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Hydrophobically Modified Polyethyleneimines and Ethoxylated Polyethyleneimines

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Hydrophobically Modified Polyethyleneimines and

Ethoxylated Polyethyleneimines

A thesis submitted in partial fulfillment

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Master of Science

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY Michael J. Simons ENTITLED <u>Hydrophobically Modified</u>
<u>Polyethyleneimines and Ethoxylated Polyethyleneimines</u> BE ACCEPTED IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF <u>Master of</u>
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Abstract

Michael Simons. M.S., Department of Chemistry, Wright State University, 2007.
Hydrophobically Modified Polyethyleneimines and Ethoxylated Polyethyleneimines.

The modification of the commercially available polymers polyethyleneimines and ethoxylated polyethyleneimines took place with approximately a 3-10% alkylbromide modification followed by, in the case of the polyethyleneimines, a 2-hydroxypropyl modification, using propylene oxide, on the order of 65-70%. The objective was to increase the hydrophobicity of the polymer while keeping the cloud point above 60°C. Another approach taken was to form hydrophobic ethers from ethoxylated polyethyleneimine. We also added a 2-hydroxy ethyl group to a hexylated polyethyleneimine avoiding the use of ethylene oxide or drying EPI.

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1. Introduction

Behavior of Thermosensitive Polymers

There are unique aqueous polymer solutions that display a lower critical solution temperature (LCST) below which they are in a hydrophilic, soluble state and above which the polymer chains become hydrophobic and precipitate from solution. The process is governed by molecular interactions between the polymer chains and the surrounding water molecules, and this is influenced by the chemical structure of the monomer units [1] (**Figure 1**).
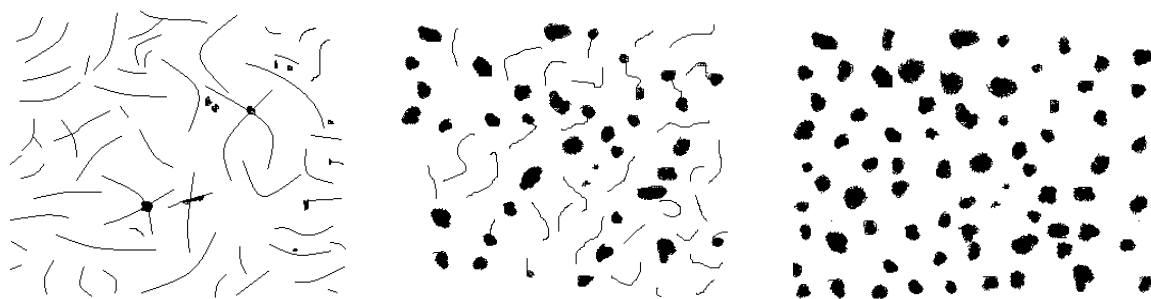
Figure 1. The Transition From Extended Chains to the Collapsed State

The factors that are responsible for conformational changes of a polymer are the type of interactions encountered. Short range interactions take place among neighboring segments where as long range interactions are the result of distant segments along the chain coming in close range to each other in space. These interactions are the result of van der Waals interactions, chemical bonds between side chains and/or solvent (e.g., hydrogen bonding), hydrophobic interactions, electrostatic interactions (electric dipoles and ions), topological interactions (e.g., entanglements) and so on. The coil-globule transition of a linear polymer is caused by these interactive forces.[2]

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At certain concentrations, a swollen to shrunken transition will take place in a cross-linked polymer. The gel will collapse at temperatures above the LCST and in the process will expel water and shrink in volume.[3] This endothermic process of the releasing of water from the polymer chain is compensated by the entropic driving force of the phase separation of the polymer due to the dissociation of the hydrophobically bound water.[4] These polymers are surrounded by complex hydration shells consisting of different local water structures.[5] The cloud point of the polymer is determined by the balance between an unfavorable decrease in the entropy of water in the hydrophobic hydration shell and a favorable interaction between polar groups and water. When a hydrophilic polymer is in an aqueous solution it becomes elongated, presumably as a result of the hydrogen bonding between the surrounding water molecules and the hydrophilic groups on the polymer. These hydrogen bonding interactions cause water molecules to become organized around the polymer chains. The solvent quality decreases with increasing temperature causing an increase in the hydrophobic polymer-polymer interactions. A thermodynamic model can be used to explain the phase transition: When the polymer is in an aqueous solution there exists a balance between the hydrophilic and hydrophobic interactions. When hydrogen bonds are formed between water and polymer there is a positive contribution to the free energy (ΔG) of solution since (ΔH) is negative and an unfavorable contribution to the free energy with a negative (ΔS) of solution.[6] There is a disruption of the hydrogen bonds between the water molecules and the polymer as the temperature of the solution increases. The cloud point temperature is the temperature at which the $T(\Delta S)$ component exceeds the (ΔH) contribution and it is at this temperature that precipitation will occur.[45]

Types of Separation

The phase transitions of polymer solutions can take on different forms such as, clear solution, opaque solution(milky), and shrunken and swollen (a two phase state consisting of a solvent layer on top of a gel.[3] Polymer solutions pass through some or all of these phases as the temperature rises. The degrees of chain precipitation and, consequently, the type of phase separation will depend on the hydrophobic character of the individual polymer chains. A low concentration of polymer chains when precipitated will give an opaque, milky solution (**Figure 2**). If the concentration of polymer chains is sufficiently high the precipitates will aggregate to form a gel. The degree of cohesiveness of the gel depends on the increasing entanglements, which increases with increasing molecular weight. The sharp phase transition at the LCST is attributable to a good balance between the hydrophilic and hydrophobic interactions in the polymer. These transitions are sharper for high molecular weight samples and they broaden for low molecular weight samples.[7] Some clouding may occur slightly below the LCST for copolymers. The reason for this might be due to a greater heterogeneity of copolymers as a result of less than ideal copolymerization.[8]
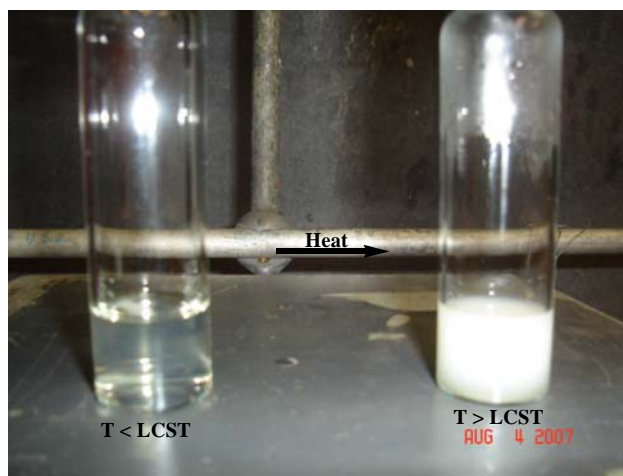
Figure 2. Precipitation of Polymer Above LCST

Uses of Stimuli-Responsive Polymers

Stimuli-responsive polymers, also called "smart polymers", undergo reversible phase transitions in response to external stimuli such as temperature[9,10], pH[11], ions[12], chemical species[13] and electric or magnetic fields[14]. The various methods for detection of the LCST include light scattering to recognize the coil-to-globule transition[15], turbidimetric measurements to detect phase separation[16], and differential scanning calorimetry (DSC) to measure the transition heat.[17] The reversibility of this phenomenon by cooling has led to the study of these polymeric materials for their application in drug delivery[18], in separation systems[19], immobilizations of enzymes[20], tissue culture substrates[21], temperature-sensitive coatings[22], flocculating agents, smart catalysts[23] and pervaporation membranes[24], thickeners in food, rheology-controlling substances in coating fluids and latex-based paints,[25] and additives in enhanced oil recovery or water treatment.[26]

Poly(N-isopropylacrylamide) PNIPAAm

Poly(*N*-isopropylacrylamide) PNIPAAm **Figure 3**, which undergoes a reversible thermosensitive-phase transition in aqueous solution, is the most studied water-soluble, thermally sensitive polymer.[27]
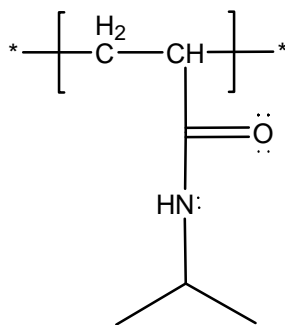
Figure 3. PNIPAAm

The good balance between the hydrophilic and hydrophobic interactions of the polymer give PNIPAAm a sharp transition at a temperature of 33° C.[28] The CONH- groups are hydrophilic and the –CH(CH$_3$)$_2$ groups are hydrophobic. At temperatures below the LCST, the strong H-bonding of the water and the hydrophilic groups outweighs the unfavorable free energy associated with the exposure of the hydrophobic groups to water, leading to good solubility of the polymer. As the temperature increases, the H-bonding between the water molecules and the carbonyl oxygen weakens, while the interactions between the isopropyl side chains improves. When the temperature passes the LCST the interactions between the hydrophobic groups become dominate, leading to a collapsed separation driven by an increase in entropy from the release of structured water around the hydrophobic groups of the polymer even though there is a reduced motional freedom of the polymer.

The Mechanism

The amount of structured water is only a function of temperature, while the phase separation temperature is determined by the relative hydrophilicity of the polymer.[29] The transition temperature is not dependent on the cross-linking density or polymer concentration and is close to the so-called Θ temperature, i.e. the temperature at which the osmotic pressure becomes zero.[30] Raising the temperature of an aqueous PNIPAAm solution above the LCST causes a coil-to-globule transition, followed by a phase separation which indicates a two step mechanism for the phase separation.[31] Through the use of techniques which probe molecular scale distances, such as static and dynamic light scattering[32] it has been ascertained that the phase separation of PNIPAM occurs in two steps: (1) the collapse of individual polymer chains from an extended coil into a globule and (2) the aggregation of the globules which triggers macroscopic phase separation.[1]

Tuning the LCST

A requirement for the different applications of the polymers is the ability to precisely tune the LCST. The LCST of PNIPAAm has been changed by adding co-solvents[33], salts[34], surfactants[35] or polyelectrolytes[26] in aqueous solutions. These studies help to understand the fundamental aspects of the LCST of PNIPAAm, but from a materials-development point of view, the incorporation of co-monomers or chemical modification of the PNIPAAm backbone is the most useful way to control the LCST.

Copolymerization of PNIPAAm

The LCST of PNIPAAm can be altered by incorporation of a co-monomer during the polymerization process. If a hydrophobic co-monomer is added, the LCST will decrease and if a hydrophilic co-monomer is added the LCST will increase.[27] A co-monomer that introduces intermolecular or intramolecular H-bonding is a hydrophobic contribution to the LCST. The introduction of co-monomers with ionizable groups, such as carboxylic acids or tertiary amines, is useful because their hydrophobicity or hydrophilicity can be modified by changes in the pH of the water since the degree of ionization is pH dependent leading to a pH-tunable LCST.[28]

A cross-linked polymer gel bearing weakly acidic or weakly basic pendant groups absorbs water to an extent that depends on the ionic composition of the gel. If the temperature sensitive gel contains acidic pendant groups, the swelling increases as the pH of the solution increases. Similarly, a weakly basic temperature-sensitive gel expands as the pH of the solution decreases. PNIPAAm and poly(acrylic acid) (pAAc) have characteristic temperature- and pH-sensitivity, respectively. Therefore, in a P(NIPAAm-co-AAc) hydrogel, where PAAc is introduced as a pH-sensitive component, the PNIPAAm will have both pH- and temperature-sensitivity.[36]

The random copolymerization of NIPAAm with the ionic monomer acrylic acid (AAc) shows a different LCST than PNIPAAm depending on the pH environment.[37] At low pH, 2.0-3.0, the hydrophilic/hydrophobic balance becomes the major factor since the dissociation of the carboxylic acid is inhibited by the presence of the counterion (H^+). Therefore the LCST of the P(NIPAAm-co-AAc) appears lower than that of PNIPAAm

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because more intra- and intermolecular hydrogen bonding between the amide group of PNIPAAm and the carboxylic acid group of PAAc occurs which increases the hydrophobicity of the polymer. This hydrogen bonding interferes with the access of water to the NIPAAm amide groups. On the other hand, the cloud point temperatures of PNIPAAm in the solution increase with AAc content in the copolymer around pH 4.0 because of the increased hydrophilicity resulting from ionized AAc components.[38] This phenomenon is mainly due to the strong electrostatic repulsive interactions introduced by charged AAc comonomers and the osmotic pressure by the counter ions.

In a poor solvent the polymer-polymer attractive interaction becomes strong which tends to make the gel shrink. However, a shrinking process gives rise to a tremendous decrease in the translational entropy of the counter ions because of the localization of ions needed to maintain the electroneutrality. Therefore, the network tends to maintain its volume by balancing the loss of entropy from the electrostatic interaction by generating concentration fluctuations. The solvent molecules are repelled from the neutral parts of the network and tend to locate near the charged groups. Then the region near the charged groups swells locally so as to maintain the entire volume of the network, leading to tremendous concentration fluctuations in the system. This situation lasts until the hydrophobic interaction dominates the electrostatic interaction and a macroscopic shrinking transition takes place.[30] LCST exists until the AAc unit can remain soluble while offsetting the aggregation caused by the hydrophobic effect of the temperature-sensitive unit.[39] Once the pH is raised above the pK of the acid groups, ionizing them to the carboxylate, the charged copolymers disrupt the complex and consequently have no ability to aggregate and therefore remain completely soluble.

Varying the Alkyl Chain Length

When temperature and pH sensitive polymers were prepared by the copolymerization of NIPAAm with varying amounts of acrylamide derivatives bearing carboxylic groups attached to different length aliphatic chain lengths (C_nAAm) in the comonomer, the hydrophobicity of the open carbon chain dominated the hydrophilicity of the carboxylic group and the LCST decreased with increasing number of carbons.[45] The one exception was the C_2AAm copolymer. For the C_2AAm copolymers an increasing amount of co-monomer led to a higher LCST indicating that the co-monomer is more hydrophilic.

Since, the LCST depends on the pK_a of the polymer, at a constant solution pH the degree of the ionization of the carboxylic acid will increase with increasing basicity of the polymer. Hoffman copolymerized PNIPAAM using the longer alkyl segment monomers propylacrylic acid and butylacrylic acid[40] which increased the pK_a and as a result increased the temperature at which the phase transition occurred.

Varying the pH

The effect of AAc content on cloud point, for random and graft copolymers of NIPAAm and AAc at pHs above and below the pH of AAc (7.4) was investigated and it could be seen that the CP of the random copolymer is always higher than the CP of the PNIPAAm homopolymer and rapidly rises as the AAc content increases. In contrast, the graft copolymers show a constant CP at either pH, independent of AAc content over a wide range of compositions. This constancy of CP over a broad composition range (especially above the pH of 7.4) is a clear demonstration of the significant difference in

the behavior between the random and graft copolymers. The higher CPs of the random copolymers, with higher AAc contents, at low pH are simply due to the hydrophilic character of the AAc monomer units along the backbone. At the same low pH, the graft copolymers show a much lower CP than homo-PNIPAAm. This is probably due to the efficient formation of hydrogen bonds between relatively long sequences of PNIPAAm and PAAc. The hydrogen bonding interferes with the access of water molecules to the NIPAAm amide groups, thus rendering the graft chains of PNIPAAm more hydrophobic, lowering their phase-separation temperature. Based on this mechanism, the CP should be insensitive to the AAc content of the graft copolymer.[41]

Formation of Micelles

Hydrophobically modified PNIPAAm copolymers form, in cold water, discrete microdomains consisting of several polymer chains "stuck" together through their hydrophobic substituents. Entities are depicted as multipolymeric aggregates consisting of a hydrophobic core which brings together the alkyl groups, surrounded by a shell made up of poly(*N*-iospropylamide) chains. The structure and properties of polymeric micelles formed in aqueous solutions of neutral amphiphilic copolymers are controlled by a delicate balance between opposing forces. The reduction in free energy when the hydrophobic side chains minimize their interface with water molecules is considered the driving force for micelle formation. The unfavorable residual contacts between water molecules in the shell region of the structures and the surface of the hydrophobic core and the organizing of several polymer chains into close proximity are the forces that oppose the formation of micelles. In the polymer rich phase that separates from solutions

at temperatures above the LCST, the original core is destroyed and the hydrophobic groups are released as isolated entities. Hydrophobic microdomains may still exist, but their structure is quite different; the alkyl groups are mostly separated from each other, although a few pairs may remain in close proximity. The collapsed polymer chains, divested of the layers of structured water molecules, provide a nonpolar environment in which hydrophobic groups are dissolved at random and kept protected by surrounding water. Upon cooling below the LCST, the collapsed polymer main chains recover their expanded conformation. To minimize contact with water, the hydrophobic side chains re-associate. This triggers the formation of hydrophobic microdomains with a gross architecture identical to the original structure. Most intriguing is the observation that the same level of intermixing exists in the cooled solutions. Further heating/cooling treatments are also ineffective in achieving any changes in intermixing. Hence, above the LCST the separated and still swollen polymer phase provides a fluid medium in which polymer chains are free to move and intermix at random. This observation may argue in favor of a transition from spherical micellar structures in cold water into longer cylindrical structures above the LCST, a mechanism proposed in the case of poly(ethylene oxide) derivatives above their LCST. Important issues on the architecture of the aggregates still remain unanswered. They concern, for example, the changes in aggregate morphology during the heat induced phase separation process and the stability of the aggregate morphology during aging of solutions below and above their cloud point. Other questions arise too on the influence on the aggregate morphology and stability of parameters such as length of the alkyl substituent, the degree of copolymer substitution, and the distribution of the alkyl groups along the polymer backbone. [1]

In Taylor and Cerankowsi's classic study of the LCST of water-soluble polymers they proposed, as a general rule, that the LCST should decrease with increasing hydrophobicity of the polymer.[6] Therefore, the LCST of amphiphilic PNIPAAm was anticipated to decrease with increasing *n*-alkyl chain length and for a constant chain length, with increasing *N*-alkylacrylamide content. This lowering of the LCST was observed for copolymers containing C_{10} and C_{14} alkyl chains. Surprisingly, this trend is reversed in the C_{18} containing polymers such that they have a lower LCST than PNIPAAm, but higher than the C_{14} containing polymers. This unusual behavior suggests that in solutions of the C_{18} substituted copolymer the alkyl chains are not exposed to water but instead form a micellar structure protected from the water by the PNIPAAm chains and as a result do not make a hydrophobic contribution to the LCST.[42]

Whether the micelles are intramolecular or involve the aggregation of several alkyl chains has not been determined. Above the LCST a polymer-rich phase forms where the PNIPAAm chains collapse and aggregate on the surface of the micellar core causing the disruption of the alkyl chains as separate entities.[6] This results in a macroscopic phase separation. From the calculated polydispersity values it is apparent that there is a broad distribution of micelle sizes. The sizes were not dependent on changes in temperature below the LCST, but significant aggregation above this temperature makes any measurements unreliable. The micelle size is dictated primarily by the action of two competing forces: (1) the hydrophobic forces[42] on the alkyl groups caused by the water which causes them to aggregate in the center and (2) the excluded-volume repulsion between the polymers which limits the aggregate size.

Polymerization Effects on Cloud Point

In addition to the comonomer composition, the comonomer distribution also has a large effect on the LCST behavior of an *N*-isopropylacrylamide based copolymer. A large displacement of the LCST results from a low fraction of comonomer for a random copolymer.[43] The LCST will be affected by the degree of uninterrupted lengths of the backbone and the swelling behavior will be influenced by the charge concentration at a particular location.[3] The behavior at the LCST is also influenced by the molecular weight and polydispersity index. Well-defined polymers (low polydispersity indices) synthesized by controlled radical polymerization show a much sharper LCST transition in comparison to ill-defined polymers that were prepared by free radical polymerization.[44]

Alkyl Groups vs Ions

The higher molecular weight component of PNIPAAm had associated with it a lower transition temperature.[34] Weaker and broader phase transitions are also found as the hydrophilicity of the polymer improves, since the polymer chains are better solvated, and the solvent is more strongly bound and as a result less water is released during the chain collapse. Also, since there is a random distribution of the comonomer units compared to the homopolymer, the water bound to the polymer chain has a slightly different structure that leads to a broader distribution of the transition temperature.[8]

When nonionic monomers containing long alkyl chains, such as octadecyl groups, were copolymerized with NIPAM there exhibited solubility problems since there is a decline in LCST due to an increase in polymer hydrophobicity. The incorporation of these groups is generally limited to up to 5 molar percent in order to remain soluble in

water. Bokias and coworkers performed a study where the copolymers contained equal amounts of alkyl groups and charged species where each charge was linked to the alkyl group. This competition between these two characteristics presented an interesting phase behavior in water. When the amount of charged octyl units in the copolymer increased the CP shifted to a higher temperature. This shows that the hydrophilic character of the charges is not over-taken by the hydrophobic nature of the octyl groups. As a result, the CP of these copolymers increases as the number of octyl groups increases. A different behavior was displayed when the modification took place with dodecyl groups. The dodecyl groups provided enough hydrophobic character to overcome the hydrophilic nature of the charges. In this case a decrease in LCST was observed as the dodecyl content increased. The hydrophobically modified charged polymers did not form two well-separated phases, even at temperatures much higher than the CP, but rather formed turbid suspensions, stable for several hours. These suspensions are probably stabilized by the charged units of the polymer.

A remarkable observation is that the turbidity of the C_{12} charged alkyl group above the LCST is lower than that of the C_8 derivatives, and the turbidity appeared to decrease with increasing alkyl content. The onset of the turbidity followed the expected order, but the turbidity at higher temperatures was progressively less intense as the length of the alkyl group increased. A possible explanation for this surprising turbidity behavior is the self assembly of the alkyl groups in aqueous solutions; micellar-like structures protected by the charged groups. The formation of micelles in nonionic hydrophobically modified copolymers of PNIPAAm has been demonstrated in solutions below the LCST and these structures are disrupted at temperatures above the LCST resulting in a phase separation

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similar to the homopolymer. The charge in these polymers seems to stabilize the formed

micelle structures and prevent the full collapse of the polymer chains and the formation

of the polymer-rich phase by keeping the mixed aggregates of the alkyl groups and

NIPAM segments in the center while the charges are on the surface. The repulsive

electrostatic interactions, between the charges, prevent the system from phase separating.

These amphiphilic units of the copolymer act in a way similar to the effect of added

surfactant. It is well known that PNIPAAm interacts with surfactants, such as sodium

dodecyl sulfate.[45]

Role of Surfactants

A series of sodium *n*-alkyl sulfates of alkyl chain lengths (*n*) in the range of 1-16

in aqueous mixtures of PNIPAAm were examined to determine the effects of the

surfactant on the LCST. The sulfate derivatives of 4 carbons or less did not form micelles

and decreased the LCST of PNIPAAm solutions. Surfactants of chain length (*n* = 5-10)

also lowered the LCST at low concentrations, but at concentrations that exceeded the

critical aggregation concentration (CAC) the phase transition temperature was elevated

and the concentration of surfactant needed to precipitate the polymer increased with

decreasing *n*. For (n > 10) the trend became more apparent as the length of the surfactant

tail increased. The precipitated aggregates formed in solution concentrations 1 order of

magnitude lower than the critical micelle concentration (CMC) of sodium *n*-dodecyl

sulfate in water. The precipitated particle sizes were smallest in surfactant solutions of the

longest alkyl chain length. The addition of a surfactant to the PNIPAAm mixture results

in changing the conformation of the polymer due to binding of anionic surfactant

micelles which gives the polymer polyelectrolyte character. Once attached, intermicellar repulsions caused by charged surfactant aggregates along the polymer chain retard intermolecular aggregation which opposes polymer collapse and aggregation while enhancing polymer solubility.[46] The spacing of the surfactants is determined by an interplay between their coulombic repulsions and their ability to bind to the polymer chain[47] which occurs around 60Å. When the polymer is saturated with surfactant micelles any additional increase in surfactant concentration will cause the formation of free micelles which will behave like salts and lower the LCST. Above the LCST of PNIPAAm two different structures of the comixture have been found depending on the surfactant concentration. At high concentrations SDS micelles bind to the individual macromolecule and solubilize them. At low surfactant concentrations the macromolecules collapse to form small colloidal particles which are not stabilized by the surfactant. These micelles do not connect to each other and therefore do not form gels indicating that a micelle can not be shared by two macromolecules.[48]

Effects of Salts

Since the transition of thermoresponsive polymers occurs by the dehydration of the polymer and the strengthening of hydrophobic interactions among side chains, which is related to the structural deformation of water around the alkyl groups, the effects of salts on the transition temperature on aqueous polymer solutions could be related to many possible factors that are included in these processes. These factors may include their effects on the polymer backbone, the direct interactions of salt ions with the side chain polar groups (such as amide or carboxyl) and the effects on the hydrogen bonding of

water. Salting-in ions are considered to break the structure and consequently stabilize hydrophobic interactions. On the other hand, salting-out anions are known as structure makers for water and as a result promote hydrophobic interactions among side chains and in the process induce the formation of the globular structures of the polymer.[49]

When PNIPAAm is dissolved in water it is surrounded by an extended hydration sheath where water has lost its normal structure. The addition of salts to aqueous PNIPAAm solutions alters the properties of the hydration layer and can cause a disruption of the highly oriented water molecules which surround the polymer. This increases the hydrophobic character of the PNIPAAm chains, resulting in a lower LCST. The type and concentration of ions will affect the degree of destruction to the hydration sheath in the case of salting out ions or strengthening in the case of salting in ions.[50]

The salt effects on the LCST of PNIPAAm have been reported and are related to the Hofmeister series. The relationship between the Hofmeister series and thermally responsive polymers can be explained on the basis of direct interactions of the anions with the macromolecule and its adjacent hydration shell. The phase transition of the polymer proceeds through separate mechanisms depending on the capacity of the ion to "make" or "break" water structure. Ions that make water structures are $CO_3^{2-} > SO_4^{2-} >$ $S_2O_3^{2-} > H_2PO_4^- > F^- > Cl^- > Br^-$ and ions that break water structures are $NO_3^- > I^- >$ $ClO_4^- > SCN$. The effects of the Hofmeister anions on the solvation of PNIPAAm can be explained by three different interactions of the ions with the polymer and its hydration waters.

First, the anions that "make" water structures can polarize a water molecule that is involved in hydrogen bonding with the amide and enhance the hydrophobic interaction.

The highly charged F^- and Cl^- ions are examples of water structure makers. Second, the anions that "break" water structures destabilize the hydrophobic hydration of the polymer by increasing the surface tension of the water/hydrophobic interface which causes the removal of the hydrophobic hydration waters from the backbone and isopropyl side chain and stabilizes the hydrophobic interactions. A large ion such as I^- is classified as a water structure breaker. Third, most weakly hydrated anions may bind directly to the polymer driven by a favorably change in the enthalpy from the anion-polymer interaction. The first and second of these effects should lead to a lowering of the LCST by a salting out of the polymer. The third effect should lead to a salting in of the polymer.[51]

The major contribution towards ΔH is the breakage of hydrogen bonds from the water molecules surrounding the hydrophobic groups of the polymer chains.[5] Under normal circumstances an increasing phase temperature would reduce ΔH because there are fewer hydrogen bonds at higher temperatures. However, the relationship between ΔH and the phase transition temperature is different for polymer solutions containing salts than for solutions without ions. In the case of solutions containing ions the lowering of the phase transition temperature is associated with a reduction in the ΔH of solution. This is a result of the dissociated ions ability to subtract water molecules from the polymer chain and strengthen hydrophobic interactions, which stabilize the globular conformation of the polymer and lower the transition temperature. Ions have effects not only on the hydration states of the macromolecules but also on the structure of bulk water. A portion of the water molecules that are removed from the polymer upon the phase transition will contribute to hydrating these ions, accompany exothermic heat and help to reduce the endothermic heat of the transition as a whole.

Sodium salts of the more weakly hydrated anions were found to lower the LCST by increasing the surface tension between the hydrophobic portions of the polymer (isopropyl group and the hydrocarbon backbone) and the adjacent hydration waters. On the other hand, the strongly hydrated ions were found to weaken the hydrogen bonding between the pendent amide group and the attached hydration waters by a polarization effect. The phase transition took place in two steps. The first was associated with the disassociation of hydrogen bonding to the amide, while the second involved the loss of the hydrophobically hydrating water molecules.[52]

When six kinds of tetraalkylammonium bromides were added to an aqueous solution of PNIPAAm the observed cloud points varied. According to the relationship between "structure makers" and the cloud point of inorganic salts, the addition of tetraalkyammonium salts might be expected to lower the transition temperature of PNIPAAm solution but experimental results did not confirm this expectation. When the salt containing no alkyl groups (NH_4-Br) was added the transition temperature was lowered and the salts containing a longer alkyl chain (CH_3-C_3H_7) lowered the temperature at which the phase transition took place. However, the LCST was raised for the alkyl groups (C_4H_9, C_5H_{11}).

The kind of interaction between the alkyl chain of the salts and the polymer networks might explain these results. The hydrophobic character of the alkyl groups probably induces a hydrophobic interaction with the isopropyl groups in the polymer segments. In addition, the hydrophobicity is known to promote the attaching of ions to the polymer segments. These ions will behave like fixed charges on the network,

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eventually raising the transition temperature.[53] This kind of behavior can be seen in a PNIPAAm-surfactant system.[54]

Hydrogels, which have been defined as cross-linked hydrophilic polymer networks, show different equilibrium degrees of swelling in response to various kinds of salts as well as their concentrations. Even though nonionic gels demonstrate the salting out (or salting in) effects, they normally bring about a far weaker salt-induced swelling change compared to the ionic gels since in nonionic polymers, salt will not lead to an abrupt change in the solubility at a "critical" concentration, because it is believed that increasing the salt concentration gradually changes either ion–dipole interactions between the ion and the polar group in the polymer or the water structure associated with the nonpolar group. When the polymer is crossed-linked and formed into a gel, the change in solubility (or change in viscosity) in the salt solution is reflected in the equilibrium swelling degree of the gel. A decreased swelling degree indicates a decrease in solubility (or viscosity). When the critical concentration of sodium chloride, at which the gel phase transition occurs, is plotted against temperature there is a good linear relationship between the two, indicating that a smaller amount of sodium chloride is needed for the phase transition as the temperature increases. A very similar behavior can be seen for un-crossed-linked poly(NIPAAm). Its LCST decreases as the concentration of sodium chloride increases. These results suggest that un-cross-linked and cross-linked polymers have the same LCST regardless of their physical state in solution.[55]

As we increase the concentration of a univalent salt (i.e., NaCl) in a neutral containing gel with a fixed acrylic acid content, the H^+ ions in the gel will be exchanged for the salt cation. The increased production of free counter ions produced by the

dissociation of the acrylic acid will cause the ion swelling pressure to increase. When the acrylic acid is completely dissociated, any further increase of salt concentration will reduce the ion swelling pressure as in a gel at high pH. It is of no consequence if the anion involved is OH⁻ or Cl⁻. In solutions of a uni-bivalent salt such as $MgCl_2$ the same swelling behavior should occur but with only half as much of the divalent cation Mg^{2+} being needed to maintain the charge balance in a gel with completely dissociated acid groups.[56]

Effects of Cosolvents

By using solvent mixtures with various compositions, the volume transition behavior based on the interaction between polymer and solvent molecules can be better understood. In a study by Hirotsu and co-workers, the solvents used were water, methanol, ethanol, *n*-propanol, and mixtures of water and alcohols. Additives such as alcohols tend to weaken hydrophobic hydration, resulting in the promotion of hydrophobic interactions. As the number of carbons in the alcohol increased while maintaining a constant concentration the greater was the shift in transition temperature. The simplest way to treat the interaction between polymer and solvent molecules in a mixed solvent is the "single liquid approximation (SLA)". In SLA a mixed solvent is treated as a homogeneous liquid having average thermodynamic properties. The difference in the behavior between NIPA gels immersed in water compared to alcohols is reflected in the thermodynamic parameters describing the interaction between solvent molecules and IPA segments. The values of ΔH in NIPA/water are two orders of magnitude larger than those in NIPA/alcohol systems (-130 x 10^{-15} erg Vs -1.5 x 10^{-15}

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erg) and also ΔS in the NIPA/water is several times more negative (-4.5 x 10^{-15} erg Vs -1.5 x 10^{-15} erg). A large absolute value of ΔH is indicative of a strong temperature dependence. The large negative value of ΔH shows that there is a strong association between water molecules and hydrophilic groups in NIPA. Specifically, a hydrogen bond formation between water molecules and –NH and –C=O groups in NIPA is taking place. A more positive ΔS for the alcohol is a result of the reduced hydrogen bonding in the vicinity of IPA segments. When small amounts of DMSO were added the transition temperature was lowered and the transition heat was changed. DMSO is an aprotic solvent and therefore interacts with water molecules differently than alcohols. The hydrated water molecules may be replaced with DMSO molecules and as a result decreases the transition heat.[57]

Project at Hand

The commercially available polymer polyethyleneimine (PEI) with a molecular weight of 25,000 g/mol and composed of primary, secondary, and tertiary amino groups in a ratio of 1:2:1[58] linked by ethylene units was obtained from BASF and utilized as the starting material for this project. The main purpose of this project was to tailor the hydrophilic and hydrophobic balance of the material and, in turn the cloud points or lower critical solution temperature, LCST, by first increasing the hydrophobicity of the polymer by alkylating the primary amines with an *n*-alkyl group ranging from *n* = 4-6,10,12 followed by propoxylating the remaining reactive primary and secondary amines with propylene oxide. A restriction on the final product was that it had to have a cloud point near or above 60 °C. The hydrophobicity and lower critical solution temperature of

the polymer were both affected by the length of the alkyl chain and the percent modification of both the alkyl group and the 2-hydroxypropyl group.

Another approach taken was to begin with ethoxylated polyethyleneimine (EPI) with 80% of the amines ethoxylated. The hydrophobicity of EPI was increased by first deprotonating 7% of the 2-hydroxyethyl ($-CH_2CH_2OH$) groups followed by alkylating the resulting alkoxide ions with an appropriate alkyl bromide such as penty, hexyl, or decyl (only 3 % modification). The ethers were used to give the polymer the hydrophobic component while the 2-hydroxyethyl groups simulated the role of the propylene oxide in the synthesis involving PEI. These synthesized samples had no cloud point up to 100°C. An alkylated PEI was also reacted with 1-Bromoethanol to provide a product with a 2-hydroxypropyl group while avoiding the use of propylene oxide or drying EPI. This product also had no cloud point up to 100°C.

Nine different classes of modified PEI were studied which included: 1) Butylated/Propoxylated Polyethyleneimines (B_uP-PEI), 2) Pentylated/Propoxylated Polyethyleneimines (P_nP-PEI), 3) Hexylated/Propoxylated Polyethyleneimines (H_xP-PEI), 4) Decylated/Propoxylated Polyethyleneimines (D_cP-PEI), 5) Dodecylated/Propoxylated Polyethyleneimines (D_dP-PEI), 6) Pentylated Ethoxylated Polyethyleneimine (P_n-EPI), 7) Hexylated Ethoxylated Polyethyleneimine (H_x-EPI), 8) Decylated Ethoxylated Polyethyleneimine (D_c-EPI), and 9) Hexylated/Ethoxylated PEI (HxE-PEI).

2. Results and Discussion

A. Synthesis and Characterizations of Pentylated/Propoxylated Polyethyleneimines (P_nP-PEI)

Commercially available polyethylenemine (PEI) was obtained from BASF and used as the starting material for all of the alkylation and propoxylation modifications. The first modification of the PEI to take place was a 7% pentylation (**Scheme 1**) followed by a 68% propoxylation **(Scheme 2)**. To alkylate the PEI with a pentyl group the PEI was first dissolved in THF using at 10% (wt/vol) concentration at a temperature of 65°C. A 7% molar amount of 1-bromopentane (based on the number of moles of average repeat units, 43.03 g/mol) was used as the alkylating agent in a reaction that involved the nucleophilic displacement of the bromide in a typical S_n2 reaction using the lone pair of electrons on nitrogen. The Br^- leaving group formed a salt with the resulting ammonium ion, which was converted to NaBr and water with the addition of a stoichiometric amount of NaOH dissolved in a 10% (wt/vol) concentration of MeOH. The resulting NaBr salts were highly soluble (approximately 90% remained) and the resulting solution was not easily filtered, thus only the salts which appeared were removed by decanting the solution. The THF was removed by vacuum and the alkylated product was dissolved in EtOH at a 10% (wt/vol) concentration.
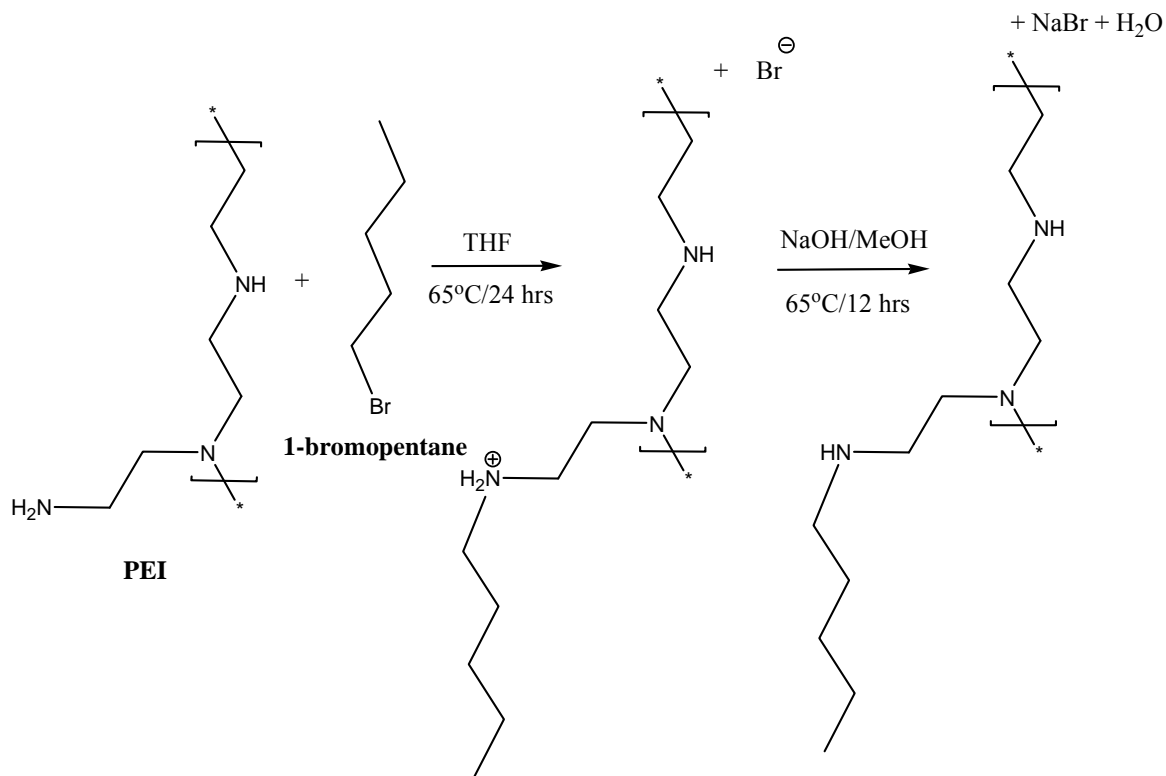
Scheme 1. Synthesis of Pentylated Polyethyleneimine, P_n-PEI

The propoxylating reaction took place in a Parr-reactor at 60°C using a 68% molar amount of propylene oxide. Attack of the lone pair of electrons on the nitrogen atom at the less sterically hindered side of the propylene oxide opened the epoxide ring and the resulting alkoxide deprotonated the concurrently formed cationic quaternary amine, thus forming a 2-hydroxypropyl functional group. In a subsequent 7% pentyl and 65% propoxyl modification the propylene oxide was added in four equal portions in an attempt to avoid the formation of short (polypropylene oxide) chains resulting from the attack of the alkoxide on any remaining propylene oxide. If this was occurring, it was considered that the cloud point would be lower since polypropylene oxide chains have a poorer affinity for water than isopropanol. After comparing the cloud point temperatures of two sets of alkylations and propoxylations while introducing the

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propylene oxide by both regular addition and batch wise addition it was found that the cloud point was not significantly affected by the incremental addition of propylene oxide and therefore all subsequent propoxylations took place by regular addition.
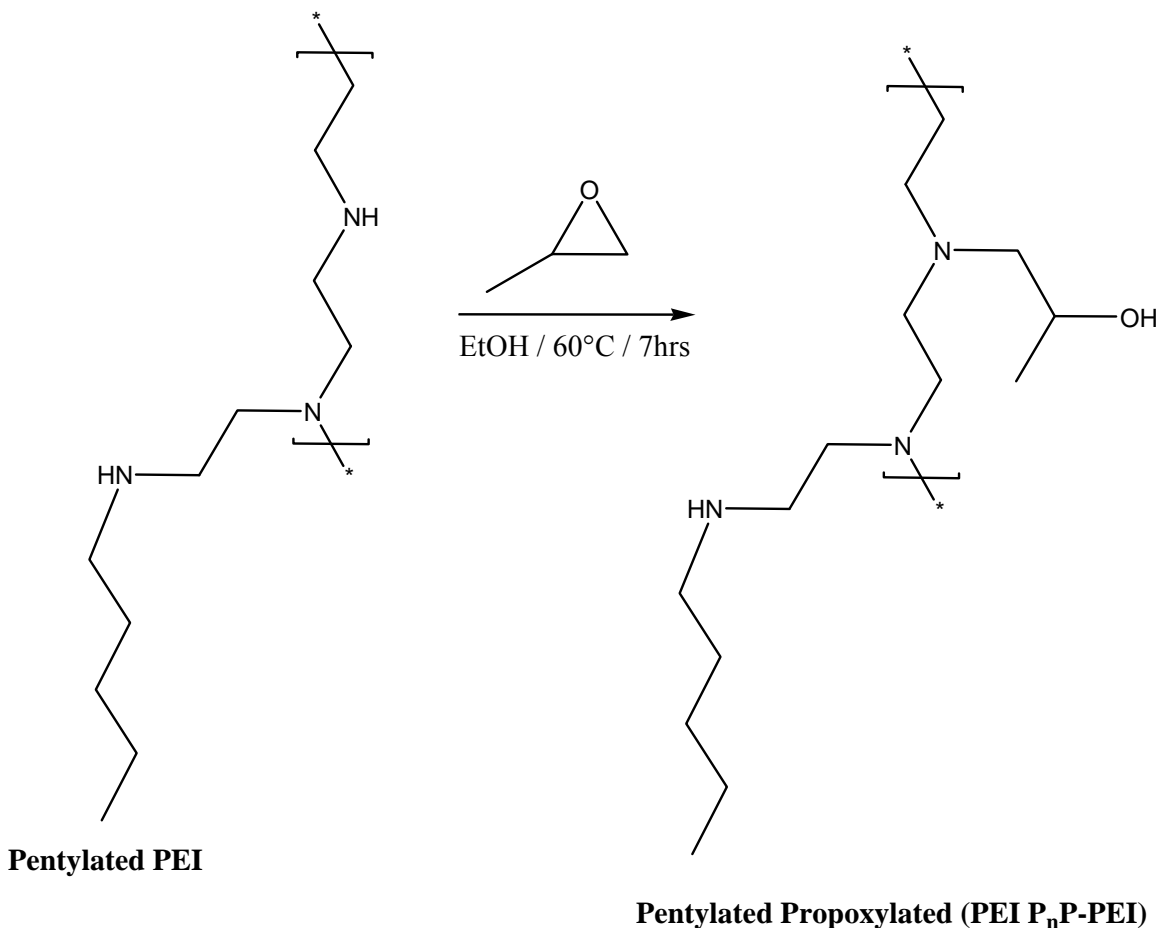
Scheme 2. Propoxylation Step of Pentylated Polyethyleneimine

Upon completion of the propoxylation reaction the ethanol was removed and the product was placed into dialysis tubing with a molecular weight cut off of 12 to 14,000 Daltons for twenty four hours in water to remove the NaBr salts and any remaining ethanol and THF. It was later determined, from a subsequent alkylation and propoxylation reaction, that six hours of dialysis was the optimal dialysis time for

removing the salts and low molecular weight compounds while avoiding unnecessary losses of the desired product. The percent modification determined by NMR was 7.6% pentylation and 77% propoxylation. The cloud point for this modified PEI was 65°C at a 2% weight concentration. An overlay of the ^{1}H NMR spectra of PEI, pentylated PEI and pentylated-propoxylated PEI (P_nP-PEI) is shown in **Figure 4.**
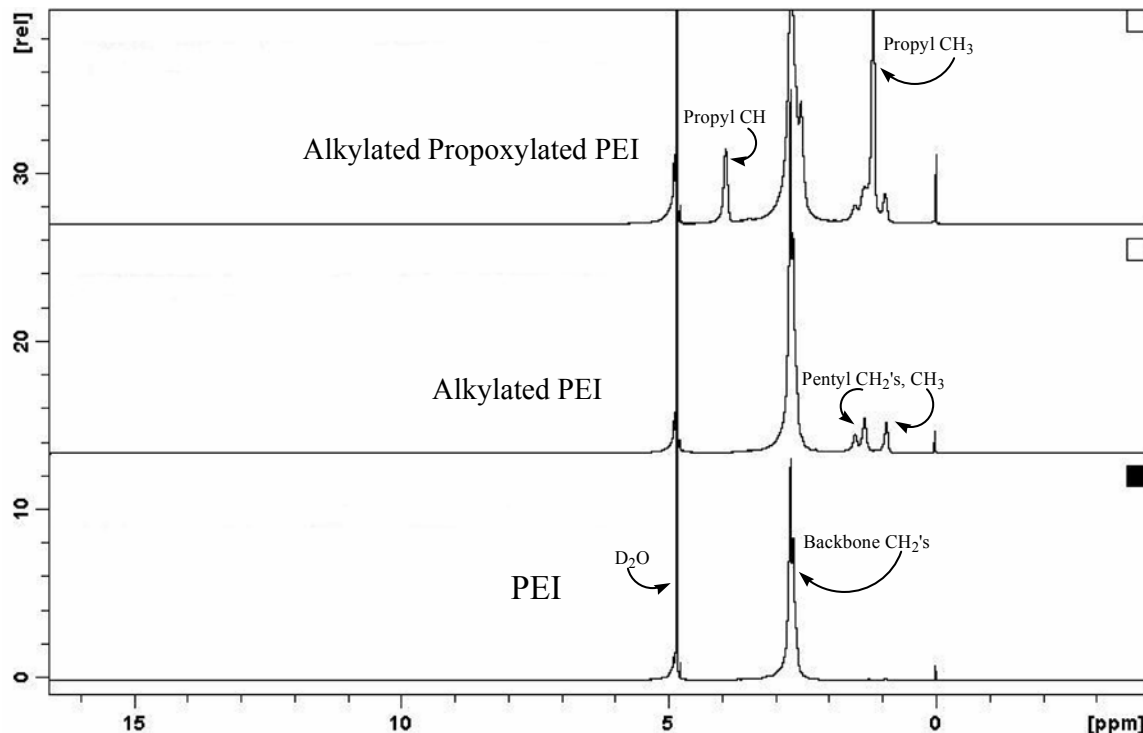
Figure 4. 300 MHz NMR of PEI, Pentylated PEI and Pentylated-Propoxylated PEI (P_nP-PEI) in D_2O

The alkylations and propoxylations with their percent modifications to follow are enumerated in **Table 1** with their cloud points, molecular weights, polydispersity index and pH.

Table 1. Modification of PEI with Cloud Points

Modification	Cloud Point (°C)	Mw	PDI	pH
7%Butyl-65%Propyl	62	9,000	5.3	9.50
7.4%Pentyl-85%Propyl	52	12,600	4.8	9.66
6.5%Pentyl-72%Propyl	59	7,900	6.8	10.12
7.1%Pentyl-69%Propyl	62	8,100	6.1	8.91
8.5%Pentyl-64%Propyl	63	8,600	4.9	9.99
7.6%Pentyl-77%Propyl	65	9,000	3.6	9.15
8.4%Pentyl-69%Propyl (PEI-P)	67	21,000	9.0	8.91
15.8%Hexyl-80%Propy	41	18,800	2.8	9.41
9.5%Hexyl-74%Propyl	50	11,900	5.6	9.17
8.1%Hexyl-71%Propyl	52	16,600	4.4	9.16
7.8%Hexyl-72%Propy	57	6,400	4.4	9.12
5.9%Hexyl-69%Propyl	59	6,900	4.3	9.63
8.1%Hexyl-81%Propyl	63	8,300	3.5	9.00
6.4%Hexyl-69%Propyl	65	8,500	5.2	9.11
3.8%Decyl-76%Propyl	67	10,400	5.2	9.86
3.5%Decyl-75%Propyl	72	7,700	5.8	9.61
3.4%Decyl-73%Propyl	74	15,000	4.0	9.17
7%Decyl-81%Propyl	66	10,200	4.1	9.4
4.9%Dodecyl-79%Propyl	66	12,300	4.9	9.81

In order to get some sense of the effects of the alkyl group and the propoxylation level the cloud points of the above alkylation and propoxylation products were plotted against the following: 1) Total number of alkyl carbon atoms, keeping the chain length and the percent propoxylation constant, 2) Alkyl Group, keeping the number of alkyl carbon atoms and the percent propoxylation constant, 3) Number of alkyl carbon atoms, keeping the percent alkylation and the percent propoxylation constant, 4) Percent propoxylation keeping the alkyl group and the percent alkylation constant, and 5) Total number of carbon atoms per OH group.

Figure 5 shows the relationship between the percent alkylations while keeping the chain length constant and the percent propoxylation constant. The percentage of propoxylation was kept constant and the same alkyl group was used so that a comparison

could be made between the percent alkylation and the cloud point. With an increase in the percent alkylation the cloud point decreased for the hexyl and decyl groups. The trends shown by the hexyl and decyl groups were consistent with the anticipated results since there is a greater hydrophobicity associated with an increased number of carbons. It is interesting to note that when a high molecular weight sample of PEI (750,000 Daltons) was compared to the regular PEI (25,000 Daltons), the pentyl alkylation which had the higher percent alkyl modification, 8.4% compared to 7.1%, had a cloud point 5°C higher. This could be caused by a higher ratio of end groups on the lower molecular weight sample. This is opposite to the effects observed by Lee and coworkers who found that lower molecular weight thermoresponsive hyperbranched polymers exhibited higher LCST.[59]
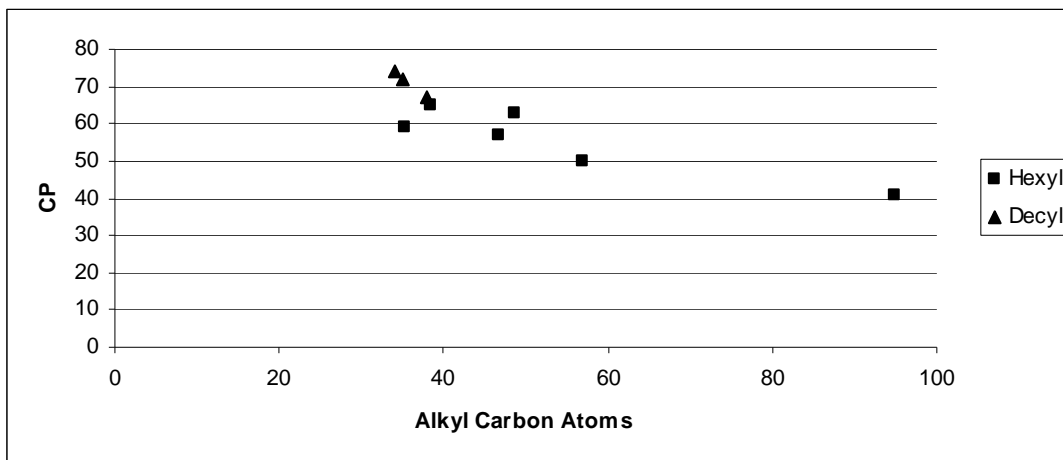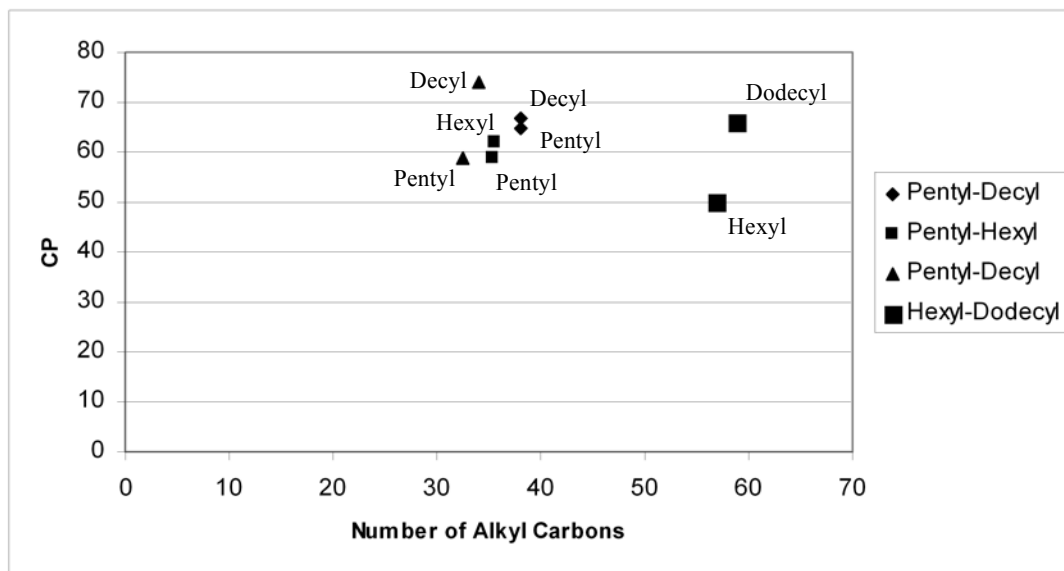

Figure 5. Cloud Point vs Alkyl Carbons, Keeping the Alkyl Group Constant and the Percent Propoxylation Constant

Figure 6 shows the correlation between the percent alkylation and the cloud point while keeping the number of carbon atoms and the percent propoxylation modification constant. In the two plots that have a pentyl group and a decyl group and in the one plot

that has a hexyl group and a dodecyl group the cloud point was higher for the modification which involved the longer chain. However, certain length chains might be forming micelles which would increase the cloud point temperature. This demonstrates that longer chains, above a certain length, will provide an equal (same number of carbons) amount of hydrophobicity while maintaining a higher cloud point.

Figure 6. Cloud Point vs Percent Alkylations, Keeping the Alkyl Group Constant and the Percent Propoxylation Constant

Figure 7 demonstrates how the cloud point varies as the length of the alkyl chain changes while maintaining a constant percent alkylation and propoxylation. The first plot is a contrast between 38 pentyl carbons (7.6% pentyl modification) and 70 decyl carbons (7% decyl modification). The second plot shows the variance between 48.6 hexyl carbons (8.1% hexyl modification) and 70 decyl carbons (7% decyl modification). In both cases the longer decyl chain imparted a higher cloud point despite the fact that it had 46% more carbon atoms when compared to the pentyl group and 31% more carbon atoms when

matched up against the hexyl group. This increased hydrophilicity might be attributable to the formation of micelles. When micelles form the alkyl chains point inwards towards a center leaving the more hydrophilic groups on the surface where the interactions between water and the polymer take place. This enhances solubility and therefore would increase the cloud point temperature.[42]
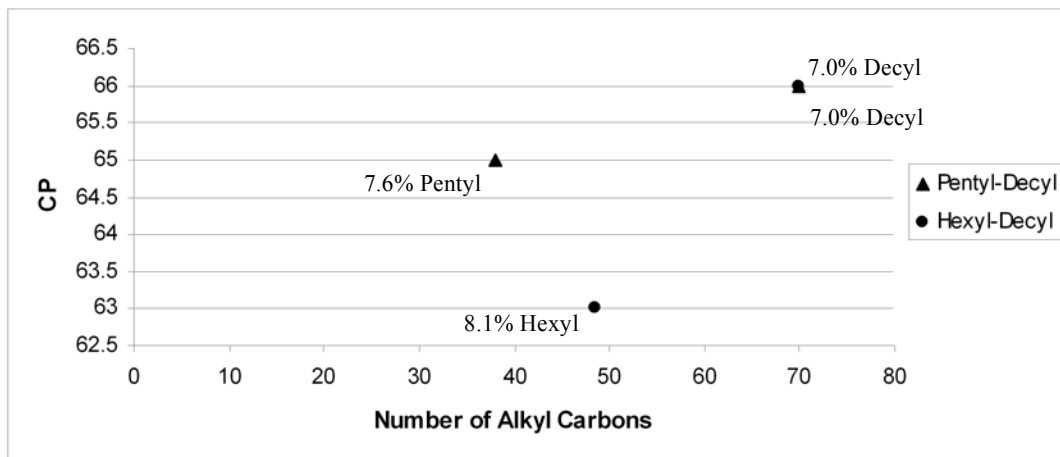

Figure 7. Cloud Point vs Chain Length, Keeping Constant the Percent Alkyl and propyl modification

Figure 8 illustrates the variation in cloud point as the percent modification of the 2-hydroxy propyl group changes while the alkyl group and the percent alkyl modification were kept constant. In the cases of the 7% pentyl, 8% pentyl and 8% hexyl the cloud point increased with an increasing percent propoxylation. This shows that the polymers had an increased affinity for water molecules with an increasing number of 2-hydroxy propyl groups.
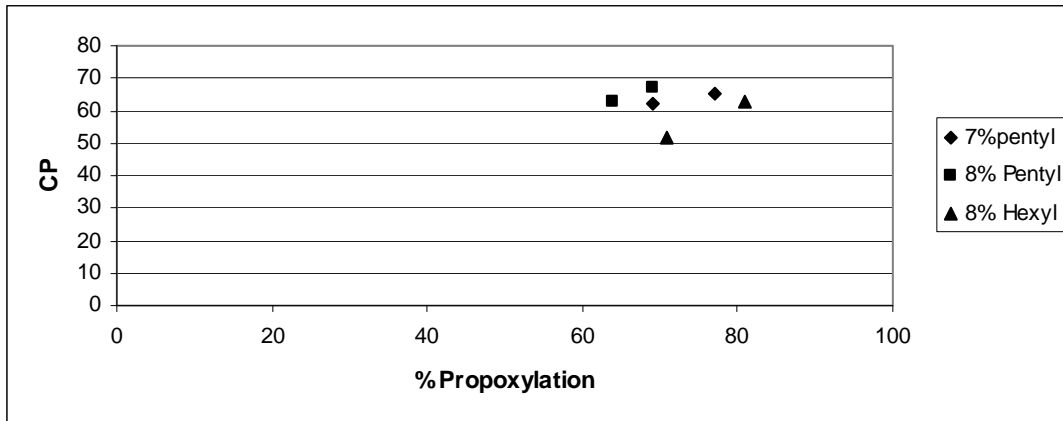
Figure 8. Cloud Point vs Percent Propoxylation, Keeping the Alkyl Group and the Percent Alkylation Constant

Figure 9 exemplifies the effect of the total number of carbon atoms and also the number of OH groups on the cloud point. The downward trend indicates that the cloud point of the polymer solution decreases with an increasing number of carbon atoms relative to the number of hydroxyl groups. This was also concluded from the analysis of Figure 2. The negative slope of the graph also signifies that the cloud point decreases as the number of OH groups decrease. This is consistent with the results of Figure 5.
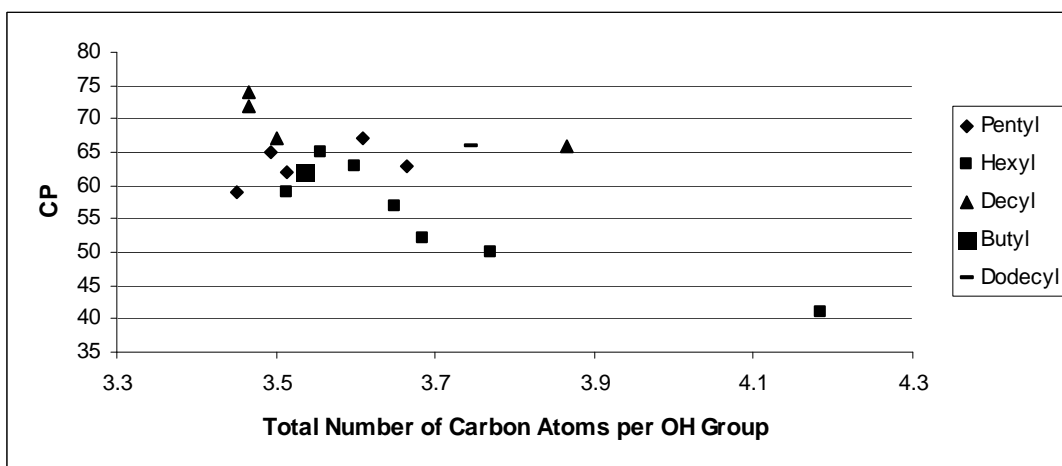
Figure 9. Cloud Point vs Alkyl Carbons per OH Group

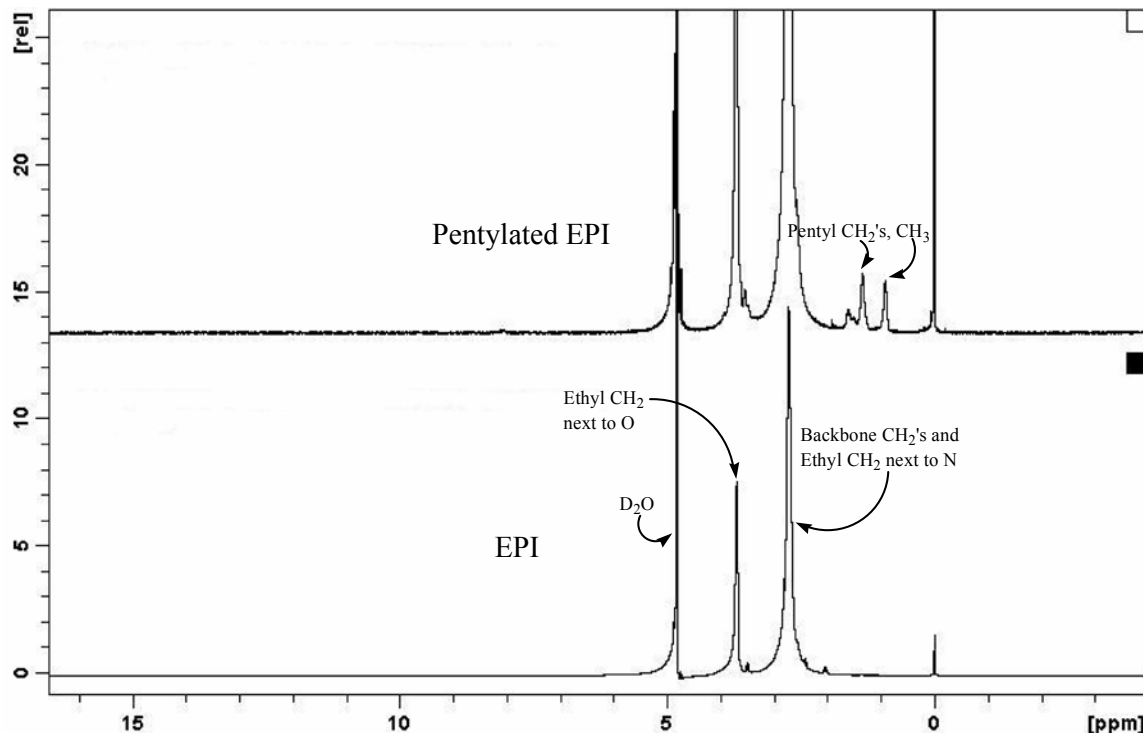# B. Synthesis and Characterizations of Pentylated Ethoxylated Polyethyleneimines

The modification of ethoxylated polyethyleneimines (**Scheme 3)** containing 80 % 2-hydroxyethyl groups began with the removal of 59% water from the EPI by vacuum leaving a residual 6% percent water in the BASF polymer specified as 35% solids and verified by NMR. This remaining water was removed through an azeotropic distillation by first dissolving the EPI in NMP at a 10% (wt/vol) concentration followed by the addition of toluene at a 5% (wt/vol) concentration. After removal of the toluene under reduced pressure, 7% of the hydroxyl groups were deprotonated using the strong base *t*-BuO⁻, over a twelve-hour period, followed by the addition of an equivalent molar amount of 1-bromopentane to alkylate the alkoxide anions for an additional twelve hours. In order to remove the solvents and KBr salts the reaction mixture was placed into dialysis tubing with a molecular weight cut off of 12 to 14,000 Daltons and submerged into water for six hours. The percent modification determined by NMR was 4.9% pentylation with a 81% yield and no cloud point up to 100°C **Table 2**. A NMR of EPI and pentylated EPI can be seen in **Figure 10**.
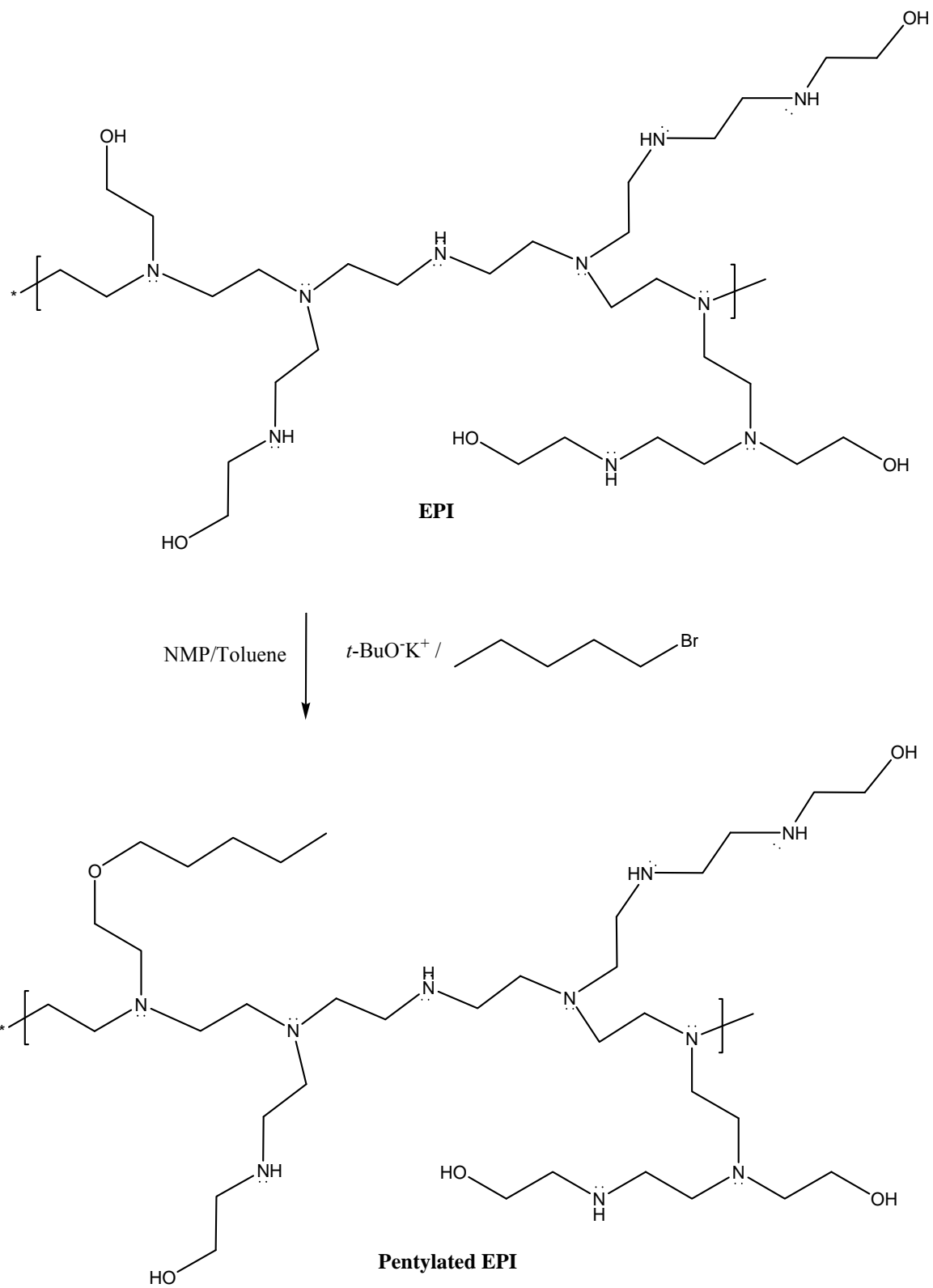
Scheme 3. Deprotonation and Pentylation of EPI

Table 2. Modification of EPI with Cloud Points

Modification	Cloud Point (°C)	Mw	PDI	pH
4.9%Pentyl-EPI	No C.P.	2400	3.7	9.28
8.6%Hexyl-EPI	No C.P.	5400	4.0	9.02
2.3%Decyl-EPI	No C.P.	3500	5.3	9.46
6.4%Pentyl-EPI	No C.P.	5200	4.7	9.06



Figure 10. NMR of EPI and Pentylated EPI

C. Synthesis and Characterizations of the Reaction of

1-Bromoethanol with 7%H-PEI

1-Bromoethanol was reacted with a 7% hexylated PEI **scheme 4** in an attempt to essentially ethoxylate an alkylated PEI without using ethylene oxide. This modified polymer would be analogous to the polymer obtained by reacting an alkylated PEI with ethylene oxide. The procedure involved four additions of bromoethanol with the addition

of a stoichiometric amount of NaOH dissolved in a 10% (wt/vol) concentration of MeOH between each addition of 1-bromoethanol in order to neutralize any ammonium ions formed. After the completion of the reaction the mixture was made clear by a 5% (wt/vol) ether wash which presumably removed any organics and the resulting product had no cloud point up to 100°C. A NMR of hexylated PEI reacted with 1-bromoethanol is shown in **Figure 11** in an overlay with EPI.
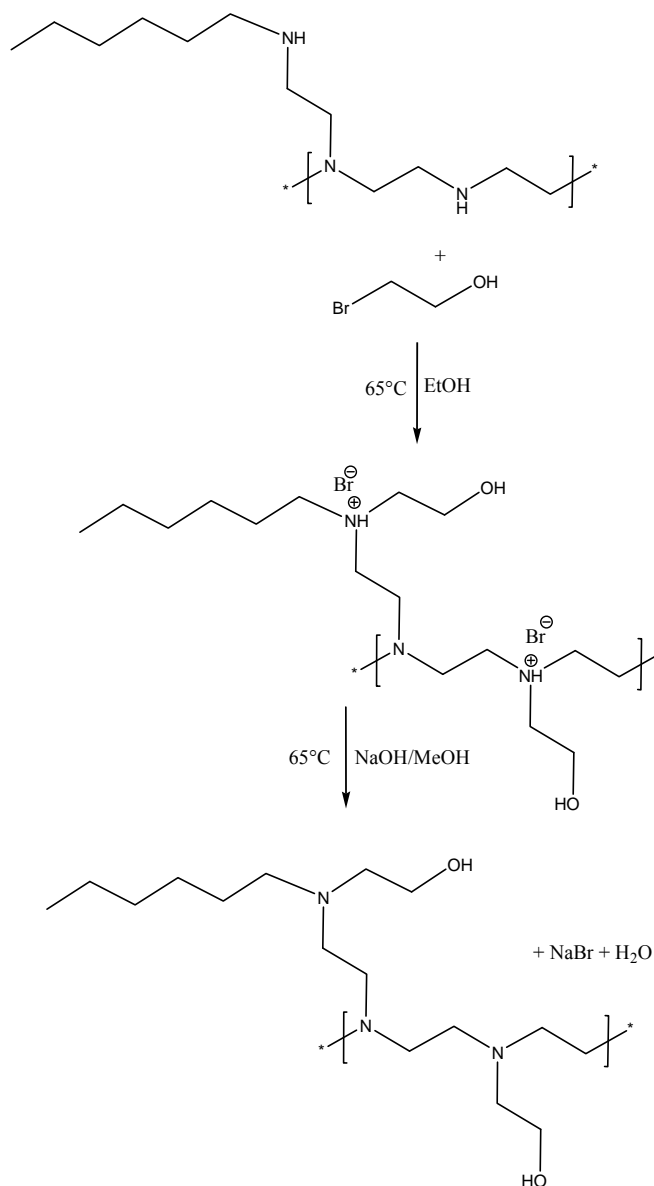
Scheme 4. Hexylated PEI reaction with 1-Bromoethanol

Table 3. Alternative modification of PEI with Cloud Points

Modification	Cloud Point (°C)	Mw	PDI	pH
7.75%Hexyl-87.5%Ethoxyl PEI	No C.P.	4300	3.5	8.48
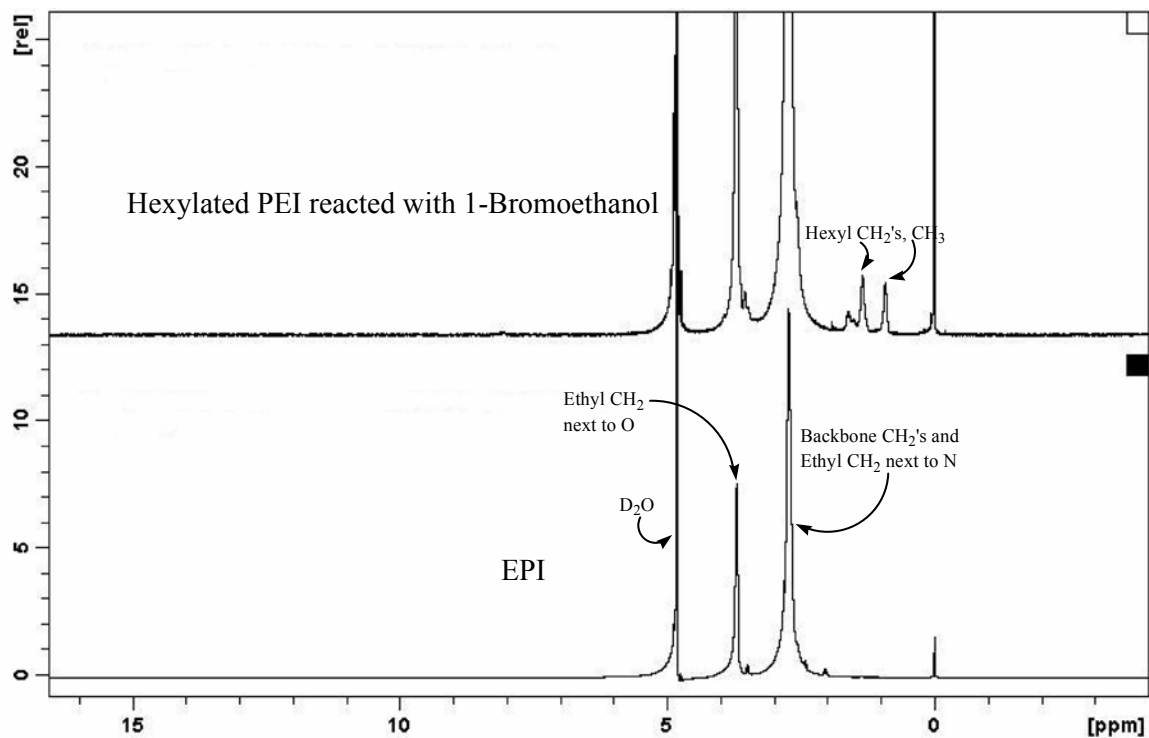
Figure 11. 300 MHz NMR of EPI and Hexylated PEI reacted with 1-Bromoethanol in D_2O

3. Experimental

Materials

All reactions were carried out under a nitrogen atmosphere and all transfers were done using syringes or cannula as required. The polyethyleneimines classified as Lupasols® and the ethoxylated polyethyleneimine were donated by BASF Chemical Co. Propylene oxide, 1-bromobutane, 1-bromopentane, 1-bromohexane, 1-bromodecane, 1-bromododecane, 2-bromoethanol and potassium *t*-butoxide were purchased from Aldrich Chemical Co. and used as received. The solvents and the company purchased from are listed as follows: tetrahydrofuran-Fisher Chemicals, methanol-VWR International, ethanol-Aaper Alcohol and Chemical Co. and toluene- VWR International. Spectra/Por® dialysis membranes with 12-14 k cut-offs were purchased from Daigger Lab Equipment and Supplies. The propoxylating reactions were performed in a Parr Pressure Reaction Apparatus controlled by a Variac® Autotransformer.

Instrumentation

^{1}H and ^{13}C NMR spectra were acquired with a Bruker Avance 300-MHZ instrument operating at 300 and 75.5 MHz, respectively. Deuterium oxide and (methyl sulfoxide)-d_6 were used as solvents to prepare NMR samples. Size exclusion chromatography (SEC) analysis was conducted with a Viscotek Model 300 TDA system, equipped with a viscosity, refractive index and light scattering detectors operating at 70°C. Polymer Laboratories 5 μm PL gel Mixed C columns were used with NMP (with

5% LiBr) as the eluent and a Thermoseparation Model P1000 operating at 0.8 mL/min. pH values were obtained using a Fisher Science Education pH Tutor Meter.

General Synthesis of Pentylated Propoxylated Polyethyleneimines (P_nP-PEI)

7-68% P_nP-PEI (All attempted percent modifications are indicated as noted)

In a 1000 ml RB flask equipped with a magnetic stir bar, condenser, gas adaptor and charged with nitrogen were placed 20.22 g (0.469 mol of repeat units) of polyethyleneimine (PEI) dissolved in 200 ml of THF. In an oil bath the mixture was heated to 65°C. Next, 4.89 g (0.033 mol) of 1-bromopentane was added and the reaction mixture was stirred for 48 hour at 65°C. This was followed by the addition of 1.32 g (0.033 mol) of NaOH dissolved in 13 ml of MeOH and the reaction mixture was stirred for a further 24 hours at 65°C. After the reaction was complete the THF was removed in vacuum and the resulting pentylated PEI was dissolved in 217 ml of EtOH and placed into a Parr-reactor, previously purged with nitrogen. Next, 21.23 ml (0.303 mol) of propylene oxide was added by syringe and the Parr-reactor was heated to 58°C for 11 hours. All subsequent propoxylating steps were heated for 7 hours. The EtOH was removed by evaporation and the product dissolved in 100 ml of water and placed into dialysis tubing with a molecular weight cut off of 12 to 14,000 Daltons and submerged into 20 gallons of water for twenty four hours which afforded 9.94 g of P_nP-PEI, based on a 0.30 g dried down sample, for a 24% yield. The percent modification 7.6% pentyl and 77% propoxyl was determined via analysis of the ^{1}H NMR spectrum. All ^{13}C data acquired using DEPT 135. ^{1}H NMR (D_2O, δ): 0.98 (CH_3); 1.20 (CH_3); 1.36-1.55 (CH_2);

2.56-2.75 (CH$_2$); 3.94 (CH). ^{13}C NMR (DMSO-d_6, δ): 13.9 (CH$_3$); 21.2 (CH$_3$); 22.1 (CH$_2$); 29.1 (CH$_2$); 47.3 (CH$_2$); 53.1 (CH$_2$); 57.3 (CH$_2$); 63.1 (CH$_2$); 64.6 (CH).

7-77% H$_x$P-PEI

       This sample was prepared by the same procedures as discussed for the 7-68% P$_n$P-PEI except 1-bromohexane was used as the alkylating agent and the propylene oxide was added in three batches (50-30-15 percent) and heated for 7 hours and cooled down to room temperature after each addition which will be described as slow addition. Starting with 23.34 g (0.542 mol) of PEI, 6.26 g (0.038 mol) of 1-bromohexane and 29.29 ml (0.418 mol) of propylene oxide gave 15.91 g of product (34% yield) at 8.1 hexyl and 81 2-hydroxypropyl percent modification. ^{1}H NMR (D$_2$O, δ): 0.95 (CH$_3$); 1.17 (CH$_3$); 1.36-1.50 (CH$_2$); 2.53-2.72 (CH$_2$); 3.94 (CH). ^{13}C NMR (DMSO-d_6, δ): 13.9 (CH$_3$); 21.2 (CH$_3$); 26.7 (CH$_2$); 31.5 (CH$_2$); 47.3 (CH$_2$); 53.1 (CH$_2$); 57.3 (CH$_2$); 63.1 (CH$_2$); 64.6 (CH).

7-65% H$_x$P-PEI

       This sample was prepared by the same procedures as discussed for the 7-68% P$_n$P-PEI except 1-bromohexane was used as the alkylating agent and the propylene oxide was added by slow addition. Starting with 21.76 g (0.505 mol) of PEI, 5.835 g (0.035 mol) of 1-bromohexane and 23.0 ml (0.328 mol) of propylene oxide gave 18.49 g of product (47% yield) at 7.8 hexyl and 72 2-hydroxypropyl percent modification.

^{1}H NMR (D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.36-1.50 (CH$_2$); 2.53-2.75 (CH$_2$); 3.94 (CH).

^{13}C NMR (DMSO-d_6, δ): 13.9 (CH$_3$); 21.2 (CH$_3$); 22.1 (CH$_2$); 26.7 (CH$_2$); 31.5 (CH$_2$); 47.3 (CH$_2$); 53.1 (CH$_2$); 57.3 (CH$_2$); 63.1 (CH$_2$); 64.6 (CH).

5-67% H$_x$P-PEI

This sample was prepared by the same procedures as discussed for the 7-68% P$_n$P-PEI except 1-bromohexane was used as the alkylating agent and the propylene oxide was added by slow addition. Starting with 21.07 g (0.489 mol) of PEI, 3.96 g (0.024 mol) of 1-bromohexane and 22.95 ml (0.328 mol) of propylene oxide gave 22.4 g of product (59% yield) at 5.9 hexyl and 69 2-hydroxypropyl percent modification.

^{1}H NMR (D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.36-1.52 (CH$_2$); 2.53-2.72 (CH$_2$); 3.94 (CH).

^{13}C NMR (DMSO-d_6, δ): 13.9 (CH$_3$); 21.2 (CH$_3$); 22.1 (CH$_2$); 26.7 (CH$_2$); 31.5 (CH$_2$); 47.3 (CH$_2$); 53.1 (CH$_2$); 57.3 (CH$_2$); 63.1 (CH$_2$); 64.6 (CH).

7-65% P$_n$P-PEI

This sample was prepared by the same procedures as discussed for the 7-68% P$_n$P-PEI except the propylene oxide was added by slow addition. Starting with 22.20 g (0.515 mol) of PEI, 5.45 g (0.036 mol) of 1-bromopentane and 23.45 ml (0.335 mol) of propylene oxide gave a 7.1 pentyl and 69 2-hydroxypropyl percent modification.

^{1}H NMR (D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.36-1.52 (CH$_2$); 2.56-2.75 (CH$_2$); 3.94 (CH).

^{13}C NMR (DMSO-d_6, δ): 13.9 (CH$_3$); 21.2 (CH$_3$); 22.1 (CH$_2$); 29.1 (CH$_2$); 47.3 (CH$_2$); 53.1 (CH$_2$); 57.3 (CH$_2$); 63.1 (CH$_2$); 64.6 (CH).

7-65% H$_x$P-PEI

This sample was prepared by the same procedures as discussed for the 7-68% P$_n$P-PEI except 1-bromohexane was used as the alkylating agent and the propylene oxide was added by slow addition. Starting with 19.7 g (0.457 mol) of PEI, 5.28 g (0.032 mol) of 1-bromohexane and 20.81 ml (0.297 mol) of propylene oxide gave 13.78 g of product (38% yield) at 8.1 hexyl and 71 2-hydroxypropyl percent modification.

^{1}H NMR (D$_2$O, δ): 0.95 (CH$_3$); 1.17 (CH$_3$); 1.33-1.50 (CH$_2$); 2.53-2.75 (CH$_2$); 3.92 (CH).

^{13}C NMR (DMSO-d_6, δ): 13.9 (CH$_3$); 18.2 (CH$_3$); 21.2 (CH$_2$); 22.1 (CH$_2$); 26.7 (CH$_2$); 31.5 (CH$_2$); 47.3 (CH$_2$); 53.1 (CH$_2$); 56.1 (CH$_2$); 57.3 (CH$_2$); 63.1 (CH$_2$); 64.6 (CH).

7-65% B$_u$P-PEI

This sample was prepared by the same procedures as discussed for the 7-68% P$_n$P-PEI except 1-bromobutane was used as the alkylating agent and the propylene oxide was added by slow addition. Starting with 19.16 g (0.445 mol) of PEI, 4.27 g (0.031 mol) of 1-bromobutane and 20.26 ml (0.289 mol) of propylene oxide gave 22.98 g of product (26% yield) at 10.6 butyl and 79 2-hydroxypropyl percent modification.

^{1}H NMR (D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.36-1.52 (CH$_2$); 2.53-2.75 (CH$_2$); 3.94 (CH).

^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 21.1 (CH$_3$); 21.2 (CH$_2$); 47 (CH$_2$); 53 (CH$_2$); 57.1 (CH$_2$); 62.7 (CH$_2$); 64.6 (CH).

3-69% D_cP-PEI

This sample was prepared by the same procedures as discussed for the 7-68% P_nP-PEI except 1-bromodecane was used as the alkylating agent and the propylene oxide was added by slow addition. Starting with 19.24 g (0.447 mol) of PEI, 2.96 g (0.013 mol) of 1-bromodecane and 21.61 ml (0.308 mol) of propylene oxide gave 18.82 g of product (48% yield) at 3.4 decyl and 73 2-hydroxypropyl percent modification.^{1}H NMR (D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.33-1.50 (CH$_2$); 2.53-2.75 (CH$_2$); 3.94 (CH). ^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 21.4 (CH$_3$); 29.3(CH$_2$); 47.6 (CH$_2$); 53.3 (CH$_2$); 57.7 (CH$_2$); 63.4 (CH$_2$); 64.6 (CH).

3-69% D_cP-PEI

This sample was prepared by the same procedures as discussed for the 7-68% P_nP-PEI except 1-bromodecane was used as the alkylating agent and the propylene oxide was added by slow addition. Starting with 20.54 g (0.477 mol) of PEI, 3.16 g (0.014 mol) of 1-bromodecane and 23.06 g (0.329 mol) of propylene oxide gave 38 g of product (92% yield) at 3.5 decyl and 75 2-hydroxypropyl percent modification. ^{1}H NMR (D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.33-1.50 (CH$_2$); 2.56-2.75 (CH$_2$); 3.94 (CH). ^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 21.4 (CH$_3$); 27.1(CH$_2$); 29.3(CH$_2$); 31.5CH$_2$); 47.6 (CH$_2$); 53.3 (CH$_2$); 57.7 (CH$_2$); 63.0 (CH$_2$); 64.6 (CH).

3-77 % D$_c$P-PEI

This sample was prepared by the same procedures as discussed for the 7-68% P$_n$P-PEI except 1-bromodecane was used as the alkylating agent. Starting with 22.6 g (0.525 mol) of PEI, 3.48 g (0.016 mol) of 1-bromodecane and 28.3 ml (0.404 mol) of propylene oxide gave 32 g of product (66% yield) at 3.8 decyl and 76 2-hydroxypropyl percent modification. ^{1}H NMR (D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.33-1.50 (CH$_2$); 2.53-2.75 (CH$_2$); 3.94 (CH).^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 17.3 (CH$_3$); 21.4 (CH$_2$); 27.1(CH$_2$); 29.3(CH$_2$); 30.3 (CH$_2$); 47.6 (CH$_2$); 53.3 (CH$_2$); 57.7 (CH$_2$); 63.0 (CH$_2$); 64.9 (CH).

7-73% P$_n$P -PEI

This sample was prepared by the same procedures as discussed for the 7-68% P$_n$P-PEI except 1-bromopentane was used as the alkylating agent. Starting with 21.82 g (0.507 mol) of PEI, 5.36 g (0.036 mol) of 1-bromopentane and 25.91 ml (0.370 mol) of propylene oxide gave 9.8 g of product (22% yield) at 7.4 pentyl and 85 2-hydroxypropyl percent modification. ^{1}H NMR (D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.36-1.55 (CH$_2$); 2.56-2.75 (CH$_2$); 3.94 (CH). ^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 21.4 (CH$_3$); 22.4 (CH$_2$); 26.8 (CH$_2$); 29.3(CH$_2$); 47.6 (CH$_2$); 53.3 (CH$_2$); 63.4 (CH$_2$); 64.9 (CH).

7-68% P$_n$P –PEI (Scale-Up)

This sample was prepared by the same procedures as discussed for the

7-68% P$_n$P-PEI except the cosolvent THF (1000 ml) and MeOH (360ml) were used for

the alkylation step and dialysis took place for six hours. Starting with 136.95 g (3.18 mol)

of PEI, 33.62 g (0.223 mol) of 1-bromopentane and 151.5 ml (2.16 mol) of propylene

oxide gave 228 g of product (81.7% yield) at 8.5 pentyl and 64 2-hydroxypropyl percent

modification. ^{1}H NMR (D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.33-1.52 (CH$_2$); 2.53-2.75

(CH$_2$); 3.94 (CH). ^{13}C NMR (DMSO -d_6, δ): 14.2 (CH$_3$); 21.4 (CH$_3$); 22.4 (CH$_2$); 26.8

(CH$_2$); 47.6 (CH$_2$); 53.3 (CH$_2$); 57.7 (CH$_2$);   63.0 (CH$_2$); 64.9 (CH).

7-68% P$_n$P –PEI (Scale-Up)

This sample was prepared by the same procedures as discussed for the

7-68% P$_n$P-PEI except EtOH was used as a solvent for the alkylation step and dialysis

took place for six hours. Starting with 137.6 g (3.19 mol) of PEI, 37.78 g (0.224 mol) of

1-bromopentane and 152.2 ml (2.17 mol) of propylene oxide gave 247 g of product

(88.5% yield) at 6.5 pentyl and 72 2-hydroxypropyl percent modification. ^{1}H NMR (D$_2$O,

δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.33-1.52 (CH$_2$); 2.53-2.75 (CH$_2$); 3.94 (CH). ^{13}C NMR

(DMSO-d_6, δ): 14.2 (CH$_3$); 21.4 (CH$_3$); 26.8 (CH$_2$); 29.3 (CH$_2$); 47.6 (CH$_2$); 53.3 (CH$_2$);

57.7 (CH$_2$);   63.0 (CH$_2$); 64.9 (CH).

3-77 % D$_c$P-PEI

This sample was prepared by the same procedures as discussed for the 7-68% P$_n$P-PEI except 1-bromodecane was used as the alkylating agent and dialysis took place for six hours. Starting with 22.6 g (0.525 mol) of PEI, 3.48 g (0.0157 mol) of 1-bromodecane and 28.3 ml (0.4040 mol) of propylene oxide gave 32 g of product (66% yield) at 3.8 decyl and 76 2-hydroxypropyl percent modification. ^{1}H NMR (D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.33-1.50 (CH$_2$); 2.53-2.75 (CH$_2$); 3.94 (CH).^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 17.3 (CH$_3$); 21.4 (CH$_2$); 27.1(CH$_2$); 29.3(CH$_2$); 30.3 (CH$_2$); 47.6 (CH$_2$); 53.3 (CH$_2$); 57.7 (CH$_2$); 63.0 (CH$_2$); 64.9 (CH).

6-74 % D$_c$P-PEI

This sample was prepared by the same procedures as discussed for the 7-68% P$_n$P-PEI except 1-bromodecane was used as the alkylating agent and dialysis took place for six hours. Starting with 10.48 g (0.2433 mol) of PEI, 3.35 g (0.015 mol) of 1-bromodecane and 12.6 ml (0.180 mol) of propylene oxide gave 18 g of product (87.3% yield) at 7 decyl and 81 2-hydroxypropyl percent modification. ^{1}H NMR (D$_2$O, δ): 0.95 (CH$_3$); 1.20 (CH$_3$); 1.33-1.50 (CH$_2$); 2.53-2.75 (CH$_2$); 3.94 (CH). ^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 21.4 (CH$_3$); 22.4 (CH$_2$); 27.1 (CH$_2$); 29.3 (CH$_2$); 31.5 (CH$_2$); 47.6 (CH$_2$); 53.3 (CH$_2$); 63.0 (CH$_2$); 64.9 (CH).

9.4-70.6% H$_x$P-PEI

This sample was prepared by the same procedures as discussed for the

7-68% P$_n$P-PEI except 1-bromohexane was used as the alkylating agent and dialysis took

place for six hours. Starting with 10.94 g (0.254 mol) of PEI, 3.94 g (0.024 mol) of 1-

bromohexane and 12.6 ml (0.179 mol) of propylene oxide gave 17.92 g of product (82%

yield) at 9.5 hexyl and 74 2-hydroxypropyl percent modification.^{1}H NMR (D$_2$O, δ): 0.95

(CH$_3$); 1.17 (CH$_3$); 1.33-1.50 (CH$_2$); 2.53-2.72 (CH$_2$); 3.94 (CH). ^{13}C NMR (DMSO-d_6,

δ): 14.2 (CH$_3$); 21.4 (CH$_3$); 26.8 (CH$_2$); 31.5 (CH$_2$); 47.6 (CH$_2$); 53.3 (CH$_2$); 57.4 (CH$_2$);

63.0 (CH$_2$); 64.9 (CH)

5-75 % D$_d$P-PEI

This sample was prepared by the same procedures as discussed for the

7-68% P$_n$P-PEI except 1-bromododecane was used as the alkylating agent and dialysis

took place for six hours. Starting with 9.96 g (0.2313 mol) of PEI, 2.88 g (0.012 mol) of

1-bromododecane and 12.2 ml (0.174 mol) of propylene oxide gave 17.56 g of product

(79.3% yield) at 4.9 dodecyl and 79 2-hydroxypropyl percent modification. ^{1}H NMR

(D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.36-1.52 (CH$_2$); 2.53-2.75 (CH$_2$); 3.94 (CH).^{13}C NMR

(DMSO-d_6, δ): 14.2 (CH$_3$); 21.4 (CH$_3$); 22.4 (CH$_2$); 27.1(CH$_2$); 29.3(CH$_2$); 31.5 (CH$_2$);

47.6 (CH$_2$); 53.3 (CH$_2$); 57.7 (CH$_2$); 63.0 (CH$_2$); 64.9 (CH).

15-65% H_xP-PEI

This sample was prepared by the same procedures as discussed for the 7-68% P_nP-PEI except 1-bromohexane was used as the alkylating agent and dialysis took place for six hours. Starting with 6.47 g (0.150 mol) of PEI, 3.72 g (0.023 mol) of 1-bromohexane and 6.84 ml (0.0976 mol) of propylene oxide gave 11.2 g of product (71% yield) at 15.8 hexyl and 80 2-hydroxypropyl percent modification. ^{1}H NMR (D$_2$O, δ): 0.95 (CH$_3$); 1.17 (CH$_3$); 1.33-1.50 (CH$_2$); 2.53-2.72 (CH$_2$); 3.94 (CH). ^{13}C NMR (DMSO-d_6, δ): 13.9 (CH$_3$); 21.2 (CH$_3$); 22.1 (CH$_2$); 26.7 (CH$_2$); 31.5 (CH$_2$); 47.3 (CH$_2$); 53.1 (CH$_2$); 57.3 (CH$_2$); 63.1 (CH$_2$); 64.6 (CH).

5-75% H_xP-PEI

This sample was prepared by the same procedures as discussed for the 7-68% P_nP-PEI except 1-bromohexane was used as the alkylating agent and dialysis took place for six hours. Starting with 6.66 g (0.155 mol) of PEI, 1.28 g (0.008 mol) of 1-bromohexane and 8.12 ml (0.116 mol) of propylene oxide gave 10.24 g of product (70% yield) at 6.4 hexyl and 69 2-hydroxypropyl percent modification. ^{1}H NMR (D$_2$O, δ): 0.98 (CH$_3$); 1.20 (CH$_3$); 1.36-1.52 (CH$_2$); 2.56-2.75 (CH$_2$); 3.94 (CH). ^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 21.4 (CH$_3$); 22.4 (CH$_2$); 27.1 (CH$_2$); 31.5 (CH$_2$); 47.6 (CH$_2$); 53.3 (CH$_2$); 63.0 (CH$_2$); 64.9 (CH).

7-68% P_nP-PEI-P

This sample was prepared by the same procedures as discussed for the 7-68% P_nP-PEI except high molecular weight PEI was used instead of PEI and dialysis took place for six hours. Approximately 9 g of water was removed from the PEI-P by vacuum and the residual water (50% solids) was accounted for in determining the amount of starting material. Starting with 20.04 g (0.465 mol) of PEI-P, 4.92 g (0.033 mol) of 1-bromopentane and 22.2 ml (0.316 mol) of propylene oxide gave 34.7 g of product (79.5% yield) at 7.1 hexyl and 69 2-hydroxypropyl percent modification.^{1}H NMR (D_2O, δ): 0.98 (CH_3); 1.20 (CH_3); 1.36-1.52 (CH_2); 2.53-2.75 (CH_2); 3.94 (CH). ^{13}C NMR (DMSO-d_6, δ): 13.9 (CH_3); 21.2 (CH_3); 22.1 (CH_2); 29.1 (CH_2); 47.3 (CH_2); 53.1 (CH_2); 57.3 (CH_2); 63.1 (CH_2); 64.6 (CH).

General Synthesis of Pentylated Ethoxylated Polyethyleneimines

7% Pentylated EPI

In a 1000 ml RBF equipped with a gas adaptor was placed a sample of EPI 72.35 g and put under vacuum and 42.61g of water was removed. A dean-stark trap was then attached to the round bottom flask containing the dried down sample and the cosolvent mixture of toluene (200ml) and NMP (250ml) was added. The solution was then heated in an oil bath to 120°C and an additional 4.08g of water was removed azeotropically bringing the total amount of EPI to 25.66g in accordance with the reported 35% solids. Next, 2.345g (0.0209m) of t-BuO⁻K⁺ was added to deprotonate 7% of the hydroxy groups followed by the addition of 3.16g (0.0209m) of 1-bromopentane to alkylate the hydroxyl

anions. The resulting solution was placed into aqueous dialysis for six hours to remove the toluene and NMP in addition to the KBr salts. The total amount of product after dialysis was 20.18 g (74% yield) at 4.9 pentyl percent modification. ^{1}H NMR (D$_2$O, δ): 0.92 (CH$_3$); 1.36 (CH$_2$); 1.63 (CH$_2$); 2.75 (CH$_2$); 3.73 (CH). ^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 17.3 (CH$_2$); 30.3 (CH$_2$); 47.3 (CH$_2$); 48.9 (CH$_2$); 51.7 (CH$_2$); 53.0 (CH$_2$); 54.2 (CH$_2$); 57.1 (CH$_2$); 58.6 (CH$_2$); 59.6 (CH$_2$).

7% Hexylated EPI

This sample was prepared by the same procedures as discussed for the 7% Pentylated EPI except water was removed from the EPI by vacuum taking into account 9% residual water and 1-bromohexane was used as the alkylating agent. Starting with 7.22 g (0.091 mol) of EPI and 1.06 g (0.0064 mol) of 1-bromohexane gave 2.9 g of product (37% yield) at 8.6 hexyl percent modification. ^{1}H NMR (D$_2$O, δ): 0.92 (CH$_3$); 1.36 (CH$_2$); 1.63 (CH$_2$); 2.75 (CH$_2$); 3.73 (CH). ^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 17.3 (CH$_2$); 30.3 (CH$_2$); 47.3 (CH$_2$); 48.9 (CH$_2$); 51.7 (CH$_2$); 53.0 (CH$_2$); 54.2 (CH$_2$); 57.1 (CH$_2$); 58.6 (CH$_2$); 59.6 (CH$_2$).

3% Decylated EPI

This sample was prepared by the same procedures as discussed for the 7% Pentylated EPI except water was removed form the EPI by vacuum taking into account 9% residual water and 1-bromodecane was used as the alkylating agent. Starting with 19.46 g (0.246 mol) of EPI and 1.64 g (0.0074 mol) of 1-bromodecane gave 12.83 g of product (63% yield) at 2.3 decyl percent modification. ^{1}H NMR (D$_2$O, δ): 0.92 (CH$_3$);

1.36 (CH$_2$); 1.63 (CH$_2$); 2.75 (CH$_2$); 3.73 (CH). ^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$);

17.5 (CH$_2$); 30.2 (CH$_2$); 47.4 (CH$_2$); 48.6 (CH$_2$); 51.9 (CH$_2$); 53.1 (CH$_2$); 54.6 (CH$_2$);

57.3 (CH$_2$); 59.4 (CH$_2$); 60.3 (CH$_2$).

7% Pentylated EPI

      This sample was prepared by the same procedures as discussed for the

7% Pentylated EPI except water was removed from the EPI by vacuum taking into

account 9% residual water. Starting with 21.92 g (0.255 mol) of EPI and 3.69 g (0.0244

mol) of 1-bromopentane gave 10.73 g of product (49% yield) at 6.4 pentyl percent

modification. ^{1}H NMR (D$_2$O, δ): 0.92 (CH$_3$); 1.36 (CH$_2$); 1.63 (CH$_2$); 2.75 (CH$_2$); 3.73

(CH). ^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 17.2 (CH$_2$); 29.3 (CH$_2$); 30.5 (CH$_2$); 48.9

(CH$_2$);

52.8 (CH$_2$); 57.0 (CH$_2$); 59.4 (CH$_2$).

General Synthesis of the Reaction of

1-Bromoethanol with 7%H-PEI

7% Hexylated 65% Ethoxylated PEI

      The PEI was alkylated with 1-bromohexane following the alkylating procedure

for 7-68% P$_n$P-PEI except 1-bromohexane was used as the alkylating agent. Then to a 50

ml RBF equipped with a magnetic stir bar, condenser, gas adaptor and flushed with N$_2$

was added 21 ml of EtOH and 2.17 g (0.046 mol) of HPEI. The RBF was then placed in a

65°C preheated oil bath. Next, 3.75 g (0.0299 mol) of 1-bromoethanol was added in four

equal increments. Each addition stirred for 48 hours and to it was added 0.27 g (.00675

mol) of NaOH in 2.7 ml of MeOH which stirred for 24 hours while maintaining a constant temperature of 65°C. The product was placed into aqueous dialysis for six hours and then washed with ether to give 1.8 g (35% yield) at 7.75 hexyl and 87.5 2-hydroxyethyl percent modification as a clear yellow solution with no cloud point up to 100°C. ^{1}H NMR (D$_2$O, δ): 0.92 (CH$_3$); 1.36 (CH$_2$); 1.55 (CH$_2$); 2.75 (CH$_2$); 3.73 (CH). ^{13}C NMR (DMSO-d_6, δ): 14.2 (CH$_3$); 22.4 (CH$_2$); 26.8 (CH$_2$); 31.5 (CH$_2$); 46.3 (CH$_2$); 53.0 (CH$_2$); 57.1 (CH$_2$); 59.6 (CH$_2$).

4. Conclusion

The commercially available polymer polyethyleneimine (PEI) was able to successfully undergo alkylation and propoxylation modifications using a bromoalkane and propylene oxide while maintaining a cloud point in the acceptable range of 60 - 70°C. The added alkyl substituent was effective in providing a hydrophobic component to the backbone of PEI. The addition of the 2-hydroxypropyl took up the remaining reactive primary and secondary amines.

The product resulting from the chemical modification of ethoxylated polyethyleneimine provided a polymer with hydrophobic ethers. Another approach taken was to treat an alkylated PEI with 1-bromethanol as a way to introduce a 2-hydroxyethyl group without having to use ethylene oxide or dry EPI.

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