ABSTRACT

Title of Thesis: FRACTIONATION OF POLY(ETHYLENE GLYCOL) BETWEEN LIQUID PHASES

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We studied the fractionation of poly(ethylene oxide) (PEO) in isobutyric acid and water at different temperatures below the critical point. To do so, different molecular weight PEO with different end groups have been used. All the solutions were prepared at the critical composition of the binary liquids. During the fractionation, the polymer distributes itself in the lower and upper phases as a function of molecular weight. The results of the higher molecular weight polymer confirmed previous studies done by Shresth. The current studies show that the molecular weight and the end group of the polymer seem to have no effect on the fractionation. The fractionation of the lower molecular weight PEO with OCH₃ termination is most powerful when compare to the higher molecular weight with OH end group.

Two non-linear equations were then used to fit the number fractions molecular weight distributions in order to determine the type of distribution. The relative mass of polymer in each phase is then calculated. Most of the polymer migrates to the upper phase leaving almost little in the lower phase. The ratio of the mass fraction in the upper phase to that in the lower phase is roughly four.
FRACTIONATION OF POLY(ETHYLENE GLYCOL) BETWEEN LIQUID PHASES

by

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Thesis submitted to the Faculty of the Graduate School of the University of Maryland, College Park in partial fulfillment of the requirements for the degree of Master of Science 2004

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Since Albertsson confirmed their use in bioseparation in the late 50s, poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG) have attracted the wide attention of the scientific world. Showing interesting and peculiar characteristics in organic and aqueous solutions, PEO has been extensively studied. Poly(ethylene oxide) with smaller molecular weight (200-20000 g/mol) is often referred as PEG. In addition, any PEO that has hydroxyl groups at each extremity of the molecule is also called PEG. The appellation of PEO is generally used for higher molecular weights or molecules with methyl oxide groups at each end.

PEO and PEG are linear polymers with interesting properties. The polymer is built up with repeating monomer units of -(CH₂-CH₂O)-. The monomer possesses hydrophobic ethylene groups and hydrophilic oxygen atoms. The hydrophobic elements (-CH₂-CH₂-) allow the polymer to be soluble in many organic solvents. Meanwhile, the presence of the oxygen atom in every third position of the polymer favors the formation of hydrogen bonds, making the polymer soluble in water. This important feature has generated its use in numerous pharmaceutical applications. Hydrogen bonding and hydrophobic interactions play vital roles in protein folding and stability. Those two
characteristics found in proteins and other biomaterials have made the PEO useful to study biomolecular interactions.

PEO or PEG has been extensively used in pharmaceutical industries because of its ability to adsorb on surfaces and at interfaces. Considered as a biomaterial, PEO has been an important tool for drug purification, drug delivery and contact lenses. PEO can be attached to drugs and vitamins to impart water solubility.

2 - Fractionation

a.) Theoretical fractionation

When a polydisperse polymer is dissolved in a binary solution of two liquid phases, we expect the polymer to distribute itself as a function of molecular weight between the upper phase and the lower phase at equilibrium. The Flory-Huggins (FH) theory, which pioneered the understanding of this effect, cannot quantitatively describe such polymer fractionation because, like Van der Waals, FH ignores all non-mean field effects. Several refined theories have helped deal with the thermodynamics of the polymer/solvent systems. Stockmayer and co-workers have proposed a “bridging” expression that considers all the interactions. That expression resulted in the addition of nonlinear terms in the Flory equation. Evans and coworkers presented a theory of a polydisperse system based on the perturbation of a monodisperse system. This theory predicted the ratio of the moments of the parent and daughter in homogeneous solutions or coexisting phases. In fact, they showed that the difference in number average molecular weight, $M_n$ of the daughter phases should be proportional to the skewness of
the parent distribution. This theory was later contradicted by Xu and Baus, “but supported by measurements on colloidal particles.”

In 1995, Ten Brinke and Szleifer constructed a new theory that takes into account the non-mean field intramolecular and mean-field intermolecular interactions. Using Monte Carlo calculations, this theory predicts the full molecular weight distribution and the distribution coefficient of the polymer.

b.) Experimental fractionation

None of the latest theories have been experimentally tested. Long before the coming of size exclusion chromatography (SEC), Okamoto et al. tried to measure the distribution coefficient and the molecular weight by viscometry. One experiment using the SEC was done by Kleintjens et al. in which they studied polystyrene in cyclohexane and polyethylene in diphenyl ether at one temperature.

In 2002, Shresth et al. studied the fractionation of higher molecular weight PEO (Mₘ = 25700) in isobutyric acid and water at different temperatures below the critical point of the mixtures using the SEC. The experiment showed the distribution of the molecular weight and the behavior of parent and daughter distributions in lower and upper phases.

3 - Coexistence Curve of Isobutyric Acid + Water

Binary liquids that mix partially at constant pressure have coexistence curves with critical points similar to any critical point. The discrete points forming the coexistence curve are called transition temperatures, Tᵣ. Tᵣ is the temperature at which a sample of a specific composition changes from a one-phase liquid to a two-phase liquids upon either
cooling or heating. $T_c$ becomes the maximum (upper critical solution temperature, UCST) or minimum (lower critical solution temperature, LCST) value of $T_t$ when $T_t$ is measured as a function of composition. $T_c$ equals $T_t$ only if the sample is at critical composition.

The coexistence curve of isobutyric acid and water shows a UCST, which yields a maximum at the critical point (see figure 1). Points in regions I and II on either side of the curve correspond to homogeneous lower and upper phases. Inside the curve, two phases are in equilibrium with specific compositions. The critical composition is 0.39 mass fraction of isobutyric acid (IBA). The critical temperature determined by Shresth et al.\textsuperscript{8} was 299.4 K ± 0.1 K; that is within 0.3 K of the values in the literature. Once the minimal amount of polymer is added to the binary solution, a decrease of transition temperature was observed and the separation of the two phases appeared at 298.7 K.\textsuperscript{12}
Figure 1: Coexistence Curve of Isobutyric Acid + Water: Coexisting Mole Fractions
4 - New Analysis and Data

This work will focus on low molecular weight PEO. A statistical analysis will be performed on Shresth’s data and on the new data in order (1) to calculate the mass of the polymer in each phase for which Dr. G. Smith, at Utah University, developed the calculations (see Appendix A), and (2) to seek the functional forms of the parent and daughter molecular weight distributions.

II - THEORETICAL BACKGROUND

1 - Flory Theory

The common discussion of polymer fractionation between binary fluid phases is based on the Flory-Huggins prediction. According to Flory Huggins, the distribution of a polymer with size n over the two phases should fit the following equation:\(^{15}\)

\[
\frac{\phi_n''}{\phi_n'} = \exp(-\sigma n) \tag{1}
\]

where \(\phi_n''\) and \(\phi_n'\) represent the volume fraction of the polymer component of size n in the diluted and concentrated phases of volumes \(V''\) and \(V'\) respectively. \(\sigma\) is a constant which depends on temperature and pressure but is independent of the polymer size. If the volumes are converted into masses of component n in each phase, then equation (1) becomes

\[
\ln \left(\frac{w_n''}{w_n'}\right) = \ln r - \sigma n \tag{2}
\]

where \(r\) is related to the ratio of the volumes of the coexisting phases and \(w_n\) denotes the mass of the polymer species n. The above equation (2) governs the fractionation of the
polymer between the two equilibrium phases, which predicts a linear chain length
dependence of the logarithm of the distribution coefficient with \( \ln r \) as intercept.

### 2 - Ten Brinke and Szleifer Theory

Ten Brinke and Szleifer\(^9\) constructed a new theory in 1995. The theory is based on
one single chain to which they added non-mean field intramolecular interactions. This
theory predicts not only the full molecular weight distribution (MWD) of the polymer in
each phase, but also the distribution coefficient for either an UCST or a LCST.

The core idea of this approach is the probability distribution function (pdf) of the
chain conformations \( P_n(\alpha_n) \), where the subscript \( n \) indicates the size of the polymer, and
\( \alpha_n \) the conformation of the polymer chain. The theory clearly explains the relationship
between the conformational degree of freedom and the thermodynamic behavior.

This theory uses the Helmholtz free energy function for a mixture of polymer
molecules. The mixture is composed of \( N_n \) polymers of length \( n \). The lattice consists of
points \( M \) where \( M = \sum_{\{n\}} nN_n + N_s \) and \( \{n\} \) denotes the different sizes of polymer and \( N_s \)
the number of solvent molecules. The volume fraction of species \( \phi_n \) is given by \( nN_n/M \),
and due to the lattice condition, the solvent volume fraction is given by \( \phi_s = 1 - \sum \phi_n \). The
Helmholtz free energy written in terms of pdf then becomes the following function:

\[
\beta F = \sum N_n \ln \phi_n + \sum P_n(\alpha_n) \ln P(\alpha_n) + \chi N_n \langle n_n \rangle \phi_s + \sum N_s \ln \phi_s,
\]

where the first term and the second term, respectively, represent the translational entropy
and the conformational entropy of the polymers. The third term denotes the interaction between the polymer molecule of size \( n \) and the solvent molecules, and the last term is the translational entropy of the solvent molecules. Since the polymer solution contains only two types of molecules, solvent and monomers of polymer, the interaction parameter

\[
\chi = \left[ \varepsilon_{ps} - \frac{1}{2} \left( \frac{\varepsilon_{e} - \varepsilon_{ss}}{k_{B}T} \right) \right]
\]

is their interaction, where \( \varepsilon_{ij} \) is the interaction between monomer type \( i \) and monomer type \( j \), \( T \) is the absolute temperature, and \( k_{B} \) is the Boltzmann constant.

By minimizing the Helmholtz equation with respect to the pdf, the following equation is obtained:

\[
P_n(\alpha n) = \frac{1}{q_n} \exp\left[ -\chi n_n (\alpha_n) \phi_s \right],
\]

where \( q_n \) is the single chain partition function that ensures the normalization of the pdf for each molecular weight.\(^9\) By substituting \( P_n(\alpha n) \) in equation (3), the Helmholtz free energy equation then becomes:

\[
\beta F = \sum_{n} \left[ N_n \ln \phi_n - N_n \ln q_n \right] + N_s \ln \phi_s.
\]

Once the polymer solution has reached its equilibrium, the distribution coefficient and the phase diagram can be calculated by finding the chemical potential of each phase. To do so, the derivative of equation (5) is taken with respect to \( n \), the size of polymer segment.

\[
\mu_n = \ln \phi_n \ln q_n - \sum \chi \langle n_n \rangle \phi_s + (1-n) \phi_s,
\]
and for the solvent the chemical potential

$$\mu_s = \ln \phi_s + (1 - \phi_s) - \sum_n \phi_n n - \sum_n \phi_n \chi <n_n’> (1 - \phi_s). \quad (7)$$

By equating both chemical potentials, the distribution coefficient that governs the fractionation of the polymer is given as follows:

$$\ln(\frac{\phi’_n}{\phi’_n}) = - \ln \chi_{\phi_n} + (1 - n)(\phi_s’ - \phi_s”) - \chi \sum [\phi_n’ <n_n’>’ \phi_s’ - \phi_n” <n_n”>”\phi_s”]. \quad (8)$$

This equation clearly does not show a linear dependence of the distribution coefficient on $n$, as predicted by FH theory.

**III - PRIOR EXPERIMENTAL WORK**

**1 - Kinetics**

All Shresth’s plots$^8,12$ suggested that equilibrium is attained after two to four days. The weight average molecular weight ($M_w$) and the number average molecular weight ($M_n$) appear to attain equilibrium at the same time. The most important observation is that the kinetics and polydispersity indexes related to those polymers are independent of the temperature, which also appears to have little effect on the fractionation into the two daughter phases. Figures 2 and 3 below show that the lower phase of the mixture contains the higher molecular weight polymer, while the upper phase has lower molecular weight polymers.
Figure 2: Poly(ethylene oxide) in Isobutyric Acid + Water, $M_n$ and $M_w$ for the Upper and Lower Phases as a Function of Time at $T_c - T = 0.1$ K
Figure 3: Poly(ethylene oxide) in Isobutyric Acid + Water, $M_n$ and $M_w$ for the Upper and Lower Phases as a Function of Time at $T_c - T = 4 \text{ K}$
2 - Molecular Weight Distribution

One of the most exciting and interesting observations from Shresth ‘s experiment on PEO in IBA + H₂O is the powerful fractionation of the poly(ethylene oxide). The lower water rich-phase contains a higher average of molecular weight of polymer with smaller polydispersity index (PI). The majority of polymer mass is in the upper phase, and the upper phase has lower molecular weights. The ratio of the average molecular weight in the lower phase to that in upper phase is approximately 2. The following table summarizes the fractionation at different temperatures and also the polydispersity index in each phase.

The plot of molecular weight distribution (see figure 4) also confirms the fact that higher molecular weights of polymer are in the lower phase.

<table>
<thead>
<tr>
<th>Tc – T (K)</th>
<th>M̄ upper</th>
<th>M̄ lower</th>
<th>Mₙ upper</th>
<th>Mₙ lower</th>
<th>PI upper</th>
<th>PI lower</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>18000</td>
<td>36700</td>
<td>13100</td>
<td>34200</td>
<td>1.37</td>
<td>1.07</td>
</tr>
<tr>
<td>1</td>
<td>18000</td>
<td>36900</td>
<td>14200</td>
<td>35000</td>
<td>1.26</td>
<td>1.05</td>
</tr>
<tr>
<td>2</td>
<td>18800</td>
<td>40500</td>
<td>13900</td>
<td>37400</td>
<td>1.35</td>
<td>1.08</td>
</tr>
<tr>
<td>4</td>
<td>20300</td>
<td>35800</td>
<td>16800</td>
<td>33600</td>
<td>1.20</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Table 1: Coexisting Phases of Poly(ethylene oxide) in Isobutyric Acid and Water¹²
Figure 4: Poly(ethylene oxide) in Isobutyric Acid and Water: Molecular Weight Distribution at $T_c - T = 0.1 \text{ K}^8$
The following table summarizes all the findings of Shresth\textsuperscript{8,12} in the fractionation of the PEO in IBA+ H\textsubscript{2}O

<table>
<thead>
<tr>
<th>Properties</th>
<th>PEO/IBA+H\textsubscript{2}O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase with more total polymer</td>
<td>Upper, IBA-rich (80-90%)</td>
</tr>
<tr>
<td>Phase with higher molecular weight polymer</td>
<td>Lower, water-rich</td>
</tr>
<tr>
<td>Reduction in PI with separation</td>
<td>23%</td>
</tr>
<tr>
<td>([\text{Mw in higher Mw phase}/\text{Mw in lower Mw phase}])</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 2: Summary of the Distribution of PEO in Isobutyric Acid and Water\textsuperscript{8}

3 - Flory Theory

All data on PEO from Shresth et al.\textsuperscript{8} came to the same conclusion that the plot of \(\ln (w_n/w_{n}'\) versus molecular weight taken at different temperatures has a negative slope and downwardly concave curvature.(see figure 5 and 6 below).
Figure 5: Poly(ethylene oxide) in Water + Isobutyric Acid. Plots of $\ln\left(\frac{w(M)'}{w(M)''}\right)$ at $T = 298.6$ K and $T = 297.7$ K where $w(M)''$ = Mass Fraction of Polymer in Concentrated Phase and $w(M)' = Mass Fraction in the Diluted Phase.
Figure 6: Poly(ethylene oxide) in Water + Isobutyric Acid. Plots of $\ln(w(M)/w(M'))$ at $T = 296.7$ K and $T = 294.7$ K, where $w(M)$ = Mass Fraction of Polymer in the Concentrated Phase and $w(M')$ = Mass Fraction in Diluted Phase.
IV - NEW ANALYSIS OF PRIOR EXPERIMENTS

1 - Functional Form of Molecular Weight Distribution

A Matlab software program created by Matt Retzer and revised by Dr. S. Greer and Michael L. Alessi (See Appendix B) was used to fit proposed functions to the data. A good fit must fulfill the following requirements: (1) the reduced chi-squared is minimized (2) the residual plot must not show any major trends, and (3) the uncertainty on each parameter is smaller than the parameters. The program requires inputs for initial values, a confidence level, and the weighted parameters. The software will produce the errors associated with the calculated values of free parameters, the reduced chi-squared, and the residual plot. If the value of the reduced chi-square is around 1 and the residual plot is random, then we can conclude that there is a good fit. All errors are reported at 99% confidence interval, based on the errors associated with the molecular weights of 10%.

Two distributions are considered. The first distribution is the Gaussian distribution because of the symmetry observed in the plot of the lower phase data. The second distribution is the lognormal distribution, because all the data plots showed a positively skewed tail. The data sets were abridged because of the larger scatter at higher molecular weights.

The Gaussian\textsuperscript{16} equation to be used is the normal distribution.

\[
n(M) = \frac{\exp\left(-\frac{(M-\mu)^2}{2 \sigma^2}\right)}{\sigma \left(2\pi\right)^{0.5}}, \quad \text{(Gaussian)}
\]

where \(n(M)\) is the number fraction as a function of molecular weight. The values \(\mu\) and \(\sigma\) are the parameters that the nonlinear fitting algorithm determined in order to have the best fit. This equation is applied only to the lower phase data points.
The parameter $\mu$ is 34.2816
The parameter $\sigma$ is 8.3543
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 0.74769
The uncertainties in parameter $\sigma$ is 0.272
The reduced chi squared is 14.647

Figure 7: Lower Phase: Fitting and Residual Plots for Gaussian Function (Equation 9) at $T_c - T = 0.1$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,12$
The parameter $\mu$ is 34.2816
The parameter $\sigma$ is 8.3543
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 0.74769
The uncertainties in parameter $\sigma$ is 0.272
The reduced chi squared is 14.647

Figure 8: Lower Phase: Fitting and Residual Plots for Gaussian Function
(Equation 9) at $T_c - T = 1$ K for Shresth’s data on PEO in Isobutyric Acid
and Water$^8,12$
The parameter $\mu$ is 38.5284
The parameter $\sigma$ is 8.1861
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 1.0511
The uncertainties in parameter $\sigma$ is 0.39867
The reduced chi squared is 18.3612

Figure 9: Lower Phase: Fitting and Residual Plots for Gaussian Function
(Equation 9) at $T_c - T = 2$ K for Shresth’s data on PEO in Isobutyric Acid
and Water$^8,12$
The parameter $\mu$ is 34.1473
The parameter is $\sigma$ 7.1325
The confidence level is 99%
The uncertainties in parameter $\mu$ is 0.85587
The uncertainties in parameter $\sigma$ is 0.3094
The reduced chi squared is 20.2162

Figure 10: Lower Phase: Fitting and Residual Plots for Gaussian Function (Equation 9) at $T_c - T = 4$ K for Shresth's data on PEO in Isobutyric Acid and Water$^8,12$
The Gaussian distribution (equation 9) did not provide a random residual plot for the lower phase (see figures 7-10). Therefore, a slightly modified Gaussian distribution (equation 10) was considered. One new constant \( a_1 \) has been added to the equation. The purpose of the modification was to scale down the Gaussian function in order to amend the fit. The values \( \mu, \sigma, \) and \( a_1 \) are the parameters needed for the nonlinear fitting algorithm in order to have the best fit.

\[
n(M) = a_1 \exp\left( -\frac{(M-\mu)^2}{2\sigma^2} \right) \times \frac{1}{\sigma(2\pi)^{0.5}}, \quad \text{(Gaussian1)} \quad (10)
\]

The above function (equation 10) was used to fit only the lower phase data. The residual plots (see figures 11-14) look fairly random.
The parameter $a_1$ is 0.32209
The parameter $\sigma$ is 14.1055
The parameter $\mu$ is 31.8339
The confidence level is 99%.
The uncertainties in parameter $a_1$ is 0.0066962
The uncertainties in parameter $\sigma$ is 0.28462
The uncertainties in parameter $\mu$ is 0.1008
The reduced chi squared is 2.448

Figure 11: Lower Phase: Fitting and Residual Plots for Gaussian1 Function (equation 10) at $T-T_c = 0.1$ K for Shrest’s data on PEO in Isobutyric Acid and Water$^{8,12}$
The parameter $a_1$ is 0.14701
The parameter $\sigma$ is 13.1778
The parameter $\mu$ is 33.065
The confidence level is 99%.
The uncertainties in parameter $a_1$ is 0.0043283
The uncertainties in parameter $\sigma$ is 0.38656
The uncertainties in parameter $\mu$ is 0.13685
The reduced chi squared is 2.243

Figure 12: Lower Phase: Fitting and Residual Plots for Gaussian1 Function (equation 10) at $T-T_c = 1$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,12$
The parameter $a_1$ is 0.28289
The parameter $\sigma$ is 15.6352
The parameter $\mu$ is 35.5143
The confidence level is 99%
The uncertainties in parameter $a_1$ is 0.0070458
The uncertainties in parameter $\sigma$ is 0.33039
The uncertainties in parameter $\mu$ is 0.1061
The reduced chi squared is 1.687

Figure 13: Lower Phase: Fitting and Residual Plots for Gaussian1 Function (equation 10) at $T-T_c=2$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,12$
The parameter $a_1$ is 0.27284
The parameter $\sigma$ is 13.9667
The parameter $\mu$ is 32.1043
The confidence level is 99%.
The uncertainties in parameter $a_1$ is 0.0064705
The uncertainties in parameter $\sigma$ is 0.30595
The uncertainties in parameter $\mu$ is 0.10635
The reduced chi squared is 2.097

Figure 14: Lower Phase: Fitting and Residual Plots for Gaussian1 Function (equation 10) at $T_r - T = 4$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,12$
The next functions tested were lognormal functions. The choice of the lognormal functions was based on the fact that the plots describing the number fraction are positively skewed. The first function, equation 11 is a standard lognormal distribution.\(^{16}\)

\[
\frac{n(M) = \exp - \left(\ln(M) - \mu\right)^2 / (2\sigma^2)}{(2\pi)^{0.5} \sigma M}, \quad \text{(lognormal)} \quad (11)
\]

None of the residual plots from the lognormal (equation 11) fits were random (see figures 15-23).
The parameter $\mu$ is 4.4982
The parameter $\sigma$ is 0.01106
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 0.25447
The uncertainties in parameter $\sigma$ is 0.00343
The reduced chi squared is 9.68441

Figure 15: One-Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T = 300$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,12$
The parameter $\sigma$ is 0.23499
The parameter $\mu$ is 32.5641
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.0096589
The uncertainties in parameter $\mu$ is 0.77379
The reduced chi squared is 13.8423

Figure 16: Lower Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c-T = 0.1$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,12$
The parameter $\mu$ is 5.8704
The parameter $\sigma$ is 0.00032913
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 0.28941
The uncertainties in parameter $\sigma$ is 0.00011673
The reduced chi squared is 18.4935

Figure 17: Upper Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c-T = 0.1$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,12$
The parameter $\sigma$ is 0.22247
The parameter $\mu$ is 33.8092
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.0083333
The uncertainties in parameter $\mu$ is 0.8083
The reduced chi squared is 38.2645

Figure 18: Lower Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c-T = 1$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^{8,12}$
The parameter $\mu$ is 5.0699
The parameter $\sigma$ is 0.0019114
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 0.21156
The uncertainties in parameter $\sigma$ is 0.00028811
The reduced chi squared is 25.0744

Figure 19: Upper Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c - T = 1$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^{8,12}$
The parameter $\sigma$ is 0.19149
The parameter $\mu$ is 35.4707
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.010122
The uncertainties in parameter $\mu$ is 1.063
The reduced chi squared is 18.7533

Figure 20: Lower Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c - T = 2$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,12$
The parameter $\mu$ is 5.1937
The parameter $\sigma$ is 0.0003762
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 0.20563
The uncertainties in parameter $\sigma$ is 0.00011265
The reduced chi squared is 11.6106

Figure 21: Upper Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c-T = 2$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,12$
The parameter $\mu$ is 3.7308
The parameter $\sigma$ is 0.0094349
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 0.18306
The uncertainties in parameter $\sigma$ is 0.002603
The reduced chi squared is 11.9585

Figure 22: Upper Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c-T = 4$ K for Shresth’s data on PEO in Isobutyric Acid and Water\textsuperscript{8,12}
The parameter $\sigma$ is 0.20137
The parameter $\mu$ is 33.0594
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.0095973
The uncertainties in parameter $\mu$ is 0.89275
The reduced chi squared is 17.5371

**Figure 23**: Lower Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c - T = 4$ K for Shresth’s data on PEO in Isobutyric Acid and Water.
The lognormal distribution did not provide random residual plots. Equation 12, a lognormal function with new constant parameter $c_1$, was applied to all the data. The purpose of the addition was to scale down the lognormal distribution in order to fit the data points.

$$n(M) = c_1 \exp \left( - \frac{(\ln(M) - \mu)^2}{2\sigma^2} \right), \quad \text{(lognormal1)}$$

(12)
The parameter $c_1$ is 4.6974
The parameter $\sigma$ is 1.9284
The parameter $\mu$ 3.8285
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 6.7757
The uncertainties in parameter $\sigma$ is 0.43076
The uncertainties in parameter $\mu$ is 3.7108
The reduced chi squared is 17.212

Figure 24: One-Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T = 300$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^{8,12}$
The parameter $c_1$ is 0.32267
The parameter $\sigma$ is 0.23224
The parameter $\mu$ is 32.3507
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.0064888
The uncertainties in parameter $\sigma$ is 0.0030538
The uncertainties in parameter $\mu$ is 0.13397
The reduced chi squared is 2.449

Figure 25: Lower Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_c - T = 0.1$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8, 12$
The parameter $c_1$ is 0.048307
The parameter $\sigma$ is 0.63012
The parameter $\mu$ is 8.0238
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.00077456
The uncertainties in parameter $\sigma$ is 0.0055445
The uncertainties in parameter $\mu$ is 0.07107
The reduced chi squared is 20.041

Figure 26: Upper Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_c - T = 0.1$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^{8,12}$
The parameter $c_1$ is 0.15391
The parameter $\sigma$ is 0.93934
The parameter $\mu$ is 18.4104
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.005849
The uncertainties in parameter $\sigma$ is 0.013532
The uncertainties in parameter $\mu$ is 0.49265
The reduced chi squared is 20.0879

Figure 27: Upper Phase: Fitting and Residual Plots for Lognormal Function (Equation 12) at $T_c - T = 1$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,12$
The parameter $c_1$ is 0.14115
The parameter $\sigma$ is 0.19873
The parameter $\mu$ is 33.3372
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.0035649
The uncertainties in parameter $\sigma$ is 0.004485
The uncertainties in parameter $\mu$ is 0.16442
The reduced chi squared is 2.241

Figure 28: Lower Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_c - T = 1$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^{8,12}$
The parameter \( c_1 \) is 0.029946
The parameter \( \sigma \) is 0.56767
The parameter \( \mu \) is 6.3054
The confidence level is 99%.
The uncertainties in parameter \( c_1 \) is 0.00035774
The uncertainties in parameter \( \sigma \) is 0.0040577
The uncertainties in parameter \( \mu \) is 0.040603
The reduced chi squared is 20.8621

Figure 29: Upper Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at \( T_c-T = 2 \) K for Shresth’s data on PEO in Isobutyric Acid and Water\(^8,12\)
The parameter $c_1$ is 0.28793
The parameter $\sigma$ is 0.2292
The parameter is $\mu$ 36.0985
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.0079052
The uncertainties in parameter $\sigma$ is 0.0038922
The uncertainties in parameter $\mu$ is 0.15563
The reduced chi squared is 1.677

**Figure 30**: Lower Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T - T_c = 2$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,12$
The parameter $c_1$ is 0.27649
The parameter $\sigma$ is 0.22726
The parameter is $\mu$ 32.585
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.0069873
The uncertainties in parameter $\sigma$ is 0.003656
The uncertainties in parameter $\mu$ is 0.14348
The reduced chi squared is 2.063

Figure 31: Lower Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_c - T = 4$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^8,_{12}$
The parameter $c_1$ is 0.13972
The parameter $\sigma$ is 0.80468
The parameter $\mu$ is 16.3393
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.0026756
The uncertainties in parameter $\sigma$ is 0.0068373
The uncertainties in parameter $\mu$ is 0.19525
The reduced chi squared is 19.349

Figure 32: Upper Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $Tc - T = 4$ K for Shresth’s data on PEO in Isobutyric Acid and Water$^{8,12}$
Like the Gaussian distribution (equation 9), the lognormal distribution (equation 11) did not yield random residuals in any phases. However, when equation 10 (Gaussian1) and equation 12 (lognormal1) are compared, they both provided reasonably random residuals for the lower phase. Thus, those two equations yielded a better fit for the lower phase.

2 - Mass in Coexisting Phases

In order to determine the mass of polymer in each phase and confirm the fact that most of the polymer is in the upper phase, the following equation from Dr. Grant Smith, University of Utah, is used.\(^\text{17}\) The derivation (see Appendix A) is based on the fact that the mass of each molecular weight is conserved. The total mass of polymer in each phase is:

\[
W^T_A = \frac{w(M) - w_B(M)}{w_A(M) - w_B(M)} W^T
\quad (13)
\]

\[
W^T_B = \frac{w(M) - w_A(M)}{w_B(M) - w_A(M)} W^T
\quad (14)
\]

where \(W^T\) denotes the initial weight of polymer, \(W^T_A, W^T_B\) respectively represent the total mass of polymer in upper and lower phases, and \(w(M)\) is the weight fraction in one phase while \(w_A(M)\) and \(w_B(M)\) are the weight fractions in the upper and lower phases respectively.

The mass in each phase was determined from each data point and then the average mass in that phase was calculated by summing all the masses and divided by the total number of data points. The standard error was determined by finding the standard
deviation of the mean and divided by the square-root of the total number of data points; errors are reported as one standard deviation. Several outliers were deleted.

The results are shown in table 3 and figure 33, which indicate that most of the PEO migrate into the upper phase. The mass fraction in the upper phase is roughly five times the mass fraction in the lower phase.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mass and Mass Fraction in Upper Phase</th>
<th>Mass and Mass Fraction in Lower Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 K</td>
<td>(0.067 ± 0.042) gram (0.817 ± 0.512)</td>
<td>(0.015 ± 0.042) gram (0.183 ± 0.512)</td>
</tr>
<tr>
<td>1 K</td>
<td>(0.046 ± 0.002) gram (0.719 ± 0.031)</td>
<td>(0.018 ± 0.002) gram (0.281 ± 0.031)</td>
</tr>
<tr>
<td>2 K</td>
<td>(0.0541 ± 0.0016) gram (0.845 ± 0.025)</td>
<td>(0.0099 ± 0.0016) gram (0.154 ± 0.025)</td>
</tr>
<tr>
<td>4 K</td>
<td>(0.0627 ± 0.0250) gram (0.979 ± 0.390)</td>
<td>(0.0013 ± 0.0250) gram (0.021 ± 0.390)</td>
</tr>
</tbody>
</table>

Table 3: Mass and Mass Fraction of Polymer in Lower and Upper Phases at Different Temperatures for Shresth’s data on PEO in Isobutyric Acid and Water.8, 12
Figure 33: Plot ($T_c - T$) vs Mass Fraction for the Upper and Lower Phases:
From Shresth’s Data on PEO ($M_w = 25700$) in Isobutyric Acid and Water$^8,^{12}$
V - NEW EXPERIMENTS

1 - Experimental methods

a.) Temperature Control

In order to achieve control of the temperature, the sample cell is completely submerged in a water bath. The bath, a large glass container surrounded by Styrofoam, allows different components to be inserted. A precision temperature controller (Tronac PTC-41), which is connected to a 60-watt light bulb, controls the temperature of the bath. The light bulb serves as a control heater. Cold diethylene glycol is circulated through a copper tube to provide cooling. Since most of the heat exchange is through the top, the bath is covered with polypropylene balls as insulator. A 9540 digital platinum resistance thermometer (Guildline) measures the temperature of the bath to ±0.001 K.

b.) Sampling Manifold

Shresth\textsuperscript{12} designed the sampling manifold based on the following requirements.

1- The polymer-solvent systems have to be free of any impurities.

2- The temperature control should be provided by a water bath; therefore the polymer solution should be immersed.\textsuperscript{18}

3- The apparatus should allow the simultaneous withdrawal of the polymer solution from both phases without disturbing the equilibrium.

The sampling process should follow this procedure:

1- Attach the vacuum pump to the sample cell.
2- Close the auxiliary and vent valves and start the vacuum pump.

3- Open the auxiliary valves.

4- Move the main valve in such a way that the polymer solution is withdrawn into the glass vials.

5- Once the sampling process is done, close the main to cut off the main valve from the vacuum line valve and then the auxiliary valves.

6- Remove the vials.

c.) Size Exclusion Chromatography

The principle of size-exclusion chromatography (SEC) or gel permeation chromatography (GPC) is the separation of polymer at different molecular weights throughout a column packed with porous beads. In the beginning, a sample of polymer solution is injected into the column. As the solvent goes through the column, the larger molecules elute first (smaller volume of solvent) leaving the smaller molecules diffusing through the porous beads to elute last (larger volume of solvent). The main factor related to the size exclusion chromatography is the hydrodynamic volume, not the molecular weight. The relative abundances of the different polymer fractions are given by the plots are called chromatograms.

The GPC analyses were performed using a Waters GPC system equipped with a column oven and differential refractometer, both maintained at 40°C, and four columns consisting of a Waters Ultrastyragel 500 angstroms, Waters Styrager HR3, Styrager HR4,
and Shodex K-806M, also maintained at 40°C. THF is used as eluant at the flowrate of 1.1 ml/min.

To obtain the molecular weight of the different polymer fractions, the chromatograph is calibrated with known sample molecular weights. Calibration involves the determination of the elution volume for a series of narrow molecular weight polymers. The SEC was calibrated with four PEO standards at Mn = 2375, 10125, 13200, 15400, 48600.

“GPC for Windows” Version 1.23, published by Chemware, Mount Waverly, Victoria, Australia,²⁰ was used to find the molecular weight distribution, the average molecular weight, the average number molecular weight, and the polydispersity index from each chromatogram.
Figure 34: A Schematic Diagram of the SEC Process:
From www.impactanalytical.com
2 - Polymer samples

The polymers studied have average molecular weights ranging from 2000 to 20000. We choose two polymers with two different end groups, hydroxyl (OH) or (OCH₃), but different molecular weights.

The different polymers obtained are the following

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source</th>
<th>Catalog # / Lot #/ Sample #</th>
<th>M₆</th>
<th>End Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fluka Chemical</td>
<td>425182/1 12401</td>
<td>20900</td>
<td>OH</td>
</tr>
<tr>
<td>2</td>
<td>Polymer Source</td>
<td>PEG-2OCH₃-2K</td>
<td>4530</td>
<td>OCH₃</td>
</tr>
</tbody>
</table>

Table 4: Polymer Samples

3 - Procedures

The purpose of the experiments was to study samples from the coexisting phases of the PEO and PEG at different temperatures below the critical point. The critical temperature of isobutyric acid and water is 298.7 K and the critical mass fraction is 0.39.¹² The different temperatures chosen were T_c - T = 0.1 K, 1 K, 2 K, and 4 K below the critical point. For each temperature, a fresh sample was prepared by the following procedures.

a.) Sample 1: Preparation of Poly(ethylene oxide): M₆ = 20900; Termination = -OH

For sample 1 only two temperatures were considered, to confirm the findings made previously by Shresth.¹²
Isobutyric acid and poly(ethylene oxide) were respectively purchased from Fluka Chemical and Aldrich Chemical Co. The isobutyric acid (lot # 14103 CL) came with 99.9% of purity while the poly(ethylene oxide) ($M_w = 20000$, lot and filling code 425182/1 12401) had to be recrystallized in methanol to increase its purity. This was the very same PEO used by Shresth. The distilled, de-ionized water came from a Barnstead Nanopure purification system located in the laboratory.

In a clean and dry sample cell, a polymer solution was made by mixing together 50.4 g of fresh distilled de-ionized water, 32.2 g isobutyric acid, and 0.0877 grams of poly(ethylene oxide). A glass stir bar was added to mix the solution. The polymer solution was placed on the manifold in a stirred water bath at 319 K for three days. On the third day, the solution was cooled down at 300 K and roughly 2 ml of polymer solution was extracted from the one-phase solution into a pre-weighed vial. This step was done to confirm the molecular weight given by the manufacturer using the SEC apparatus described above. The solution was then cooled down to 298.6 K and held constant for five days. Approximately 2 ml from each phase were extracted at various times over five days into pre-weighed vials. Any liquid left in the capillaries was removed by discarding the first few drops for each sample collection. All the vials from the above experiments were placed under vacuum for a couple of days to dry and remove any trace of water and isobutyric acid. The vials were weighed and the mass of polymer was determined. The polymer was then dissolved in THF at roughly 2 mg/ml. All the samples were then analyzed by the SEC as described above.
A fresh sample of polymer and isobutyric acid and water was made by mixing 87 mg of polymer, 50.38 g of water, and 32.3 g of isobutyric acid. The above experiment was repeated at 294.7 K.

b.) Sample 2: Preparation of Poly (ethylene glycol): $M_w = 4530$; Termination = OCH$_3$

The poly(ethylene glycol) (Sample # PEG2OCH$_3$-2K) (Manufacturer’s analysis $M_w = 2200$, $M_n = 2000$, PI = 1.10) used in this experiment was obtained from Polymer Source Inc. Dorval, Canada. The polymer was used as received from Polymer Source. The isobutyric acid with 99.9% of purity was obtained from Aldrich Chemical Corporation (Lot # 062K3482). Distilled and de-ionized fresh samples of water were obtained from a Barnstead Nanopure system.

The first sample was made by mixing 87 milligrams of poly(ethylene glycol) with 50.34 grams of water and 32.3 grams of isobutyric acid in a cell. To that polymer solution was added a glass stir bar. The sample cell was then placed in a mixed water bath for three days at 319 K. The solution was then cooled down to 300 K and after five hours the stirrer was stopped and a one-phase sample was extracted into a pre-weighed vial in order to verify the accuracy of the information provided by the company. The solution was then cooled down at 297.7 K and held at constant temperature for five days. Prior to each sample extraction, any liquid left in the capillaries was discarded. Each day, samples from both phases were extracted into a pre-weighed vial.

The second, and the third experiments were made by mixing fresh samples of 32.3 grams of isobutyric acid, 50.34 grams of water, and 87 milligrams of poly(ethylene
glycol) in a cell. Each time the polymer solutions were mixed with a glass stir bar and the above experiment was repeated at 296.7 K and 294.7 K.

VI - RESULTS OF NEW EXPERIMENTS

1 - Sample 1: $M_w = 20900$; Termination = -OH

a.) Kinetics

The results shown in Figure 15-16 are similar to the previous experiments done by Shresth. The parent phase (day 0) gives $M_w = 20900$, $M_n = 15900$, and $PI = 1.31$. The only information provided by the manufacturer was $M_w = 20000$. The lower phase yields higher molecular weight with a very narrow polydispersity when compared to the upper phase. The equilibrium is reached between day 2 and day 4 for the upper and the lower phases. In addition, $M_n$ and $M_w$ reach the equilibrium at the same time.
Figure 35: $M_n$ and $M_w$ for the Upper and the Lower Phases as a Function of Time at $T = 298.6$ K for Sample 1: $M_w = 20900$; Termination = -OH
Figure 36: $M_n$ and $M_w$ for the Upper and the Lower Phases as a Function of Time at $T = 294.7$ K for Sample 1: $M_w = 20900$; Termination = -OH
b.) Molecular Weight Distribution

The trends analyzed here show that higher molecular weight PEO migrates to the lower phase, while shorter chains with higher polydispersity move to the upper phase. Table 5 summarizes all the results.

<table>
<thead>
<tr>
<th>T - T_c (K)</th>
<th>M_n upper</th>
<th>M_w upper</th>
<th>M_n lower</th>
<th>M_w lower</th>
<th>PI upper</th>
<th>PI lower</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 K</td>
<td>12.7</td>
<td>16.7</td>
<td>34.6</td>
<td>36.3</td>
<td>1.32</td>
<td>1.07</td>
</tr>
<tr>
<td>4 K</td>
<td>14.6</td>
<td>19.9</td>
<td>34.9</td>
<td>38.2</td>
<td>1.36</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Table 5: Mass of Polymer in Lower and Upper Phase at Different Temperatures for Sample 1: M_w = 20900; Termination = -OH

The following plots (figures 38-39) show extensive noise due to the fact that the lower phase has a very weak signal because of the lower concentration of polymer. To make the plots readable, data at larger and smaller molecular weights that showed scatter have been left out. The normalization process included all the data in the fits. The following figures demonstrate the fact that the lower phase has higher average molecular weight as compared to the upper phase.
Figure 37: Comparison of Molecular Weight Distributions in the Upper and Lower Phases at 298.6 K for Sample 1: $M_w = 20900$; Termination = -OH
Figure 38: Comparison of the Molecular Weight Distributions in the Upper and Lower phases at 294.7 K for Sample 1: $M_w = 20900$; Termination = -OH
c.) Flory - Huggins Theory

The plot generated from FH theory (see figure 19) is a concave downward, disagreeing with FH.

![Figure 39: Ln \( w(M)/w(M') \) vs. Molecular Weight at 298.6 K for Sample 1: \( M_w = 20900 \); Termination = -OH](image)
Figure 40: \( \ln \left( \frac{w(M)^\gamma}{w(M)'^\gamma} \right) \) vs. Molecular Weight at 294.7 K for Sample 1: \( M_w = 20900 \); Termination = -OH
d.) Statistical Analysis

The different equations in section IV-1 were used to test the different data sets. The first equation (equation 9), which is a Gaussian distribution\textsuperscript{16} was applied to the lower phase of the samples with $M_w = 20900$. Like Shresth’s\textsuperscript{12} data, the residual plots are not random. They all seem to have a pattern (see figures 41-42).
The parameter $\mu$ is 53.2794
The parameter $\sigma$ is 12.1364
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 1.0734
The uncertainties in parameter $\sigma$ is 0.37163
The reduced chi squared is 7.7672

Figure 41: Lower Phase: Fitting and Residual Plots for Gaussian Function (Equation 9) at $T_c-T = 0.1$ K for $M_w = 20900$; Termination-OH
The parameter $\mu$ is 63.4491
The parameter $\sigma$ is 15.9432
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 1.1033
The uncertainties in parameter $\sigma$ is 0.40502
The reduced chi squared is 17.7705

Figure 42: Lower Phase: Fitting and Residual Plots for Gaussian Function (equation 9) at $T_c-T = 4$ K for $M_w = 20900$; Termination-OH
Because the residual plots from the Gaussian distribution (equation 9) did not show any randomness, we decided to use the slightly modified Gaussian (equation 10) that has provided fairly random residuals for Shresth’s lower phase. Again, equation 10 yielded quite random residual plots (see figures 43-44).
The parameter $a_1$ is 0.43158
The parameter $\sigma$ is 18.8017
The parameter $\mu$ is 48.0294
The confidence level is 99%.
The uncertainties in parameter $a_1$ is 0.0016273
The uncertainties in parameter $\sigma$ is 0.092502
The uncertainties in parameter $\mu$ is 0.039496
The reduced chi squared is 4.7423

Figure 43: Lower Phase: Fitting and Residual Plots for Gaussian1 Function (equation 10) at $T_c-T = 0.1 \, \text{K}$ for $M_w = 20900$; Termination-OH
The parameter $a_1$ is 0.26674  
The parameter $\sigma$ is 17.6148  
The parameter $\mu$ is 52.5295  
The confidence level is 99%. 
The uncertainties in parameter $a_1$ is 0.002889  
The uncertainties in parameter $\sigma$ is 0.22434  
The uncertainties in parameter $\mu$ is 0.090266  
The reduced chi squared is 4.1407

Figure 44: Lower Phase: Fitting and Residual Plots for Gaussian1 Function (equation 10) at $T_c-T = 4$ K for $M_w = 20900$; Termination-OH
Like previous plots from Shresth’s data\textsuperscript{12}, the lognormal distribution (equation 11) and the modified lognormal (equation 12) were considered. The two equations were applied to all the phases. Equation 11 did not provide random residual, (see figures 45-49), therefore, we decided to consider equation 12, which is a slightly modified lognormal distribution. Equation 12 gave fairly random residual plots (see figures 50-54) for the lower phase only.
The parameter $\sigma$ is 0.40304
The parameter $\mu$ is 7.0478
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.019601
The uncertainties in parameter $\mu$ is 0.39048
The reduced chi squared is 4.6391

Figure 45: One-Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T = 300$ K for Sample 1: $M_w = 20900$; Termination = -OH
The parameter $\sigma$ is 0.37176
The parameter $\mu$ is 54.35
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.0082238
The uncertainties in parameter $\mu$ is 1.1842
The reduced chi squared is 4.1224

Figure 46: Lower Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c - T = 0.1 \text{ K from Sample 1: } M_w = 20900; \text{ Termination = -OH}$
The parameter $\sigma$ is 0.34782
The parameter $\mu$ is 8.8109
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.026803
The uncertainties in parameter $\mu$ is 0.5594
The reduced chi squared is 3.2964

Figure 47: Upper Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T-T_c$ - T = 0.1 K for Sample 1: $M_w = 20900$; Termination = -OH
The parameter $\sigma$ is 0.37262
The parameter $\mu$ is 58.0076
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.010965
The uncertainties in parameter $\mu$ is 1.082
The reduced chi squared is 12.0413
The parameter $\sigma$ is 0.13489
The parameter $\mu$ is 18.9411
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.0063316
The uncertainties in parameter $\mu$ is 0.47826
The reduced chi squared is 42.5819

Figure 49: Upper Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T-T_c - T = 4$ K for Sample 1: $M_w = 20900$; Termination = -OH
The parameter $c_1$ is 0.011126
The parameter $\sigma$ is 0.053668
The parameter $\mu$ is 21.8725
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.00012566
The uncertainties in parameter $\sigma$ is 0.0008272
The uncertainties in parameter $\mu$ is 0.017345
The reduced chi squared is 19.408

Figure 50: One-Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T = 300$ K for Sample 1: $M_w = 20900$; Termination = -OH
The parameter $c_1$ is 0.63515
The parameter $\sigma$ is 0.33551
The parameter $\mu$ is 49.4527
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.040842
The uncertainties in parameter $\sigma$ is 0.012604
The uncertainties in parameter $\mu$ is 1.7702
The reduced chi squared is 8.617

Figure 51: Lower Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_c - T = 0.1$ K from Sample 1: $M_w = 20900$; Termination = -OH
The parameter $c_1$ is 0.030369
The parameter $\sigma$ is 0.11443
The parameter $\mu$ is 19.624
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.00068082
The uncertainties in parameter $\sigma$ is 0.0031172
The uncertainties in parameter $\mu$ is 0.056286
The reduced chi squared is 19.508

Figure 52: Upper Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T-T_c$ $T = 0.1$ K for Sample 1: $M_w = 20900$; Termination = -OH
The parameter $c_1$ is 0.0029527
The parameter $\sigma$ is 0.15596
The parameter $\mu$ is 20.5337
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 3.9378e-005
The uncertainties in parameter $\sigma$ is 0.0025669
The uncertainties in parameter $\mu$ is 0.054877
The reduced chi squared is 16.495

Figure 53: Upper Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_e - T = 4$ K for Sample 1: $M_w = 20900$; Termination = -OH
The parameter $c_1$ is 0.33257
The parameter $\sigma$ is 0.2102
The parameter $\mu$ is 51.4059
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.034735
The uncertainties in parameter $\sigma$ is 0.014607
The uncertainties in parameter $\mu$ is 1.6194
The reduced chi squared is 3.058

Figure 54: Lower Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_c - T = 4 \text{ K}$ for Sample 1: $M_w = 20900$; Termination = -OH
e.) Mass in Coexisting Phases

The mass of the polymer in each phase was then calculated as described in section IV-2. Data considered as outliers were removed. To be removed, the mass point in the lower or upper had to be greater than the initial mass. As Table 6 and figure 56 show, most of the polymer migrates to the upper phase, leaving little in the lower phase. The statistical analysis done on the data shows the error (one standard deviation) to be greater than the mass of the polymer in the lower phase at T_c-T = 4 K. This finding suggests that the PEO prefers the organic solvent, which is the isobutyric acid.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mass and mass fraction in lower phase</th>
<th>Mass and mass fraction in upper phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 K</td>
<td>(0.216 ± 0.126) (0.019 ± 0.011) gram</td>
<td>(0.783 ± 0.126) (0.068 ± 0.011) gram</td>
</tr>
<tr>
<td>4 K</td>
<td>(0.057 ± 0.103) (0.005 ± 0.009) gram</td>
<td>(0.943 ± 0.103) (0.082 ± 0.009) gram</td>
</tr>
</tbody>
</table>

Table 6: Mass of Polymer in Lower and Upper Phases at Different Temperatures for Sample 1: M_w = 20900; Termination = -OH
Figure 55: Mass Fraction of Polymer in Lower and Upper Phase at Different Temperatures for Sample 1: $M_w = 20900$; Termination = -OH
Table 7 summarizes the coexisting mass fraction for PEO (M_w = 20000) as calculated from Shresth’s data\textsuperscript{12} and from the new data reported above.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mass and mass fraction in lower phase from Shresth</th>
<th>Mass and mass fraction in lower phase from Niamke</th>
<th>Mass and mass fraction in upper phase from Shresth</th>
<th>Mass and mass fraction in upper phase from Niamke</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 K</td>
<td>(0.015 ± 0.042) gram (0.183 ± 0.512)</td>
<td>(0.019 ± 0.011) gram (0.216 ± 0.126)</td>
<td>(0.067 ± 0.042) gram (0.817 ± 0.512)</td>
<td>(0.068 ± 0.011) gram (0.783 ± 0.126)</td>
</tr>
<tr>
<td>1 K</td>
<td>(0.018 ± 0.002) gram (0.281 ± 0.031)</td>
<td>(0.046 ± 0.002) gram (0.718 ± 0.031)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 K</td>
<td>(0.0099 ± 0.0016) gram (0.154 ± 0.025)</td>
<td>(0.0541 ± 0.0016) gram (0.845 ± 0.025)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 K</td>
<td>(0.0013 ± 0.0250) gram (0.021 ± 0.390)</td>
<td>(0.005 ± 0.009) gram (0.057 ± 0.103)</td>
<td>(0.0627 ± 0.0250) gram (0.979 ± 0.390)</td>
<td>(0.082 ± 0.009) gram (0.943 ± 0.103)</td>
</tr>
</tbody>
</table>

Table 7: Comparison of Coexisting Mass and Mass Fractions of PEO (M_w = 20000) from Shresth and Niamke

Table 7 confirms that most of the polymer migrates into the upper phase. The mass fraction in the upper phase is roughly five times greater than the mass fraction in the lower phase. When we compared the different results, we found that previous and current data behave in the same way. The mass fractions are close to each other (see figure 56).
Figure 56: Comparison of the Coexisting Mass Fractions as Calculated from Shresth’s data\cite{12} and from New Data Reported Here
2 - Sample 2- PEG-OCH$_3$: Molecular Weight of 4530

a.) Kinetics

The day 0 data correspond to the polymer in the one-phase solution. This step was performed in order to verify the information provided by the manufacturer. The GPC at day 0 gives $M_n = 4080$, $M_w = 4530$ and $PI = 1.11$, which is different from the manufacturer’s information ($M_n = 2000$, $M_w = 2200$ and $PI = 1.1$).

Figures 57-59 show that the equilibrium molecular weight is attained after 3-4 days in both phases. In addition, $M_n$ and $M_w$ reach equilibrium at the same time either in the lower or upper phase. The lower phase contains the higher molecular weight, while the upper phase contains smaller polymer segments.

![Figure 57: PEG-OCH$_3$, $M_w = 4530$: $M_n$ and $M_w$ for the Upper and Lower Phase as a Function of Time, $T_c - T = 1$ K](image)
Figure 58: PEG-OCH$_3$, $M_w = 4530$: $M_n$ and $M_w$ for the Upper and Lower Phase as a Function of Time, $T_c - T = 2$ K
Figure 59: PEG-OCH₃, $M_w = 4530$: $M_n$ and $M_w$ for the Upper and Lower Phases as a Function of Time, $T_c - T = 4$ K
b.) Molecular Weight Distribution

Again, the plots (figures 60-62) indicate that the water-rich phase contains the higher molecular weight and the isobutyric-rich phase contains smaller molecular weight.

At all the temperatures, the average molecular weight in the upper phase is roughly twice the average molecular weight in the lower phase. The following table summarizes the different moments and the polydispersity of the PEG-OCH$_3$ at different temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$M_n$ upper</th>
<th>$M_n$ lower</th>
<th>$M_w$ upper</th>
<th>$M_w$ lower</th>
<th>PI upper</th>
<th>PI lower</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 K</td>
<td>2826</td>
<td>6208</td>
<td>3286</td>
<td>6404</td>
<td>1.16</td>
<td>1.03</td>
</tr>
<tr>
<td>2 K</td>
<td>4104</td>
<td>9574</td>
<td>4646</td>
<td>10076</td>
<td>1.13</td>
<td>1.05</td>
</tr>
<tr>
<td>4 K</td>
<td>4964</td>
<td>7664</td>
<td>5580</td>
<td>8124</td>
<td>1.12</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Table 8: PEG-OCH$_3$, $M_w = 4530$: $M_n$ and $M_w$ for the Lower and Upper Phases at Different Temperatures
Figure 60: PEG-OCH$_3$, $M_w = 4530$: Comparison of the Molecular Weight Distributions in the Upper and Lower Phases at $T = 297.7$ K
Figure 61: PEG-OCH$_3$, $M_w = 4530$: Comparison of the Molecular Weight Distributions in the Upper and Lower phases at $T = 296.7$ K
Figure 62: PEG-\text{OCH}_3, M_w = 4530: Comparison of the Molecular Weight Distributions in the Upper and Lower Phases at T = 294.7 K
c.) Flory - Huggins Plot

The different data (figures 63-65) obtained do not fit a straight line as suggested by the theory. Therefore, we can conclude that Flory-Huggins theory does satisfy our observations.

![Flory-Huggins Plot](image)

**Figure 63**: PEG-OCH$_3$, $M_w = 4530$: $\ln(w(M)/w(M'))$ versus Molecular Weight at $T = 297.7$ K
Figure 64: PEG-OCH$_3$, $M_w = 4530$: Ln($w(M)/w(M)'$) versus Molecular Weight at $T = 296.7$ K
Figure 65: PEG-OCH₃, Mᵢ = 4530: \( \ln(w(M)/w(M)) \) versus Molecular Weight at \( T = 294.7 \) K
d.) Analysis

Because of the similarities in the shape, we decided to apply the Gaussian
distribution (equation 9) and also the slightly modified Gaussian distribution (equation
10) from section IV-1. Only the lower phase will be considered because the shapes of the
parent and upper phases indicate that they are not even pseudo-gaussian.

Equation 9 gave residuals that are not random (see figures 66-68). The second
distribution (equation 10) provided reasonable random residuals (see figures 69-71).
The parameter $\mu$ is 14.2662
The parameter $\sigma$ is 2.5451
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 0.27836
The uncertainties in parameter $\sigma$ is 0.064432
The reduced chi squared is 42.2913

Figure 66: Lower Phase: Fitting and Residual Plots for Gaussian Function (Equation 9) at $T_c - T = 1$ K for $M_w = 4530$; Termination-OCH$_3$
The parameter $\mu$ is 13.3998
The parameter $\sigma$ is 1.8164
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 0.3009
The uncertainties in parameter $\sigma$ is 0.05975
The reduced chi squared is 22.9757

Figure 67: Lower Phase: Fitting and Residual Plots for Gaussian Function (Equation 9) at $T_c - T = 2$ K for $M_w = 4530$; Termination-OCH$_3$
The parameter $\mu$ is 12.0794
The parameter $\sigma$ is 2.5156
The confidence level is 99%.
The uncertainties in parameter $\mu$ is 0.23658
The uncertainties in parameter $\sigma$ is 0.079096
The reduced chi squared is 29.3081

Figure 68: Lower Phase: Fitting and Residual Plots for Gaussian Function (Equation 9) at $T_c - T = 4$ K for $M_w = 4530$; Termination-OCH$_3$
The following plots are from equation 10:

The parameter $a_1$ is 0.11357
The parameter $\sigma$ is 4.1232
The parameter $\mu$ is 14.3407
The confidence level is 99%.
The uncertainties in parameter $a_1$ is 0.00052929
The uncertainties in parameter $\sigma$ is 0.025707
The uncertainties in parameter $\mu$ is 0.011784
The reduced chi squared is 8.2319

Figure 69: Lower Phase: Fitting and Residual Plots for Gaussian1 Function (Equation 10) at $T_c - T = 1 \text{ K}$ for $M_w = 4530$; Termination-$\text{OCH}_3$
The parameter $a_1$ is 0.10701
The parameter $\sigma$ is 5.6677
The parameter $\mu$ is 11.7959
The confidence level is 99%.
The uncertainties in parameter $a_1$ is 0.00068114
The uncertainties in parameter $\sigma$ is 0.040731
The uncertainties in parameter $\mu$ is 0.015963
The reduced chi squared is 7.5783

Figure 70: Lower Phase: Fitting and Residual Plots for Gaussian1 Function (Equation 10)
at $T_c-T = 2$ K for Mw = 4530; Termination-OCH$_3$
The parameter $a_1$ is 0.00031864
The parameter $\sigma$ is 1.222
The parameter $\mu$ is 12.1359
The confidence level is 99%.
The uncertainties in parameter $a_1$ is $3.2308\times10^{-6}$
The uncertainties in parameter $\sigma$ is 0.0072885
The uncertainties in parameter $\mu$ is 0.0035456
The reduced chi squared is 19.8583

Figure 71: Lower Phase: Fitting and Residual Plots for Gaussian1 Function (Equation 10) at $T_c-T = 4$ K for Mw = 4530; Termination-OCH$_3$
As previously, the Gaussian distribution (equation 9) did not yield random residuals for any phases. However, the modified Gaussian distribution (equation 10) provided some fairly random residuals.

The next equations considered were the different lognormal distributions (equation 11 and equation 12). The lognormal distribution (equation 11) like the Gaussian (equation 9) did not show randomness in residual plots (see figures 72-75). However, the lower phase residual plots from equation 12 are quite random except for $T_c - T = 4$ K (see figures 76-82).
The parameter $\sigma$ is 0.28161
The parameter $\mu$ is 14.6826
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.006732
The uncertainties in parameter $\mu$ is 0.25105
The reduced chi squared is 34.3455

Figure 72: Lower Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c - T = 1$ K for Sample 2: $M_w = 4530$; Termination = -OCH$_3$
The parameter $\sigma$ is 0.21188
The parameter $\mu$ is 12.182
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.0041673
The uncertainties in parameter $\mu$ is 0.18692
The reduced chi squared is 43.4462

Figure 73: Lower Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c - T = 2$ K for Sample 2: $M_w = 4530$; Termination = -OCH$_3$
The parameter $\sigma$ is 0.15438
The parameter $\mu$ is 9.4152
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.0045557
The uncertainties in parameter $\mu$ is 0.17824
The reduced chi squared is 51.1661

Figure 74: Upper Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c - T = 2$ K for Sample 2: $M_w = 4530$; Termination = -OCH$_3$
The parameter $\sigma$ is 0.28951
The parameter $\mu$ is 13.1896
The confidence level is 99%.
The uncertainties in parameter $\sigma$ is 0.0069021
The uncertainties in parameter $\mu$ is 0.22598
The reduced chi squared is 9.764

Figure 75: Lower Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at $T_c - T = 4\, K$ for Sample 2: $M_w = 4530$; Termination = -OCH$_3$
The parameter $c_1$ is 0.0093738
The parameter $\sigma$ is 0.066513
The parameter $\mu$ is 4.9885
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 9.3155e-005
The uncertainties in parameter $\sigma$ is 0.00084948
The uncertainties in parameter $\mu$ is 0.0037589
The reduced chi squared is 18.782

Figure 76: One-Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at T= 300 K for Sample 2: $M_w = 4530$; Termination = -OCH$_3$
The parameter $c_1$ is 0.11545
The parameter $\sigma$ is 0.14829
The parameter $\mu$ is 14.4206
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.00032211
The uncertainties in parameter $\sigma$ is 0.00047892
The uncertainties in parameter $\mu$ is 0.0075575
The reduced chi squared is 8.231

Figure 77: Lower Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_c - T = 1$ K for Sample 2: $M_w = 4530$; Termination = -OCH$_3$
The parameter $c_1$ is $0.010931$
The parameter $\sigma$ is $0.069935$
The parameter $c_2$ is $5.3055$
The confidence level is 99%.
The uncertainties in parameter $c_1$ is $9.3083e-005$
The uncertainties in parameter $\sigma$ is $0.00079325$
The uncertainties in parameter $\mu$ is $0.0039791$
The reduced chi squared is $19.304$

Figure 78: Upper Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_c - T = 1$ K for Sample 2: $M_w = 4530$; Termination = -OCH$_3$
The parameter $c_1$ is 0.11546
The parameter $\sigma$ is 0.26958
The parameter $\mu$ is 12.1003
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.00046264
The uncertainties in parameter $\sigma$ is 0.0012028
The uncertainties in parameter $\mu$ is 0.018545
The reduced chi squared is 7.592

Figure 79: Lower Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_c - T = 2$ K for Sample 2: $M_w = 4530$; Termination = -OCH$_3$
The parameter $c_1$ is 0.0077707
The parameter $\sigma$ is 0.042193
The parameter $\mu$ is 5.1317
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 0.00021403
The uncertainties in parameter $\sigma$ is 0.001126
The uncertainties in parameter $\mu$ is 0.0041901
The reduced chi squared is 20.849

Figure 80: Upper Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_c - T = 2$ K for Sample 2: $M_w = 4530$; Termination = -OCH$_3$
The parameter $c_1$ is 0.00075388
The parameter $\sigma$ is 0.050864
The parameter $\mu$ is 12.147
The confidence level is 99%.
The uncertainties in parameter $c_1$ is 2.9761e-006
The uncertainties in parameter $\sigma$ is 0.00027587
The uncertainties in parameter $\mu$ is 0.0033042
The reduced chi squared is 19.874

Figure 81: Lower Phase: Fitting and Residual Plots for Lognormal Function (Equation 12) at $T_c - T = 4$ K for Sample 2: $M_w = 4530$; Termination = -OCH₃
The parameter $c_1$ is 0.011603
The parameter $\sigma$ is 0.073085
The parameter $\mu$ is 5.3011
The confidence level is 99%.
The uncertainties in parameter $c_1$ is $7.5717e^{-005}$
The uncertainties in parameter $\sigma$ is 0.0006376
The uncertainties in parameter $\mu$ is 0.0032822
The reduced chi squared is 12.6065

Figure 82: Upper Phase: Fitting and Residual Plots for Lognormal1 Function (Equation 12) at $T_c - T = 4$ K for Sample 2: $M_w = 4530$; Termination = -OCH$_3$
e.) Mass in Coexisting Phases

The same calculations described previously in section IV-2 were used to determine
the mass of polymer in each phase. To do so, several outliers were eliminated. Any mass
value that was greater than the initial mass of polymer was considered as an outlier.

The following table summarizes all the results related to PEG-OCH3 – 2 K (Sample
2).

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Average mass and mass fraction in lower phase</th>
<th>Average mass and mass fraction in upper phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 K</td>
<td>(0.0180 ± 0.0017) gram (0.207 ± 0.0195)</td>
<td>(0.0689 ± 0.0017) gram (0.793 ± 0.0195)</td>
</tr>
<tr>
<td>2 K</td>
<td>(0.021 ± 0.003) gram (0.241 +/- 0.034)</td>
<td>(0.065 ± 0.003) gram (0.748 +/- 0.034)</td>
</tr>
<tr>
<td>4 K</td>
<td>(0.025 ± 0.005) gram (0.288 +/- 0.057)</td>
<td>(0.062 ± 0.005) gram (0.712 +/- 0.057)</td>
</tr>
</tbody>
</table>

Table 9: PEG-OCH3, M_w = 4530: Mass Fraction of Polymer in Lower and Upper Phases at Different Temperatures
Figure 83: PEG-OCH$_3$, $M_w = 4530$: Plot of $T_c - T$ vs Mass Fraction for the Upper and Lower Phases
Figure 85 summarizes all data on coexisting mass fractions. All data fit the same graph within error.
VII - DISCUSSION AND CONCLUSIONS

The results obtained here confirmed the previous experiments done by Shresth in 2002 and also refuted the Flory-Huggins theory. As shown before, \( \ln \left( \frac{w'(M)}{w'(M)} \right) \) versus molecular weight did not yield a straight line, but a downward concave curve for all the samples studied.

The upper phase contains most of the smaller molecular weights of polymer, while the polymer in the lower phase contains the larger molecular weights. The migration of the polymer seems to be completely independent of the end group and molecular weight. In fact, higher molecular weight \((M_w = 20000)\) with termination –OH and lower molecular weight \((M_w = 4530)\) with end group OCH\(_3\) yield the same results.

Because no theory was able to explain all the molecular weight distributions, two empirical distribution equations were used to fit to the data. The first experiments done by Shresth gave a pseudo-Gaussian distribution in the lower phase. All the plots show a positively skewed tail; therefore a pseudo-lognormal function was fitted to all the phases.
APPENDIX A: Mass Fraction in Coexisting Phases\textsuperscript{17}

\[ W^T w(M) = W^T_A w_A(M) + W^T_B w_B(M) \]

where

\[ W^T = \text{the initial weight of polymer} \]

\[ w(M) = \text{molecular weight distribution in one phase} \]

\[ W^T_A = \text{total weight of polymer in phase A} \]

\[ w_A(M) = \text{molecular weight distribution in phase A} \]

\[ W^T_B = \text{total weight of polymer in phase B} \]

\[ w_B(M) = \text{molecular weight distribution in phase B} \]

The total polymer mass:

\[ W^T = W^T_A + W^T_B. \]

Solving for \( W^T_A \)

\[ W^T_A w_A(M) = W^T w(M) - (W^T - W^T_A) w_B(M) \]

\[ W^T_A (w_A(M) - w_B(M)) = W^T [w(M) - w_B(M)] \]

The mass fractions in both phases

\[ \frac{W^T_A}{W^T} = \frac{w(M) - w_B(M)}{w_A(M) - w_B(M)} \]

\[ \frac{W^T_B}{W^T} = \frac{w(M) - w_A(M)}{w_B(M) - w_A(M)} \]
APPENDIX B: Matlab Nonlinear Least Squares Fitting Program

This function returns the error squared between the guessed function and the data. The data are input from the global variables x, y, sigma_y, and sigma_x

function err = errorfun(a)

global x y newy sigma_y F Lx weightedx sigma_x sigma_y_sqr

newy = feval(F,x,a); % evaluates the fitting function with new a

if 'y' == weightedx % if there is uncertainty in x
    dy_dx = (feval(F,(x+0.000001 .* x),a)-feval(F,(x-.000001 .* x),a))./(.000002 .* x);
    % simple numerical derivative
    sigma_y_sqr = sigma_y.^2+(sigma_x).^2 .* (dy_dx).^2; % evaluates the new uncertainty in y by propagating uncertainty in x
else
    sigma_y_sqr = sigma_y.^2;
end

err = sum(((newy-y).^2)./sigma_y_sqr);
The data file must be a .txt file. If it isn't, change line 7 to eval(['load ' s '.yourchoice]).

The model equation has to be a function of one array from the data, like x, and the fitting parameters like y = a(1)*x.^2 + a(2). The first column of the data file should be x, the second the uncertainty in x, the third y, and fourth the uncertainty in y.

The fifth column is a run number (1, 2, 3, or 4) used in the residual plot.

The current incarnation only allows 68.3% and 99% confidence for functions with a maximum of SIX coefficients. This will be remedied in a later version.
clear all

global x y z newy sigma_y F Lx weightedx sigma_x sigma_y_sqr V D pprime error p

%sdefines global variables which will be used in errorfun

s = input('Enter .txt data file name without extension: ','s'); %collects input from the user
F = input('Enter the model equation: ','s');
conf = input('Enter 1 for 68 percent level or 2 for 99 percent '); %gets the desired confidence interval

weightedy = input('Are the y data weighted? (y/n): ','s');
weightedx = input('Are the x data weighted? (y/n): ','s');
st = input('Enter the number of runs included in the file (1-4) ');
a_0 = input('Enter initial guess array: ');
eval(['load ' s '.txt']); %load the user specified data file

X = eval(s);
x = X(:,1); %splits the data file into x and y coordinates
y = X(:,3);

z = X(:,5);
Lx = length(x);
La = length(a_0);
newy = zeros(Lx,La);

Chi square table-this table was copied from Numerical Recipes in C,
delchi = [[1 2.3 3.53 4.72 5.89 7.04];[6.63 9.21 11.3 13.3 15.1 16.8]];
nu = La;
if 'y' == weightedy
    sigma_y = X(:,4);  %loads the uncertainty in y from the user
else
    sigma_y = ones(Lx,1);
end

if 'y' == weightedx
    sigma_x = X(:,2);
else
    sigma_x = zeros(Lx,1);
end

options = optimset('TolFun',1e-8,'TolX',1e-8,'MaxIter',10000);
disp('Minimizing the error function...')
a = fminsearch('errorfun',a_0);  %minimizes the objective function (finds "a" so that the
    %error is minimized)
disp('Finding error...')
if 'n' == weightedy
    sigma_y = sqrt(sum(((newy - y).^2))./(Lx - La));  %makes new uncertainty if it is not
        %specified
    sigma_y_sqr = sigma_y.^2;
end
red_chi_sqr = sum((y - newy).^2 ./sigma_y_sqr)./(Lx - La);
da = .000001*a;
for i = 1:La;  %takes the numerical derivative so that the error in the
b = a;     %parameters can be found
b(i) = b(i) + da(i);
forward = feval(F,x,b);
b(i) = b(i) - 2*da(i);
backward = feval(F,x,b);
dy_da(:,i) = (forward-backward)/(2*da(i));
end
disp('Calculating the error matrix...')
for j = 1:La;  %the alpha matrix is found as is defined in Numerical Recipes in c pg.
  for k = 1:La;
    alpha(j,k) = sum((1./(sigma_y_sqr)).*(dy_da(:,k).*dy_da(:,j)));
  end
end
delta = delchi(conf,nu); %Reads the value from the delta chi table
[V,D]=eig(alpha);  %Finds the eigenvalues and eigenvectors of the error matrix
p=delta*inv(D);
pprime = p.^0.5;  %Takes the square root of the elements in p
error = V*pprime;
error = error.';
sigma_a = max(abs(error));  %Takes the maximum value of each row
xmin = min(x);  %setting limits for plots
xmax = max(x);
xnew = xmin:(xmax-xmin)/100:xmax;
disp('Plotting function and residuals...')
figure(1)
handle = plot(x,y,'ro',xnew,feval(F,xnew,a)); %plotting the fitted function
title('Fitted Function')
figure(2)
if st == 1
    res = (y-feval(F,x,a))./(sigma_y_sqr).^0.5;
    handle2 = plot(x,res,'x'); %plotting the residuals
    set(handle2,'markersize',12)
    grid
    title('Residual Plot')
end
if st==2
    z = 0;
    for i = 1:Lx-1
        if X(i,5)<=X(i+1,5)
            z = i;
        end
    end
    set1x = x(1:z);
end
set2x = x(z+1:Lx);
set1y = y(1:z);
set2y = y(z+1:Lx);
sigma_y_sqr1 = sigma_y_sqr(1:z);
sigma_y_sqr2 = sigma_y_sqr(z+1:Lx);
res1 = (set1y-feval(F,set1x,a))./(sigma_y_sqr1).^.5;
res2 = (set2y-feval(F,set2x,a))./(sigma_y_sqr2).^.5;
handle2 = plot(set1x,res1,'x',set2x,res2,'o');  %plotting the residuals
set(handle2,'markersize',12)
grid
title('Residual Plot')
figure(3)
handle3 = plot(set1x,set1y,'x',set2x,set2y,'o',xnew,feval(F,xnew,a));  %plotting the fitted function
title('Fitted Function')
end

if st==3
    z1 = 0;
z2 = 0;
z3 = 0;
sos = 0;
for i = 1:Lx-1
if X(i,5)~=X(i+1,5)
    z1 = i;
    set1x = x(1:z1);
    set1y = y(1:z1);
    sigma_y_sqr1 = sigma_y_sqr(1:z1);
    for j = i+1:Lx-1
        if X(j,5)~=X(j+1,5)
            z2 = j;
            set2x = x(z1+1:z2);
            set2y = y(z1+1:z2);
            sigma_y_sqr2 = sigma_y_sqr(z1+1:z2);
            set3x = x(z2+1:Lx);
            set3y = y(z2+1:Lx);
            sigma_y_sqr3 = sigma_y_sqr(z2+1:Lx);
            sos = 1;
            break
        end
    end
end
if sos == 1
    break
end
if st == 3
    res1 = (set1y - feval(F, set1x, a))./(sigma_y_sqr1).^0.5;
    res2 = (set2y - feval(F, set2x, a))./(sigma_y_sqr2).^0.5;
    res3 = (set3y - feval(F, set3x, a))./(sigma_y_sqr3).^0.5;
    handle2 = plot(set1x, res1, 'x', set2x, res2, 'o', set3x, res3, '+');  %plotting the residuals
    set(handle2, 'markersize', 12)
    grid
    title('Residual Plot')
    figure(3)
    handle3 = plot(set1x, set1y, 'x', set2x, set2y, 'o', set3x, set3y, '+', xnew, feval(F, xnew, a));
    %plotting the fitted function
    title('Fitted Function')
end

if st == 4
    z1 = 0;
    z2 = 0;
    z3 = 0;
    sos = 0;
    for i = 1:Lx-1
        if X(i,5)~=X(i+1,5)
            z1 = i;
            set1x = x(1:z1);
set1y = y(1:z1);
sigma_y_sqr1 = sigma_y_sqr(1:z1);
for j = i+1:Lx-1
    if X(j,5)~=X(j+1,5)
        z2 = j;
        set2x = x(z1+1:z2);
        set2y = y(z1+1:z2);
        sigma_y_sqr2 = sigma_y_sqr(z1+1:z2);
    end
    for ii = j+1:Lx-1
        if X(ii,5)~=X(ii+1,5)
            z3 = ii;
            set3x = x(z2+1:z3);
            set3y = y(z2+1:z3);
            sigma_y_sqr3 = sigma_y_sqr(z2+1:z3);
            set4x = x(z3+1:Lx);
            set4y = y(z3+1:Lx);
            sigma_y_sqr4 = sigma_y_sqr(z3+1:Lx);
            sos = 1;
            break
        end
    end
end
end

if sos == 1
    break
end
end
end
end
end
if sos == 1
    break
end
end
end
end
end
end

if st == 4

    res1 = (set1y-feval(F,set1x,a))./(sigma_y_sqr1);
    res2 = (set2y-feval(F,set2x,a))./(sigma_y_sqr2);
    res3 = (set3y-feval(F,set3x,a))./(sigma_y_sqr3);
    res4 = (set4y-feval(F,set4x,a))./(sigma_y_sqr4);

    handle2 = plot(set1x,res1,'x',set2x,res2,'o',set3x,res3,'+',set4x,res4,'*');   %plotting the residuals

    set(handle2,'markersize',12)

    grid

    title('Residual Plot')

    figure(3)
handle3 = plot(set1x,set1y,'x',set2x,set2y,'o',set3x,set3y,'+',set4x,set4y,'*',xnew,feval(F,xnew,a));

%plotting the fitted function
    title('Fitted Function')
end
for i = 1:La;
    disp(['The parameter a(' num2str(i) ') is ' num2str(a(i))])
end
if '1' == conf
    disp(['The confidence level is 68%.'])
else
    disp(['The confidence level is 99%.'])
end
for i = 1:La
    disp(['The uncertainties in parameter a(' num2str(i) ') is ' num2str(sigma_a(i))])
end
for i = 1:length(sigma_y)
    disp(['The uncertainty in y(' num2str(i) ') is ' num2str(sqrt(sigma_y_sqr(i)))])
end
    disp(['The reduced chi squared is ' num2str(red_chi_sqr)]);
REFERENCES:


(3) Private Communication with Dr. Mikhail Anisimov.


(17) Private Communication with Dr. Grant Smith.
