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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FRACTIONATION OF POLY(ETHYLENE GLYCOL) BETWEEN LIQUID PHASES

I - INTRODUCTION

1 - Poly(ethylene oxide)

Since Albertsson confirmed their use in bioseparation in the late 50s,¹ 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 $-(CH_2-CH_2O)$. The monomer possesses hydrophobic ethylene groups and hydrophilic oxygen atoms. The hydrophobic elements $(-CH_2-CH_2-)$ 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.² Those two

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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.³ Several refined theories have helped deal with the thermodynamics of the polymer/solvent systems. Stockmayer and co-workers⁴ have proposed a "bridging" expression that considers all the interactions. That expression resulted in the addition of nonlinear terms in the Flory equation. Evans⁵ 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

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the parent distribution. This theory was later contradicted by Xu and Baus⁶, "but supported by measurements⁷ on colloidal particles.⁸"

In 1995, Ten Brinke and Szleifer⁹ 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), Okamoto¹⁰ et al. tried to measure the distribution coefficient and the molecular weight by viscometry. One experiment using the SEC was done by Kleintjens¹¹ et al. in which they studied polystyrene in cyclohexane and polyethylene in diphenyl ether at one temperature.

In 2002, Shresth¹² et al. studied the fractionation of higher molecular weight PEO $(M_w = 25700)$ 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.¹³ The discrete points forming the coexistence curve are called transition temperatures, T_t . T_t 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.⁸ was 299.4 K \pm 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.¹²



Figure 1: Coexistence Curve of Isobutyric Acid + Water: Coexisting Mole Fractions¹⁴

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

$$\phi_n \gamma \phi_n = \exp(-\sigma n) \tag{1}$$

where ϕ_n " and ϕ_n ' represent the volume fraction of the polymer component of size n in the diluted and concentrated phases of volumes V" and V' respectively. σ 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

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 Szleifer⁹ 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 α_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 ϕ_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:

$$\beta F = \sum N_n \ln \phi_n + \sum P_n (\alpha_n) \ln P(\alpha_n) + \chi N_n < n_n > \phi_s] + N_s \ln \phi_s, \qquad (3)$$

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

$$\chi = \begin{bmatrix} \epsilon_{ps} - \frac{1 (\epsilon_{p} - p \epsilon_{ss})}{2 K_B T} \end{bmatrix}$$
 is their interaction, where ϵ_{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:

$$Pn(\alpha n) = \underline{1} \exp[-\chi n_n (\alpha_n)\phi_s], \qquad (4)$$

"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:

$$\beta F = \sum_{n} [N_n \ln \phi_n - N_n \ln q_n] + N_s \ln \phi_s.$$
(5)

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.

$$\mu_{n} = \ln \phi_{n} - \ln q_{n} - \sum \phi_{n} \chi \langle n_{n} \rangle \rangle \phi_{s} + (1 - n) \phi_{s}, \qquad (6)$$

and for the solvent the chemical potential

$$\mu_{s} = \ln \phi_{s} + (1 - \phi_{s}) - \underline{\sum \phi_{n}} - \underline{\sum \phi_{n}} \chi < n_{n}' > (1 - \phi_{s}).$$
(7)

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

$$\ln(\phi''_{n} / \phi'_{n}) = -\ln q_{n}(\phi'_{n}) + (1-n)(\phi_{s}' - \phi_{s}'') - \chi \sum [\phi_{n}' < n_{n}' > \phi_{s}' - \phi_{n}'' < n_{n}' > \phi_{s}''].$$
(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 K⁸



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 K⁸

2 - Molecular Weight Distribution

One of the most exciting and interesting observations from Shresth 's experiment on PEO in IBA + H_2O 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.

$T_{c}-T(K)$	M _w upper	M _w lower	M _n upper	M _n lower	PI upper	PI lower
0.1	18000	36700	13100	34200	1.37	1.07
1	18000	36900	14200	35000	1.26	1.05
2	18800	40500	13900	37400	1.35	1.08
4	20300	35800	16800	33600	1.20	1.06

Table 1:	Coexisting Phases	of Polv(ethylene	oxide) in Isobu	tvric Acid and	Water ¹²
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Figure 4: Poly(ethylene oxide) in Isobutyric Acid and Water: Molecular Weight Distribution at T_c -T = 0.1 K⁸

The following table summarizes all the findings of $\mathsf{Shresth}^{8,\,12}$ in the fractionation of the PEO in IBA+ H_2O

Properties	PEO/IBA+H ₂ O
L	-
Phase with more total polymer	Upper, IBA-rich (80-90%)
Phase with higher molecular weight polymer	Lower, water-rich
Reduction in PI with separation	23%
[Mw in higher Mw phase]/Mw in lower Mw phase	1.8

 Table 2: Summary of the Distribution of PEO in Isobutyric Acid and Water⁸

3 - Flory Theory

All data on PEO from Shresth et al.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(w(M)"/w(M) 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 Phase⁸



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 Phase⁸

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 Gaussian¹⁶ equation to be used is the normal distribution.

$$n(M) = \frac{\exp(-(M-\mu)^2/2\sigma^2)}{\sigma(2\pi)^{0.5}}, \quad (Gaussian)$$
(9)

where n(M) is the number fraction as a function of molecular weight. The values μ and σ 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 μ is 34.2816 The parameter σ is 8.3543 The confidence level is 99%. The uncertainties in parameter μ is 0.74769 The uncertainties in parameter σ 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 μ is 34.2816 The parameter σ is 8.3543 The confidence level is 99%. The uncertainties in parameter μ is 0.74769 The uncertainties in parameter σ 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 μ is 38.5284 The parameter σ is 8.1861 The confidence level is 99%. The uncertainties in parameter μ is 1.0511 The uncertainties in parameter σ 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 μ is 34.1473 The parameter is σ 7.1325 The confidence level is 99%. The uncertainties in parameter μ is 0.85587 The uncertainties in parameter σ 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 μ , σ , and a_1 are the parameters needed for the nonlinear fitting algorithm in order to have the best fit.

$$n(M) = \underline{a_1 exp(-(M-\mu)^2/2\sigma^2)}_{\sigma (2\pi)^{0.5}}, \quad (Gaussian1)$$
(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 σ is 14.1055 The parameter μ is 31.8339 The confidence level is 99%. The uncertainties in parameter a_1 is 0.0066962 The uncertainties in parameter σ is 0.28462 The uncertainties in parameter μ 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 σ is 13.1778 The parameter μ is 33.065 The confidence level is 99%. The uncertainties in parameter a_1 is 0.0043283 The uncertainties in parameter σ is 0.38656 The uncertainties in parameter μ 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 σ is 15.6352 The parameter μ is 35.5143 The confidence level is 99% The uncertainties in parameter a_1 is 0.0070458 The uncertainties in parameter σ is 0.33039 The uncertainties in parameter μ 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 σ is 13.9667 The parameter μ is 32.1043 The confidence level is 99%. The uncertainties in parameter a_1 is 0.0064705 The uncertainties in parameter σ is 0.30595 The uncertainties in parameter μ 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_c -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

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

None of the residual plots from the lognormal (equation 11) fits were random (see figures 15-23).

The parameter μ is 4.4982 The parameter σ is 0.01106 The confidence level is 99%. The uncertainties in parameter μ is 0.25447 The uncertainties in parameter σ 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 σ is 0.23499 The parameter μ is 32.5641 The confidence level is 99%. The uncertainties in parameter σ is 0.0096589 The uncertainties in parameter μ 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 μ is 5.8704 The parameter σ is 0.00032913 The confidence level is 99%. The uncertainties in parameter μ is 0.28941 The uncertainties in parameter σ 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 σ is 0.22247 The parameter μ is 33.8092 The confidence level is 99%. The uncertainties in parameter σ is 0.0083333 The uncertainties in parameter μ 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 μ is 5.0699 The parameter σ is 0.0019114 The confidence level is 99%. The uncertainties in parameter μ is 0.21156 The uncertainties in parameter σ 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 σ is 0.19149 The parameter μ is 35.4707 The confidence level is 99%. The uncertainties in parameter σ is 0.010122 The uncertainties in parameter μ 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 μ is 5.1937 The parameter σ is 0.0003762 The confidence level is 99%. The uncertainties in parameter μ is 0.20563 The uncertainties in parameter σ 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 μ is 3.7308 The parameter σ is 0.0094349 The confidence level is 99%. The uncertainties in parameter μ is 0.18306 The uncertainties in parameter σ 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^{8, 12}

The parameter σ is 0.20137 The parameter μ is 33.0594 The confidence level is 99%. The uncertainties in parameter σ is 0.0095973 The uncertainties in parameter μ 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^{8, 12}

The lognormal distribution did not provide random residual plots. Equation 12, a lognormal function¹⁶ 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.

$$n(\mathbf{M}) = \underline{c_1 \exp - (\ln(\mathbf{M}) - \mu)^2 / (2\sigma^2)}_{(2\pi)^{0.5} \sigma \mathbf{M}}, \quad \text{(lognormal1)}$$
(12)

The parameter c_1 is 4.6974 The parameter σ is 1.9284 The parameter is μ 3.8285 The confidence level is 99%. The uncertainties in parameter c_1 is 6.7757 The uncertainties in parameter σ is 0.43076 The uncertainties in parameter μ 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 σ is 0.23224 The parameter μ is 32.3507 The confidence level is 99%. The uncertainties in parameter c_1 is 0.0064888 The uncertainties in parameter σ is 0.0030538 The uncertainties in parameter μ 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 σ is 0.63012 The parameter μ is 8.0238 The confidence level is 99%. The uncertainties in parameter c_1 is 0.00077456 The uncertainties in parameter σ is 0.0055445 The uncertainties in parameter μ 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 σ is 0.93934 The parameter μ is 18.4104 The confidence level is 99%. The uncertainties in parameter c_1 is 0.005849 The uncertainties in parameter σ is 0.013532 The uncertainties in parameter μ is 0.49265 The reduced chi squared is 20.0879



Figure 27: Upper 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 0.14115 The parameter σ is 0.19873 The parameter μ is 33.3372 The confidence level is 99%. The uncertainties in parameter c_1 is 0.0035649 The uncertainties in parameter σ is 0.004485 The uncertainties in parameter μ 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 σ is 0.56767 The parameter μ is 6.3054 The confidence level is 99%. The uncertainties in parameter c_1 is 0.00035774 The uncertainties in parameter σ is 0.0040577 The uncertainties in parameter μ 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 σ is 0.2292 The parameter is μ 36.0985 The confidence level is 99%. The uncertainties in parameter c_1 is 0.0079052 The uncertainties in parameter σ is 0.0038922 The uncertainties in parameter μ 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 - Tc = 2 K for Shresth's data on PEO in Isobutyric Acid and Water^{8, 12}

The parameter c_1 is 0.27649 The parameter σ is 0.22726 The parameter is μ 32.585 The confidence level is 99%. The uncertainties in parameter c_1 is 0.0069873 The uncertainties in parameter σ is 0.003656 The uncertainties in parameter μ is 0.14348 The reduced chi squared is 2.063



Figure 31: Lower 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}

The parameter c_1 is 0.13972 The parameter σ is 0.80468 The parameter μ is 16.3393 The confidence level is 99%. The uncertainties in parameter c_1 is 0.0026756 The uncertainties in parameter σ is 0.0068373 The uncertainties in parameter μ 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.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:

$$W_{A=}^{T} \underline{w(M) - w_{B}(M)}_{W_{A}(M) - w_{B}(M)} W^{T}$$
(13)

$$W^{T}_{B=} \frac{w(M) - w_{\underline{A}}(M)}{w_{B}(M) - w_{A}(M)} W^{T}$$
(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.

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

 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

Shresth¹² 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.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 value 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.¹⁹ 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 Styragel HR3, Styragel HR4,

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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

Sample	Source	Catalog # / Lot #/ Sample #	M _W	End Group
1	Fluka Chemical	425182/1 12401	20900	ОН
2	Polymer Source	PEG-2OCH ₃ -2K	4530	OCH ₃

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): $M_w = 20900$; 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.^{8,12} 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.

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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 = OCH₃

The poly(ethylene glycol) (Sample # PEG2OCH₃-2K) (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

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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.²⁷ 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.

$T-T_{c}(K)$	M _n upper	M _w upper	M _n lower	M _w lower	PI upper	PI lower
0.1 K	12.7	16.7	34.6	36.3	1.32	1.07
4 K	14.6	19.9	34.9	38.2	1.36	1.09

Table 5: Mass of Polymer in Lower and Upper Phase at Different Temperaturesfor Sample 1: Mw = 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





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



Figure 40: Ln (w(M)"/ w(M)') 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 distribution¹⁶ was applied to the lower phase of the samples with $M_w = 20900$. Like Shresth's¹² data, the residual plots are not random. They all seem to have a pattern (see figures 41-42).

The parameter μ is 53.2794 The parameter σ is 12.1364 The confidence level is 99%. The uncertainties in parameter μ is 1.0734 The uncertainties in parameter σ 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 μ is 63.4491 The parameter σ is 15.9432 The confidence level is 99%. The uncertainties in parameter μ is 1.1033 The uncertainties in parameter σ is 0.40502 The reduced chi squared is 17.7705

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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

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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 σ is 18.8017 The parameter μ is 48.0294 The confidence level is 99%. The uncertainties in parameter a_1 is 0.0016273 The uncertainties in parameter σ is 0.092502 The uncertainties in parameter μ 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 K for M_w = 20900; Termination-OH

The parameter a_1 is 0.26674 The parameter σ is 17.6148 The parameter μ is 52.5295 The confidence level is 99%. The uncertainties in parameter a_1 is 0.002889 The uncertainties in parameter σ is 0.22434 The uncertainties in parameter μ 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 data¹², 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 σ is 0.40304 The parameter μ is 7.0478 The confidence level is 99%. The uncertainties in parameter σ is 0.019601 The uncertainties in parameter μ 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 σ is 0.37176 The parameter μ is 54.35 The confidence level is 99%. The uncertainties in parameter σ is 0.0082238 The uncertainties in parameter μ 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 K from Sample 1: M_w = 20900; Termination = -OH

The parameter σ is 0.34782 The parameter μ is 8.8109 The confidence level is 99%. The uncertainties in parameter σ is 0.026803 The uncertainties in parameter μ 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 σ is 0.37262 The parameter μ is 58.0076 The confidence level is 99%. The uncertainties in parameter σ is 0.010965 The uncertainties in parameter μ is 1.082 The reduced chi squared is 12.0413





Figure 48: Lower Phase: Fitting and Residual Plots for Lognormal Function (Equation 11) at T_c - T = 4 K from Sample 1: M_w = 20900; Termination = -OH

The parameter σ is 0.13489 The parameter μ is 18.9411 The confidence level is 99%. The uncertainties in parameter σ is 0.0063316 The uncertainties in parameter μ 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 σ is 0.053668 The parameter μ is 21.8725 The confidence level is 99%. The uncertainties in parameter c_1 is 0.00012566 The uncertainties in parameter σ is 0.0008272 The uncertainties in parameter μ 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 σ is 0.33551 The parameter μ is 49.4527 The confidence level is 99%. The uncertainties in parameter c_1 is 0.040842 The uncertainties in parameter σ is 0.012604 The uncertainties in parameter μ 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 σ is 0.11443 The parameter μ is 19.624 The confidence level is 99%. The uncertainties in parameter c_1 is 0.00068082 The uncertainties in parameter σ is 0.0031172 The uncertainties in parameter μ 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 σ is 0.15596 The parameter μ is 20.5337 The confidence level is 99%. The uncertainties in parameter c_1 is 3.9378e-005 The uncertainties in parameter σ is 0.0025669 The uncertainties in parameter μ 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_c - T = 4 K for Sample 1: M_w = 20900; Termination = -OH

The parameter c_1 is 0.33257 The parameter σ is 0.2102 The parameter μ is 51.4059 The confidence level is 99%. The uncertainties in parameter c_1 is 0.034735 The uncertainties in parameter σ is 0.014607 The uncertainties in parameter μ 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 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.

Temperature	Mass and mass fraction in	Mass and mass fraction in		
	lower phase	upper phase		
0.1 K	(0.216 ± 0.126)	(0.783 ± 0.126)		
	(0.019 ± 0.011) gram	(0.068 ± 0.011) gram		
4 K	(0.057 ± 0.103)	(0.943 ± 0.103)		
	(0.005 ± 0.009) gram	(0.082 ± 0.009) gram		

Table 6: Mass of Polymer in Lower and Upper Phases at Different Temperaturesfor Sample 1: Mw = 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 data¹² and from the new data reported above.

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

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 data¹² and from New Data Reported Here

2 - Sample 2- PEG-OCH₃: 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-OCH₃, M_w = 4530: M_n and M_w for the Upper and Lower Phase as a Function of Time, T_c -T= 1 K



Figure 58: PEG-OCH₃, 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-OCH₃ at different temperatures

Temperature	M _n upper	M _n lower	M _w upper	M _w lower	PI upper	PI lower
1 K	2826	6208	3286	6404	1.16	1.03
2 K	4104	9574	4646	10076	1.13	1.05
4 K	4964	7664	5580	8124	1.12	1.06

Table 8: PEG-OCH3, $M_w = 4530$: M_n and M_w for the Lower and Upper Phases at
Different Temperatures



Figure 60: PEG-OCH₃, M_w = 4530: Comparison of the Molecular Weight Distributions in the Upper and Lower Phases at T = 297.7 K



Figure 61: PEG-OCH₃, M_w = 4530: Comparison of the Molecular Weight Distributions in the Upper and Lower phases at T = 296.7 K



Figure 62: PEG-OCH₃, 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.



Figure 63: PEG-OCH₃, M_w = 4530: Ln(w(M)["]/w(M)') versus Molecular Weight at T = 297.7 K



Figure 64: PEG-OCH₃, M_w = 4530: Ln(w(M)"/w(M)') versus Molecular Weight at T = 296.7 K



Figure 65: PEG-OCH₃, M_w = 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 μ is 14.2662 The parameter σ is 2.5451 The confidence level is 99%. The uncertainties in parameter μ is 0.27836 The uncertainties in parameter σ 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 Mw = 4530; Termination-OCH₃

The parameter μ is 13.3998 The parameter σ is 1.8164 The confidence level is 99%. The uncertainties in parameter μ is 0.3009 The uncertainties in parameter σ 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 Mw = 4530; Termination-OCH₃

The parameter μ is 12.0794 The parameter σ is 2.5156 The confidence level is 99%. The uncertainties in parameter μ is 0.23658 The uncertainties in parameter σ 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-OCH₃

The following plots are from equation 10:

The parameter a_1 is 0.11357 The parameter σ is 4.1232 The parameter μ is 14.3407 The confidence level is 99%. The uncertainties in parameter a_1 is 0.00052929 The uncertainties in parameter σ is 0.025707 The uncertainties in parameter μ 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 K for Mw = 4530; Termination-OCH₃

The parameter a_1 is 0.10701 The parameter σ is 5.6677 The parameter μ is 11.7959 The confidence level is 99%. The uncertainties in parameter a_1 is 0.00068114 The uncertainties in parameter σ is 0.040731 The uncertainties in parameter μ 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-OCH₃

The parameter a_1 is 0.00031864 The parameter σ is 1.222 The parameter μ is 12.1359 The confidence level is 99%. The uncertainties in parameter a_1 is 3.2308e-006 The uncertainties in parameter σ is 0.0072885 The uncertainties in parameter μ 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-OCH₃
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 σ is 0.28161 The parameter μ is 14.6826 The confidence level is 99%. The uncertainties in parameter σ is 0.006732 The uncertainties in parameter μ 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 = -OCH₃

The parameter σ is 0.21188 The parameter μ is 12.182 The confidence level is 99%. The uncertainties in parameter σ is 0.0041673 The uncertainties in parameter μ 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 = -OCH₃

The parameter σ is 0.15438 The parameter μ is 9.4152 The confidence level is 99%. The uncertainties in parameter σ is 0.0045557 The uncertainties in parameter μ 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 = -OCH₃

The parameter σ is 0.28951 The parameter μ is 13.1896 The confidence level is 99%. The uncertainties in parameter σ is 0.0069021 The uncertainties in parameter μ 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 = -OCH₃

The parameter c_1 is 0.0093738 The parameter σ is 0.066513 The parameter μ is 4.9885 The confidence level is 99%. The uncertainties in parameter c_1 is 9.3155e-005 The uncertainties in parameter σ is 0.00084948 The uncertainties in parameter μ 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 = -OCH₃

The parameter c_1 is 0.11545 The parameter σ is 0.14829 The parameter μ is 14.4206 The confidence level is 99%. The uncertainties in parameter c_1 is 0.00032211 The uncertainties in parameter σ is 0.00047892 The uncertainties in parameter μ 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 = -OCH₃

The parameter c_1 is 0.010931 The parameter σ 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 σ is 0.00079325 The uncertainties in parameter μ 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 = -OCH₃

The parameter c_1 is 0.11546 The parameter σ is 0.26958 The parameter μ is 12.1003 The confidence level is 99%. The uncertainties in parameter c_1 is 0.00046264 The uncertainties in parameter σ is 0.0012028 The uncertainties in parameter μ 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 = -OCH₃

The parameter c_1 is 0.0077707 The parameter σ is 0.042193 The parameter μ is 5.1317 The confidence level is 99%. The uncertainties in parameter c_1 is 0.00021403 The uncertainties in parameter σ is 0.001126 The uncertainties in parameter μ 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 = -OCH₃

The parameter c_1 is 0.00075388 The parameter σ is 0.050864 The parameter μ is 12.147 The confidence level is 99%. The uncertainties in parameter c_1 is 2.9761e-006 The uncertainties in parameter σ is 0.00027587 The uncertainties in parameter μ is 0.0033042 The reduced chi squared is 19.874



Figure 81: Lower Phase: Fitting and Residual Plots for Lognormal1 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 σ is 0.073085 The parameter μ is 5.3011 The confidence level is 99%. The uncertainties in parameter c_1 is 7.5717e-005 The uncertainties in parameter σ is 0.0006376 The uncertainties in parameter μ 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 = -OCH₃

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).

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

Table 9: PEG-OCH3, Mw = 4530: Mass Fraction of Polymer in Lower and Upper Phases atDifferent Temperatures



Figure 83: PEG-OCH₃, $M_w = 4530$: 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.



Figure 84: Summary of Mass Fractions at Different Temperatures

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, $\ln(w'(M)/w'(M))$ 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 OCH₃ 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 Phases¹⁷

$$\mathbf{W}^{\mathrm{T}} \mathbf{w}(\mathbf{M}) = \mathbf{W}^{\mathrm{T}}_{\mathrm{A}} \mathbf{w}_{\mathrm{A}}(\mathbf{M}) + \mathbf{W}^{\mathrm{T}}_{\mathrm{B}} \mathbf{w}_{\mathrm{B}}(\mathbf{M})$$

where

 \mathbf{W}^{T} = the initial weight of polymer

w(M) = molecular weight distribution in one phase

 W_{A}^{T} = total weight of polymer in phase A

 $w_A(M) =$ molecular weight distribution in phase A

 W_{B}^{T} = total weight of polymer in phase B

 $w_B(M) =$ molecular weight distribution in phase B

The total polymer mass:

$$\mathbf{W}^{\mathrm{T}} = \mathbf{W}^{\mathrm{T}}_{\mathrm{A}} + \mathbf{W}^{\mathrm{T}}_{\mathrm{B}}.$$

Solving for W_{A}^{T}

$$W^{T}_{A} w_{A}(M) = W^{T} w(M) - (W^{T} - W^{T}_{A}) w_{B}(M)$$
$$W^{T}_{A} (w_{A}(M) - w_{B}(M)) = W^{T} [w(M) - w_{B}(M)]$$

The mass fractions in both phases

$$\frac{W_{A}^{T}}{W^{T}} = \frac{w(M) - w_{B}(M)}{w_{A}(M) - w_{B}(M)}$$

 $\frac{W^T_{B}}{W^T} = \frac{w(M) - w_A(M)}{w_B(M) - w_A(M)}$

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);

Matt Retzer 10/13/98

revised by S. Greer 3/23/01, error analysis revised by Mike Alessi 5/16/01 run labeling added 7/03/01

y the data height, the dependent variable

x the independent variable

a_0 the initial parameters

a the final parameters, fitted to minimum chi squared

newy the fitted y value from the a values

sigma_y the uncertainty in the y value, either supplied or derived

sigma_x the uncertainty in the x value, supplied

z plotting color and symbol

F the objective function

tol the tolerance for the fmins function

trace determines the outputs from the fmins function

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 %defines 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.

683

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 = $p.^{5}$; % 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

 $res = (y-feval(F,x,a))./(sigma_y_sqr).^.5;$

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);

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) \sim = X(j+1,5)
         z^{2} = 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
end
```

end

```
if st == 3
res1 = (set1y-feval(F,set1x,a))./(sigma_y_sqr1).^.5;
res2 = (set2y-feval(F,set2x,a))./(sigma_y_sqr2).^.5;
res3 = (set3y-feval(F,set3x,a))./(sigma_y_sqr3).^.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);
```

```
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
      if sos == 1
        break
       end
    end
  end
  if sos == 1
    break
  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)]);

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