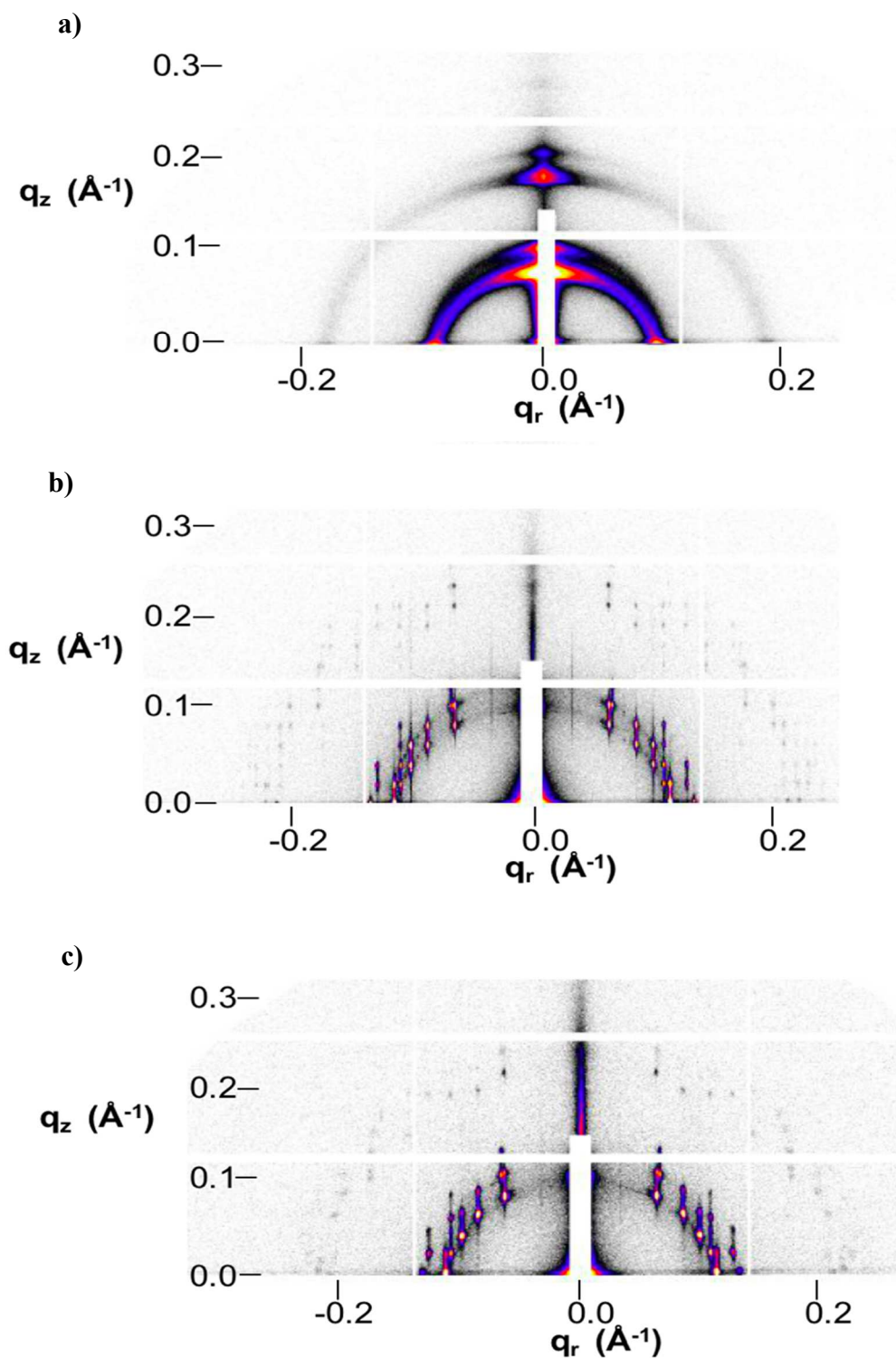
Table S5.1: Information on **35** in bulk

Phase	Peak #	<i>(hkl)</i> indices	<i>q</i> -value ratio	Exp. <i>q</i> (Å ⁻¹)	calc. <i>d</i> (nm)
LAM	1		1	0.107	5.87
	2		2	0.214	2.94
HPL	1	(101)	1	0.110	5.71
	2	(003)	1.09	0.122	5.15
	3	(102)	1.18	0.130	4.83
	4	(104)	1.73	0.190	3.31
	5	(201)	1.90	0.210	2.99
	6	(202)	1.95	0.218	2.88
	7	(105)	2.05	0.226	2.78
	8	(006)	2.18	0.242	2.59
	9	--	3.33	0.367	1.71
GYR	1	(211)	√6	0.123	5.11
	2	(220)	√8	0.143	4.39
	3	(321)	√14	0.189	3.32
	4	(420)	√20	0.226	2.78
	5	(332)	√22	0.238	2.64
	6	(422)	√24	0.248	2.53
	7	(431)	√26	0.258	2.44
	8	(521)	√30	0.278	2.26
	9	(532),(611)	√38	0.312	2.01
	10	--	√47	0.345	1.82
	11	--	√51	0.358	1.76

Table S5.2: Information on **34** in bulk

Phase	Peak #	(hkl) indices	q -value ratio	Exp. q ($\text{\AA}^{-1}$)	calc. d (nm)
LAM	1		1	0.0962	6.53
	2		2	0.193	3.23
	3		3	0.289	2.17
	4		4	0.386	1.63
HPL	1	(101)	1	0.105	5.98
	2	(003)	1.09	0.115	5.46
	3	(102)	1.18	0.123	5.11
	4	(104)	1.73	0.182	3.45
	5	(201)	1.90	0.202	3.11
	6	(105)	2.05	0.214	2.94
	7	(006)	2.18	0.229	2.74
	8	--	3.33	0.349	1.80
GYR	1	(211)	$\sqrt{6}$	0.117	5.35
	2	(220)	$\sqrt{8}$	0.135	4.64
	3	(400)	$\sqrt{16}$	0.191	3.28
	4	(420)	$\sqrt{20}$	0.214	2.93
	5	(332)	$\sqrt{22}$	0.225	2.78
	6	(422)	$\sqrt{24}$	0.234	2.68
	7	(431)	$\sqrt{26}$	0.245	2.56
	8	(521)	$\sqrt{30}$	0.262	2.39
	9	(532),(611)	$\sqrt{38}$	0.295	2.12
	10	--	$\sqrt{42}$	0.311	2.01
	11	--	$\sqrt{46}$	0.324	1.93
	12	--	$\sqrt{48}$	0.332	1.89
	13	--	$\sqrt{50}$	0.338	1.85
HEX	1	(100)	1	0.126	4.99
	2	(110)	$\sqrt{3}$	0.219	4.36
	3	(210)	$\sqrt{7}$	0.335	1.88

Figure S5.7: 2D GISAXS patterns of **34** at an incident angle of 0.15 °C showing the stability of the GYR phase. A 65 nm film was recorded at room temperature (a), then held at 175 °C for 1 h (b), and cooled back to room temperature (c)



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