

Chapter 6: Effect of Temperature on Nonionic Polymer Adsorption on SiO₂ in Aqueous Media

6.1. Goal

The objective of the work described in this chapter was to determine if the adsorption of a hydrogen-bonding homopolymer on SiO₂ could be enhanced by thermal manipulation of solvent quality above or near the cloud point. It was shown in Chapter 2 from the studies of Killman and Malmsten that insolubility alone will not drive polymer adsorption, when the polymer is well solvated.^{1,2} However, by approaching the cloud point of the solution, the favorable interactions between the solvent and polymer are eliminated or significantly reduced. It may then be possible to drive adsorption with decreased solubility, should the effect of polymer insolubility be stronger than the decrease in hydrogen-bonding between the polymer and the substrate, as the temperature is increased. Lowering the temperature will drive the soluble polymer chains back into solution. Given the slow kinetics of polymer desorption,³ no significant immediate desorption of polymer would be expected as the temperature is lowered. If adsorption is promoted, this approach could lead to a brushlike layer for a well designed copolymer stabilizer due to enhanced adsorption.

6.2. Introduction

The physical chemistry of water-soluble polymers is not as well understood as their behavior in organic solvents. The tendency for specific interactions between the polar water molecules and the polymer chains, such as hydrogen-bonding, results in very different solution behavior from that which is observed for polymers in organic media. Dominated by the entropy of mixing of water, polymer/water solutions exhibit phase behavior not observed for similar solutions in organic solvents.⁴ Water-soluble polymers may exhibit phase separation at upper critical solution temperatures, UCST or at lower critical solution temperatures, LCST, as illustrated in Figure 6.2.1. (a). At the point of phase separation, the solution turns turbid. The cloud point is defined as the temperature at which a solution becomes turbid, and it is equivalent to the UCST or LCST of the

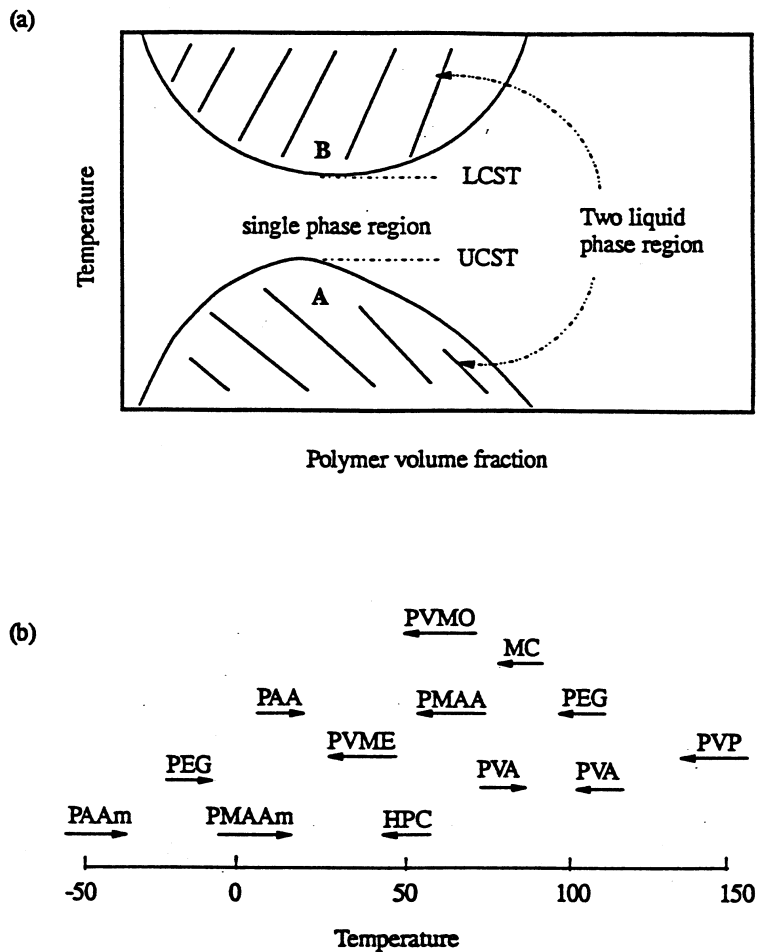


Figure 6.2.1. (a) Illustration of commonly observed phase behavior of polymer solutions. Region A represents the region characterized by a upper critical solution temperature, UCST. Region B illustrates the phase region for a lower critical solution temperature, LCST. LCST behavior is observed frequently in aqueous systems. (b) cloud points for a the most common water-soluble polymers referenced to 25 °C. Arrows indicate direction of temperature change to promote phase separation (ref. 4).

water-soluble polymer. For infinite molecular weight, the cloud point may be related to the theta temperature as:

$$\frac{1}{T_c} = \frac{1}{\Theta} \left(1 + M^{\frac{-1}{2}} \right) \quad [6.2.1]$$

where T_c is the critical temperature, Θ is the theta temperature, and M is the infinite molecular weight. As indicated in equation [6.2.2], the cloud point is a decreasing function of molecular weight. Equation [6.2.2] was derived from the Flory-Huggins solution theory. In the F-H theory, the temperature at which phase separation occurs is given by:

$$\frac{1}{T_c} = \frac{1}{\Theta} \left(1 + \frac{1}{\Psi_1} \left(\frac{1}{\sqrt{x_n}} + \frac{1}{2x_n} \right) \right) \quad [6.2.2]$$

where T_c and Θ are defined as above, Ψ_1 is an entropy term, and x_n is the degree of polymerization of the polymer. Ψ_1 is defined from the modified F-H theory in equation [6.2.3]:

$$\Delta S_1^E = R\Psi_1\phi_2^2 \quad [6.2.3]$$

where ΔS_1^E is the excess entropy of dilution, R is the gas constant, and ϕ_2 is the volume fraction of polymer in the system. The theta temperature is obtained from the intercept of equation [6.2.2], and Ψ_1 from the slope.^{4,5}

The original F-H theory of polymer solutions does a qualitatively good job of describing polymer behavior in non-polar solvents, but fails to adequately describe aqueous solution behavior. Since it was derived for non-polar solvents, this is not surprising. The F-H

theory is incapable of predicting the LCST behavior of water-soluble polymers as the χ parameter was defined to increase when temperature decreases. By design, the F-H theory can only predict a UCST as temperature is decreased.⁵ A rigorous equation of state that fully describes the behavior of nonionic polymers in aqueous media does not exist. Figure 6.2.1. (b) illustrates the cloud points of several water soluble polymers.⁴

Chen et al.⁴ measured the cloud point of PEOX at several molecular weights, as shown in Figure 6.2.2. From this figure, it is seen that LCST behavior is observed, and a theta temperature of approximately 60°C was determined from equation [6.2.2]. A negative value of Ψ_1 was obtained, indicating entropy of dilution for water is negative. Typically, Ψ_1 is positive for non-polar organic solvents. The negative value is a result of the specific interaction of the polymer with water through hydrogen-bonding. Hydrogen-bonding, the proposed mechanism for the interactions of the PEOX and modified PEI homopolymers and metal oxide surfaces, for interactions between water and water-soluble polymers, and for water and metal oxide surfaces,⁶ is known to decrease as temperature increases. Thus increasing temperature decreases the solubility of the polymers due to a decrease in hydrogen-bonding.

Given that hydrogen-bonding decreases with temperature, it is feasible that the interactions between the water and SiO₂ may be reduced as well. If the insolubility is a stronger driving force for adsorption than the loss of hydrogen-bonding between the polymer and the surface, increased adsorption may be feasible. While it has been shown for the case of sulfapyridine, an electrolyte, on Al₂O₃ that adsorption decreases with increasing temperature,⁷ there is no evidence in the literature of this type of study concerning nonionic water-soluble polymers. It is therefore not known if insolubility can drive adsorption as the hydrogen-bonding of the polymer and surface are reduced. The solubility of the sulfapyridine increases as the temperature is increased, while the polymers in this study are known to decrease in solubility.

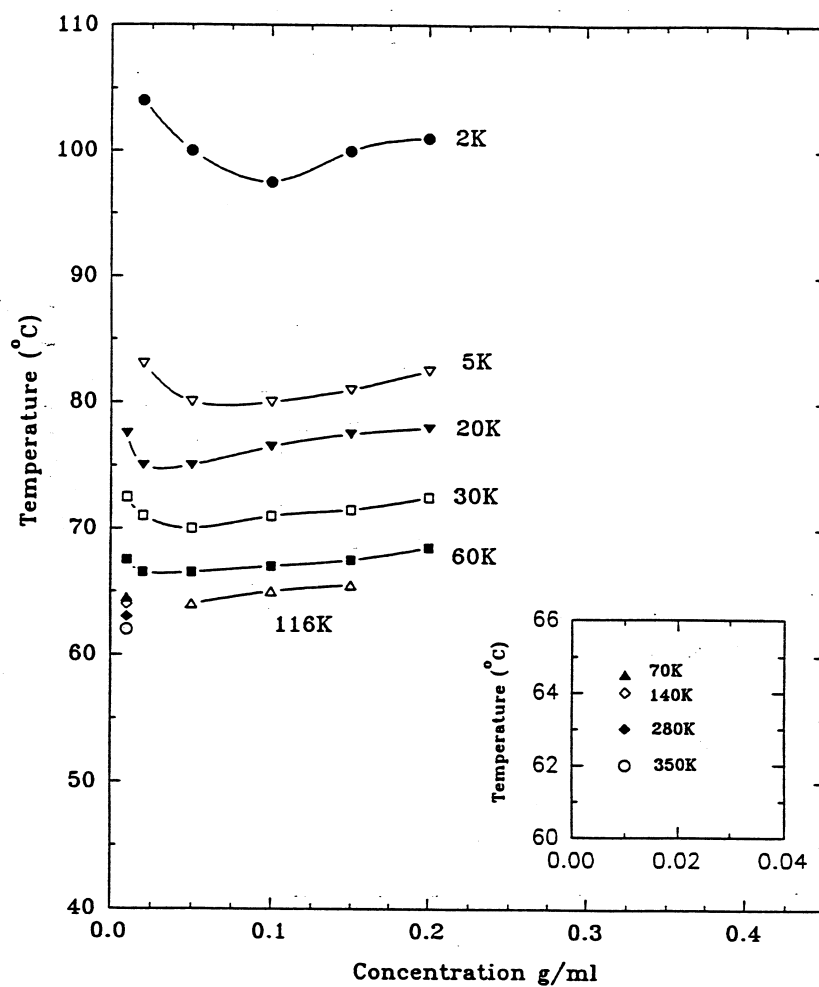


Figure 6.2.2. Cloud point temperature as a function of molecular weight for PEOX homopolymer in dilute solution. Inset is a list of cloud points of higher molecular weight PEOX polymers as listed in the literature. (ref. 4).

6.3. Materials

The PEOX sample to be studied had an $M_w = 30K$ g/mole and a $PI = 1.1$. The modified PEI sample was P100G100, with $N = 100$, $M_w = 11,700$ g/mol and containing 200 hydroxyl groups. The dendritic material studied was PA32G100 with $G = 4$ and $M_w = 8250$ g/mol. All the polymers were supplied by Oxazogen, Inc. Figure 6.3.1 shows the structure of the PEOX and hydroxyl modified PEI. The SiO_2 used was grade Cab-O-Sil L-90 amorphous fumed SiO_2 from Cabot Corporation, Lot 1F139 and Lot 1E102. The density was 1.8 g/ml, the surface area for Lot 1F139 was reported by Cabot Corporation as 96 m²/g, while for Lot 1E102 a surface area of 83 m²/g was measured on a Micromeritics ASAP 2010 Accelerated Surface Area and Porosimetry System. The particle size of the L-90 was 270 nm.

6.4. Experimental Procedure

6.4.1. Cloud Point Determination

PEOX $M_w = 30K$, P100G100, and PA32G100 samples at added concentrations of 3×10^{-3} g polymer/g solution in water were heated in 25 ml erlenmeyer flasks. A Thermolyne MIRAK™ stirring hotplate was used to heat and stir the samples. A control 25ml erlenmeyer flask with water containing the type K thermocouple probe that controls the hot plate was used as a reference for the polymer solution temperature. Using data for PEOX from Chen et al.⁴ as a reference, the solutions were brought quickly up to 68°C. After stabilizing at 68°C for 60 minutes, the temperature was increased 1°C every 30 minutes they turned cloudy. Once the solution appeared turbid, the temperature was dropped 2°C. When the solutions had been clear for 30 minutes, the temperature was increased 1°C per hour until turbidity was observed, and the temperature recorded as the cloud point. The cloud point was determined in this manner to within ± 1.5 °C.

6.4.2. Adsorption Experiments

Polymer/ SiO_2 samples were prepared as detailed in Chapter 3, except that a teflon coated magnetic stir bar turning at 750 rpm was used to mix the suspension rather than a wrist action shaker. The samples were mixed for 24 hours at the desired temperature, then cooled to room temperature quickly by refrigeration. No more than 30 minutes elapsed

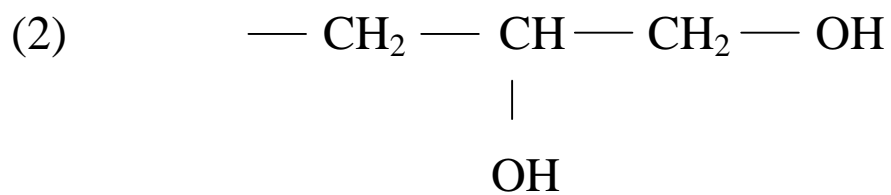


Figure 6.3.1 Structures of PEOX and hydroxyl modified PEI homopolymers. R = (1) is PEOX. R = (2) is modified PEI.

between the end of the adsorption experiment and reaching room temperature. Once at room temperature, the SiO₂ particles were removed by centrifugation at 10,000 Gs in a Marathon 21K centrifuge, as described in Chapter 3. The concentration of polymer in the supernatant was determined by the UV absorbance technique and gravimetric analysis. These techniques were described in Chapter 3. The time from the end of the experiment to separation of the particles from the supernatant did not exceed 60 minutes.

6.5. Results

6.5.1. Cloud Point Determination

The cloud point of PEOX $M_w = 30K$ was determined to be $73^\circ\text{C} \pm 1.5^\circ\text{C}$. This result was repeated three times to insure its accuracy. The modified P100G100 material did not have a cloud point. Solutions were heated from 68°C to 97°C and never observed to turn turbid. Given that this was the highest molecular weight linear modified PEI sample, the lower molecular weight polymers are not expected to have a cloud point below 97°C . Adsorption as a function of temperature was not studied for the linear modified PEI samples. Based on the P100G100 results, the cloud point of the largest molecular weight water soluble dendritic polymer was investigated, PA32G100. Once again, upon heating to 97°C no turbidity was observed at any temperature. No elevated temperature adsorption experiments were performed with the PA32G100.

6.5.2. Elevated Temperature Adsorption Experiments

To determine the effect of temperature on the adsorption of PEOX homopolymer, three experiments were performed. The first two determined the plateau adsorbed amount at 70°C and 75°C , in which the PEOX/SiO₂ samples were heated from room temperature to 70°C and 75°C , respectively. From the results in Chapter 3, it was known that at room temperature a PEOX concentration of 3×10^{-3} g PEOX/g solution was on the adsorption plateau. Figure 6.5.1 shows that the plateau adsorbed amount as a function of temperature. As seen in the figure, the adsorbed amount was observed to decrease with increasing temperature. The line was added to guide the eye, not as a fit of the data. These results indicate that the decreased solubility of the polymer does not lead to increased adsorption, and that the decrease in hydrogen-bonding interaction with the SiO₂

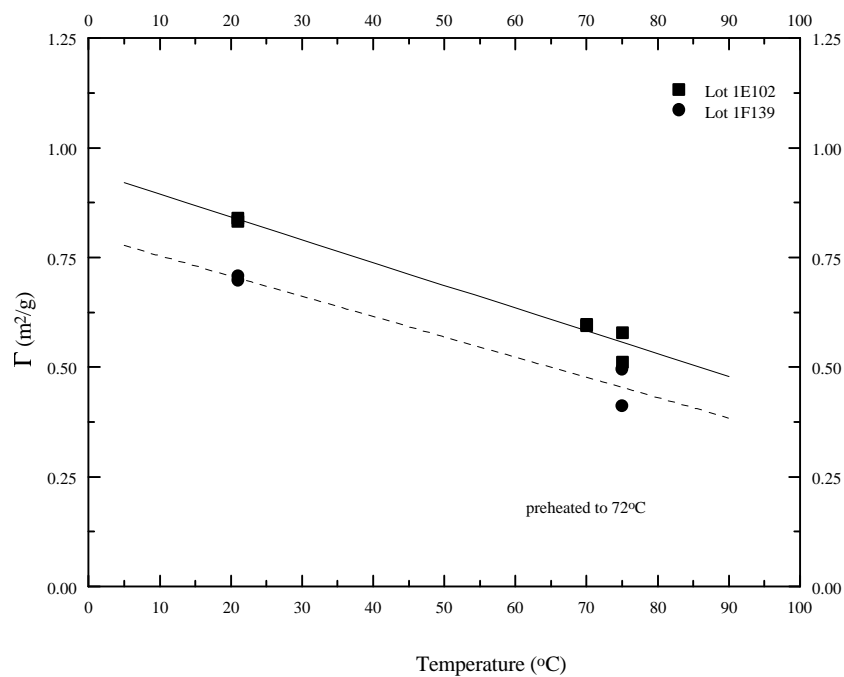


Figure 6.5.1. Elevated temperature adsorption study of PEOX $M_w = 30K$ homopolymer on SiO_2 . The cloud point of PEOX $M_w = 30K = 73^\circ C$.

surface leads to a decrease in polymer adsorption. To determine if the adsorption was completely prevented or just reduced, the 75 °C experiment was repeated, except that the polymer solution was preheated from room temperature to 72 °C. Once at 72 °C, a known weight of the L-90 silica particles were added to the hot PEOX solution. By preheating the solution, the adsorption at low temperatures was prevented, and all PEOX adsorption would be forced to occur at temperatures above 72 °C. As seen in Figure 6.5.1, the decrease in the plateau adsorbed amount was similar to the amount obtained when the samples were heated from room temperature. The slightly lower values of the plateau adsorbed amount appear to be a function of the lot of SiO₂, not an effect due to temperature, as the plateau adsorbed amount at room temperature was observed to be slightly decreased as well. Again, the line is provided to guide the eye, not as a fit of the data.

6.6. Conclusions

The experiments described in this chapter examined the effect of solvent goodness on the adsorption properties of PEOX. After establishing the cloud point of the PEOX $M_w = 30K$ homopolymer, the adsorbed amount was determined as a function of temperature, and thus PEOX solubility. As the plateau adsorbed amount was observed to decrease as the temperature was varied near and above the cloud point, it was concluded that the decrease in PEOX solubility was not able to drive adsorption. Since insolubility failed to drive the adsorption, the affinity for the surface must have been reduced. This would mean a decrease in hydrogen-bonding between the PEOX homopolymer and the SiO₂ surface. Thus, while insolubility has been observed to drive adsorption of polymers in organic media, thermally induced insolubility was not found to be an effective method for increasing the plateau adsorbed amount of the nonionic hydrogen-bonding PEOX homopolymer. These results imply that insolubility alone does not drive adsorption, rather it enhances adsorption. Without an affinity for the surface, such as hydrogen-bonding, an insoluble polymer may prefer to associate with itself rather than the surface.

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