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Investigation of Temperature Sensitivity Behaviors of Water Soluble Polyacrylamides

Erdal Uğuzdoğan,[1] Emir Baki Denkbaş,[2] Osman Sermet Kabasakal[3]

[1]Chemical Engineering Department, Pamukkale University, Kinikli 20070, Denizli, Turkey

[2]Chemistry Department, Hacettepe University, Beytepe 06800, Ankara, Turkey

[3]Chemical Engineering Department, Eskisehir Osmangazi University, Meselik Campus 26480, Eskisehir, Turkey

Correspondence to: O. S. Kabasakal (E-mail: osk@ogu.edu.tr)

ABSTRACT: Temperature sensitive polymers with a lower critical solution temperature (LCST) are used in a variety of industries such as the pharmaceutical, cosmetic, food, and paint. These polymers are generally of the poly(*N*-alkylacrylamide) type, of which poly(*N*-isopropylacrylamide) (PNIPA) is the most commonly used. More novel poly(*N*-alkylacrylamide)s have also been the subject of much attention recently. In this study, *N*-alkylacrylamides containing different alkyl groups were synthesized by nucleophylic substitution reactions of various amines with acryloyl chloride. They were polymerized using the solution polymerization method, and the temperature sensitivities of the polymers were investigated. For this purpose, three monomers, *N*,*N*-diethylacrylamide, *N*-cyclopropylacrylamide, and 4-piperidineethanolacrylamide, were synthesized using diethylamine, cyclopropylamine, and 4-piperidineethanol, as the amines, respectively. The obtained polymers, poly(*N*,*N*-diethylacrylamide) (PDEA), poly(*N*-cyclopropylacrylamide) (PCPA), and poly(4-piperidineethanolacrylamide) (PPEA), were found to be thermoresponsive, particularly PPEA is a potential novel material that can be utilized as an alternative to the common temperature sensitive polymers. The effects of several conditions on the LCST and the critical flocculation temperature (CFT) of the polymers were also investigated. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: lower critical solution temperature; critical flocculation temperature; stimuli-sensitive polymers; water-soluble polymers; solution properties

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INTRODUCTION

Temperature-responsive water-soluble polymers that are extensively used as additives by pharmaceutical, cosmetic, food, and paint industries are of great scientific and technological importance. These polymers are soluble in water at low temperatures but become insoluble as the temperature rises above the lower critical solution temperature (LCST). This feature has led to applications in bioengineering[1–5] and nanotechnology[6–8] and provides superiority to the future applications in the area of biosensors and membranes. Drug delivery systems,[9,10] human gene delivery vectors,[11,12] biocatalysts,[13,14] super absorbents,[15,16] the separation and purification of metal ions,[17,18] and biomolecules[19,20] are among the most important fields in which temperature sensitive polymers are used.

The phase separation behavior of the aqueous solutions of temperature-sensitive polymers is generally associated with the temperature dependency of hydrogen bonding and hydrophobic interactions,[21–23] but the mechanisms of this behavior have not been fully examined. Generally, poly(*N*-alkylacrylamide)s have temperature sensitivity properties. Poly(*N*-isopropylacrylamide) (PNIPA) that has been extensively studied as a thermo-responsive homopolymer, has a repeat unit that consists of hydrophilic (amide) and hydrophobic (isopropyl) groups. The LCST for linear forms of PNIPA is about 32°C[24,25] in water, being close to the human body temperature that is 37°C. This value might restrict the usage of PNIPA in biomedical and biotechnological applications such as improving new controlled drug releasing systems and the use of polymeric-based materials as micro carriers in enzymes. Both rapid changes in the application fields of temperature-sensitive polymers and the diversity of these applications require synthesis of novel polymers with different LCST values. Therefore, the synthesis of temperature sensitive polymeric materials having different LCST values has been extensively studied. These researches have been focused on two areas. One of them is about getting the LCST of known temperature sensitive polymers (i.e., PNIPA) to a specific value by chemical modification and the second area is synthesizing a novel

temperature-sensitive polymer, which might have a different LCST value. Although several N-substituted alkylacrylamide and methacrylamide polymers (*N*-alkyl-substituted polyacrylamides), belonging to an important family of temperature sensitive polymers, underwent a phase separation in water at different levels of LCST, these polymers have not yet drawn as much attention as poly(*N*-isopropylacrylamide). The LCST values of the homopolymers of *N*-(3-ethoxypropyl)acrylamide,[26] 2-amino-1-methoxypropylacrylamide,[27] isopropylmethacrylamide,[28,29] diethylacrylamide,[30] *N*-*n*-propylmethacrylamide,[31] cyclopropylacrylamide,[32] propylacrylamide,[22,33] and ethoxyethylacrylamide[34] have been reported as 32, 35, 43, 31, 28, 58, 24, and 38°C, respectively. The LCSTs of the temperature-responsive homopolymers decrease with increasing number of carbon atoms on the alkyl groups or the number of alkyl groups present. The temperature sensitive homopolymers have repeat units that contain amide groups (*N*-alkyl-substituted polyacrylamides), hydroxyl groups (alkyl substituted celluloses) or ether groups (alkyl substituted celluloses and *N*-alkyl-alkoxy-substituted polyacrylamides). These groups affect the LCSTs of polymeric materials and they have hydrophilic character. Some temperature-sensitive polymers that do not contain acrylamide-based repeat units such as poly(*N*-vinyl-2-pyrrolidone),[35] poly(vinylmethylether),[36] poly(*N*-vinylcaprolactam),[37] and poly(propryleneoxide)[38] have also attracted interest.

In previous studies, the linear and hydrogel matrix forms of poly(*N*-(3-ethoxypropyl)acrylamide) (PEPA)[26,39] and poly(2-amino-1-methoxypropylacrylamide) (PAMPA)[27,40] were proposed as novel temperature-sensitive polymers. In this study, the aim was to synthesize the novel water soluble temperature sensitive polymeric materials and to perform their thermal characterizations. For this purpose, the monomers, *N,N*-diethylacrylamide, *N*-cyclopropylacrylamide, and 4-piperidineethanolacrylamide were initially synthesized by the nucleophilic substitution reactions of acryloyl chloride with the amines diethylamine, cyclopropylamine, and 4-piperidineethanol, respectively. Then, linear poly(*N, N*-diethylacrylamide) (PDEA), poly(*N*-cyclopropylacrylamide) (PCPA), and poly(4-piperidineethanolacrylamide) (PPEA) were obtained by the solution polymerization of the monomers. The thermosensitivity behaviors of these polymers were determined. In this context, the lower critical solution temperature (LCST) and critical flocculation temperature (CFT) of the synthesized soluble polymers were determined, and the effects of various factors on the temperature-sensitivities of the polymers were investigated. Furthermore, ethyl alcohol was used for the investigation of the cononsolvency effect on the LCST of the prepared temperature sensitive polymers.

EXPERIMENTAL

Materials

The monomers, *N,N*-diethylacrylamide, *N*-cyclopropylacrylamide, and 4-piperidineethanolacrylamide, were synthesized by reacting acryloyl chloride (Aldrich Chemicals, Milwaukee, WI) with diethylamine, cyclopropylamine, and 4-piperidineethanol (Aldrich Chemicals, Milwaukee, WI), respectively. In the synthesis of the monomers, dichloromethane was used as the solvent, triethylamine as the base, *p*-hydroquinone as the inhibitor and magnesium sulfate as drying agent. All reagents were purchased from Aldrich Chemicals (Milwaukee, WI), and they were used without further purification. In the polymerizations, azobisisobutyronitrile (AIBN, BDH Chemicals, Poole, UK), recrystallized from methanol, and absolute ethyl alcohol (Merck A. G., Darmstad, Germany) were used as the initiator and the solvent, respectively. Petroleum ether (Birpa, Ankara, Turkey) was used in the purification of the polymers. All polymerization and characterization studies were performed in distilled water.

The Synthesis of the Monomers

N-alkylacrylamide monomers used in the syntheses of the temperature sensitive polymers were obtained by the nucleophilic substitution reactions of the amines with acryloyl chloride.[26,27,41] Monomers were obtained by the procedure given by Shea et al.[42] Briefly, triethylamine was dissolved in dichloromethane and the solution was cooled to 0°C in an ice bath. Amines and *p*-hydroquinone were added to the solution. Acryloyl chloride-dicholoromethane mixture was slowly added in a dropwise manner into the solution stirring magnetically at 0°C for 2 h. The solution was then continued to be stirred magnetically at the same temperature for 2 h. After that, the salts formed during the reaction were removed by washing the solution in cold water. The organic phase dried over magnesium sulfate was evaporated in vacuum for the isolation of the monomers.

The Synthesis of the Temperature Sensitive Polymers

Monomers were polymerized by solution polymerization method as follows. Initially, the monomer and AIBN were dissolved in ethyl alcohol in a sealed cylindrical glass polymerization reactor. Prior to the polymerization, for the purpose of removing oxygen in the polymerization medium, the reaction mixture was purged with nitrogen for 10 min and the reactor was sealed. Then the reactor was placed into a shaking water bath equipped with a temperature control system at room temperature. The water bath was heated to the polymerization temperature in $\sim$ 30 min shaking at 120 cpm. The polymerization was conducted at 70°C for 12 h at a 120 cpm shaking rate. After polymerization, the reactor was cooled to room temperature and ethyl alcohol was removed in a rotary evaporator under vacuum at 40°C. The polymer was precipitated by adding excess petroleum ether. The obtained polymer was redissolved in distilled water and the solution was reheated to the lower critical solution temperature of the polymer. The dissolution–precipitation was repeated several times for the complete removal of impurities in the precipitated polymer. After dissolution and precipitation, polymer was purified and dried for about 2 days in vacuum at 50°C.

Determining the Temperature Sensitivities of the Polymers

The LCST values of the polymers PDEA, PCPA, and PPEA were determined in aqueous media. The absorbance values of the prepared aqueous polymer solutions were measured in a UV–visible spectrophotometer (Shimadzu, Kyoto, Japan) equipped with a flow-through cell at 500 nm in a temperature range of 15.0–80.0°C. The aqueous solution which had a significant polymer concentration with pH 7 was put in a glass reservoir

(50.0 mL) in a water bath equipped with a temperature controlling system, and the temperature of water bath was adjusted to 15.0°C. During the circulation, the temperature was measured on the flow-cell with home-made equipments. After cooling to the adjusted temperature, the polymer solution was circulated with a pump through the flow cell at a flow rate of 10.0 mL min^{-1}. The temperature of the solution in the reservoir was increased at a rate of 1°C min^{-1} and the absorbance was periodically recorded in every minute.

The Effect of Polymer Concentration on the LCST for Aqueous Polymer Solutions. The 0.1, 0.5, 1.0, and 5.0 wt % polymer solutions in aqueous media with pH 7 were prepared to examine the effects of PDEA, PCPA, and PPEA concentrations on LCST. The LCST values were determined for each polymer concentration (C_P). Thus, the effect of polymer concentrations on the LCSTs of the obtained temperature sensitive polymers was determined.

The Effect of Added Salt (Sodium Chloride) on the Thermoresponsive Behavior (CFT) of the Aqueous Polymer Solutions. A number of experiments were performed to determine the critical flocculation temperature CFT variations of the polymer solutions in the presence of salt. In the study, sodium chloride (NaCl) was used as the salt to investigate the effect of salt. The experimental system used for LCST measurements was also used to determine the CFT as explained above. Therefore, the aqueous polymer solutions (C_P (polymer concentration): 0.1 and 1.0 wt %), containing NaCl with different concentrations ranging between 0.1 and 1.0*M*, were prepared. The absorbance-temperature curves of the solutions were obtained at 500 nm by using the spectrophotometer. The CFT values of the solutions were determined from these curves.

The Effect of Ethyl Alcohol Concentration on the LCST Values of the Polymers. The LCST values of the polymer solutions were determined via spectrophotometric method in the medium containing 0–100% volume of alcohol (ethyl alcohol) as it is explained in the experimental system used for the LCST determinations. In these experiments, the concentration of polymer in the solutions was 1.0 wt %.

RESULTS AND DISCUSSION

The variations of polymerization yields with the initiator concentrations are shown in Table I for PDEA, PCPA, and PPEA. Satisfactorily, high polymer yields were achieved in all the initiator concentrations for all of the three polymers. When the results were carefully analyzed, it was observed that the higher polymerization yield was obtained with the higher initiator concentration for PPEA. The production rate of the initiator radicals is proportional to initiator concentration, which makes possible to initiate the polymerization via more monomer molecules and provides higher propagation rate. The propagation rate may be proportional to the polymerization yield. On the other hand, a significant effect of the initiator concentrations on the polymerization yields could not be observed for PCPA and PDEA.

Table I. The Effect of Initiator Concentration on the Polymerization Yield for the Polymers PPEA, PCPA, and PDEA

AIBN (mg mL^{-1})	PPEA C_T (wt %)	PCPA C_T (wt %)	PDEA C_T (wt %)
0.75	74.1	79.2	70.8
1.417	76.2	79.2	71.2
5.833	84.3	79.2	72.5
11.667	84.4	87.3	72.5

The polymerization yields (C_T % w/w) were determined according to eq. (1), where the M_p and M_m are the weight of the polymer isolated and the weight of the monomers charged into the reactor, respectively.

$$C_T(\text{wt \%}) = \left(M_p/M_m\right) \times 100 \quad (1)$$

Water soluble polymers with thermosensitivity undergo a thermally induced, reversible phase transition. The macroscopic phenomenon is the same for all thermosensitive polymers; a clear polymer solution suddenly changes from a transparent homogeneous state into a uniform milky state (in other words opaqueness) when it is heated to a specific temperature referred to as the cloud point. At the same time, the temperature at which the first opaqueness appeared in the solution is also referred to as lower critical solution temperature (LCST). The values of the LCST for temperature sensitive polymers may be determined by the use of various methods such as turbidity, differential scanning calorimetry (DSC), fluorescence, size exclusion chromatography (SEC), or light scattering, etc. In this present study, the LCSTs of the obtained polymers were determined using UV turbidimetry technique. For the solutions of various concentrations of PCPA, PDEA, and PPEA, the change in the visible region absorbance values with temperature is shown in Figure 1. The curves showing the variation of absorbance with temperature were formed by using the absorbance values, which were measured versus temperature. In the absorbance–temperature curves, the temperature corresponding to 10% of the total absorbance increase was evaluated as the LCST. The LCST values can be expected to increase with the hydrophobicity of the substituents.

The chemical structures of the synthesized polymers are shown in Scheme 1.

The thermal aggregation behavior is seen for PCPA at all studied temperatures considering that the absorbance–temperature graphs are in bell shape (Figure 1). This shows that the solubility of PCPA in aqueous media is lower than that of PPEA. It may be said that the lower solubility of PCPA is due to the triple cyclic structure present in each mer unit. The thermoaggregation behavior was not observed only at the lowest polymer concentration for PDEA. The occurrence of aggregation at polymer concentrations higher than 0.1% indicates that PDEA has a hydrophobic structure especially upon the thermal phase separation. For PPEA, it is seen from the plot of variation of the visible region absorbance values with temperature for the polymer solutions of various concentrations that stable polymer dispersions are obtained after the thermal phase separation at all the

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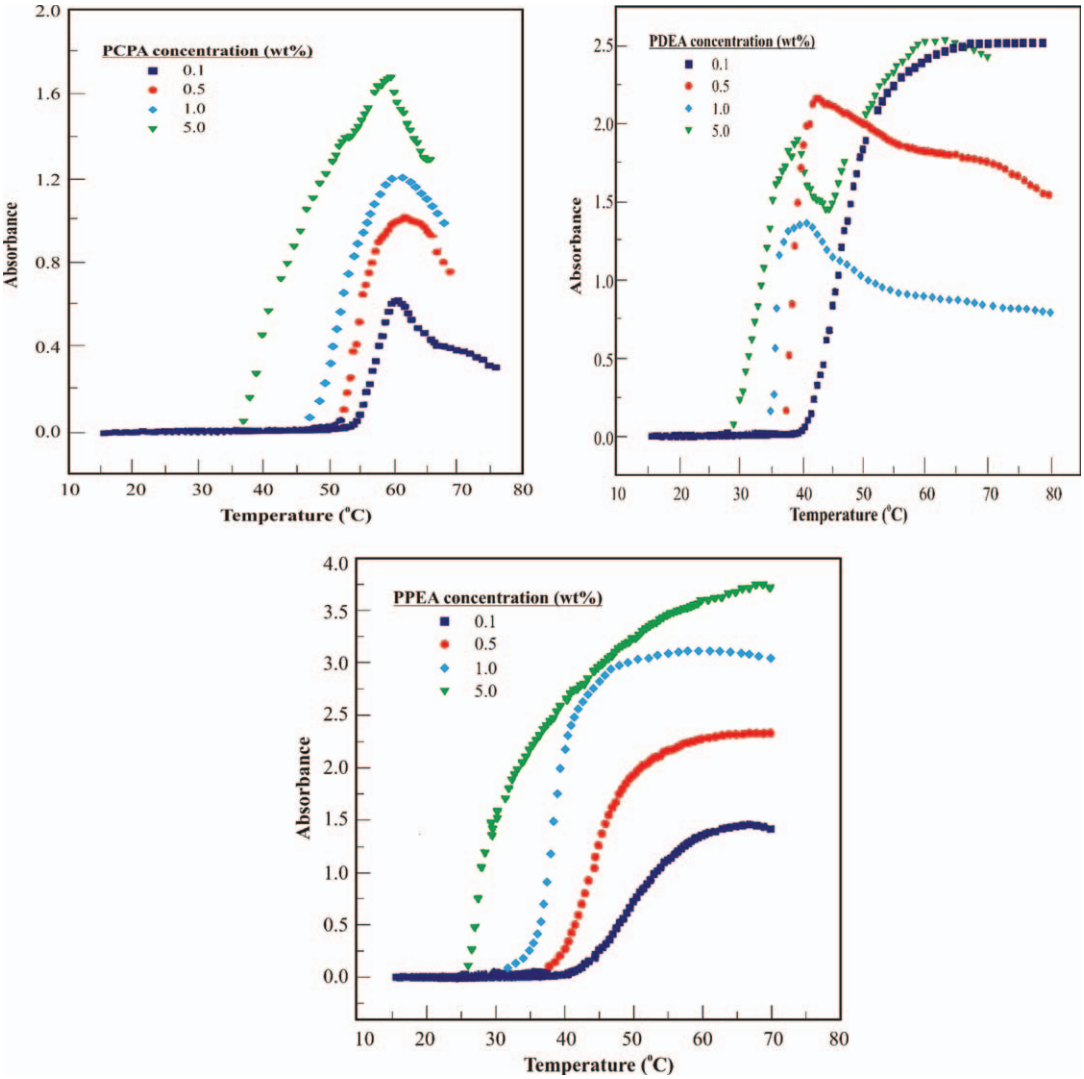
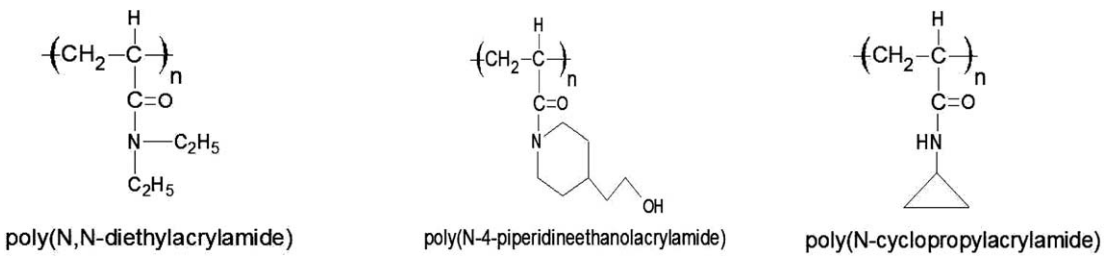


Figure 1. The curves showing the effect of PCPA, PDEA, and PPEA concentrations on the variation of absorbance with temperature (wavelength: 500 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer concentrations studied. This is due to the presence of the piperidine groups having a considerable polarity in the structure of the polymer.

Recently, much effort has been extensively focused on better understanding the phase transition behavior and the parameters affecting the phase transition temperature. These studies have been invested for the effects of molecular weight,[24,43] polymer concentration,[44–46] cosolvent,[46–51] the presence of salts,[51–53] and the polymers' end groups[54,55] on the LCSTs of temperature sensitive polymers. Furthermore, the LCSTs of temperature-sensitive polymers may change according to the conditions used in the measurements of LCST, especially heating or cooling rates.[56,57]

Figure 2 shows the variations of the LCST values, determined from the graphs in Figure 1, with increasing PCPA, PDEA, and PPEA concentrations. Here, the LCST value decreases linearly



Scheme 1. The chemical structures of the synthesized polymers.

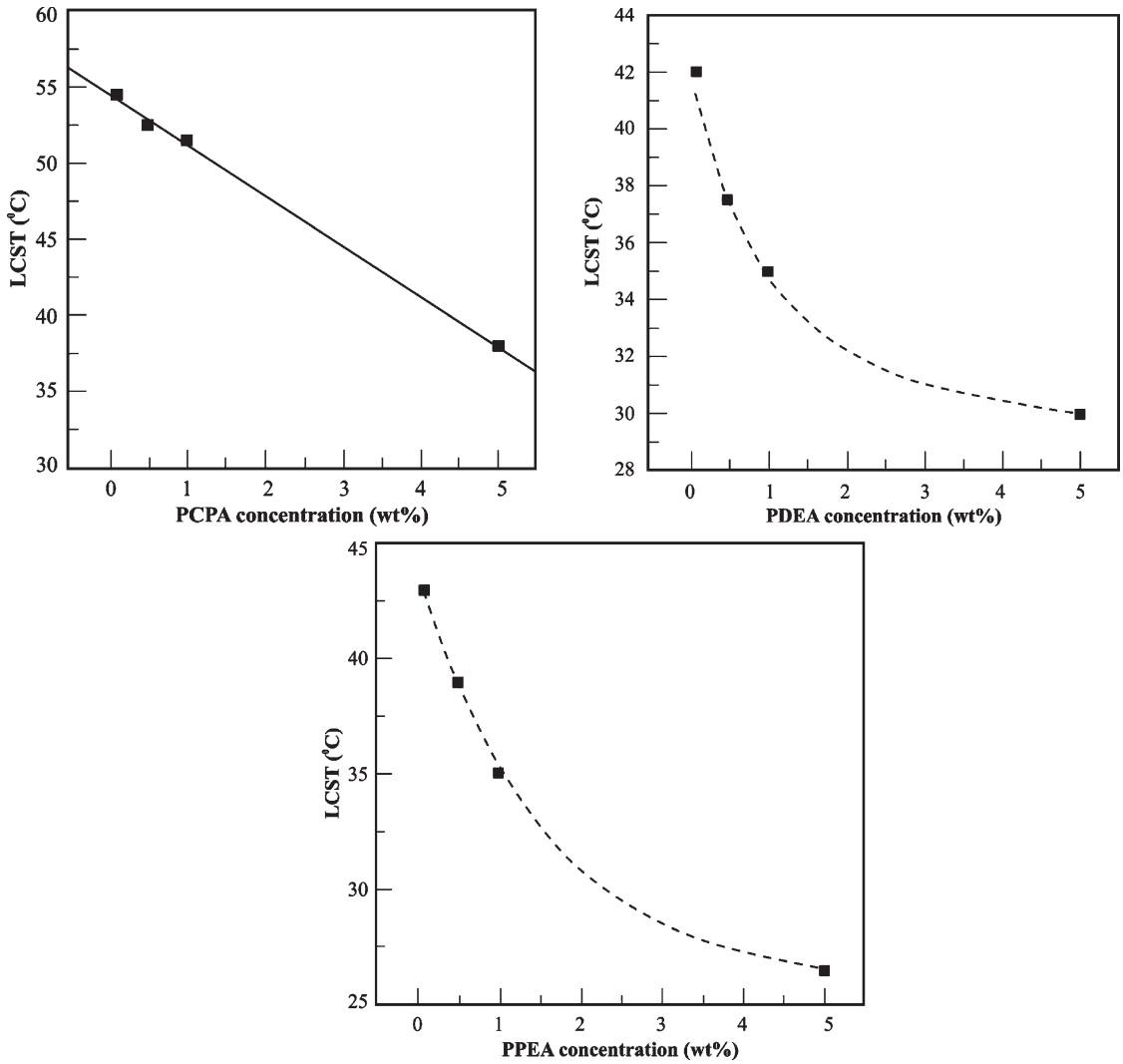


Figure 2. The effect of PCPA, PDEA, and PPEA concentrations on the LCST.

with increasing PCPA concentration and a considerable decrease is observed in the PDEA concentration range of 0.1–2.5 wt %, while the LCST decreases regularly with increasing polymer concentration in the temperature range of 25.0–42.5°C for PPEA. These situations indicate that the studied polymers have profound properties for biotechnological uses.

For all PCPA, PDEA, and PPEA concentrations, the LCST values, which were determined as the temperatures corresponding to 10% of the total absorbance change observed in Figure 1, are shown in Figure 2. The LCST values of the polymers synthesized in this study and previous studies[26,27] are given in Table II.

In the presence of salt, the temperature corresponding to the maximum point of the absorbance–temperature curve was described as critical flocculation temperature (CFT). Meanwhile, CFT is a particular temperature that is observed in flocculation behaviors with the increase of salt concentration in aqueous media for temperature sensitive polymers.

Table II. The LCST Values of the Obtained Polymers

C_p (wt %)	The LCST of PAMPA[27] (°C)	The LCST of PCPA (°C)	The LCST of PEPA[26] (°C)	The LCST of PDEA (°C)	The LCST of PPEA (°C)
0.1	56.5	54.5	42.0	42.0	43.0
0.5	46.5	52.5	35.5	37.5	39.0
1.0	43.5	51.5	33.5	35.0	35.0
5.0	35.0	38.0	32.0	30.0	26.5

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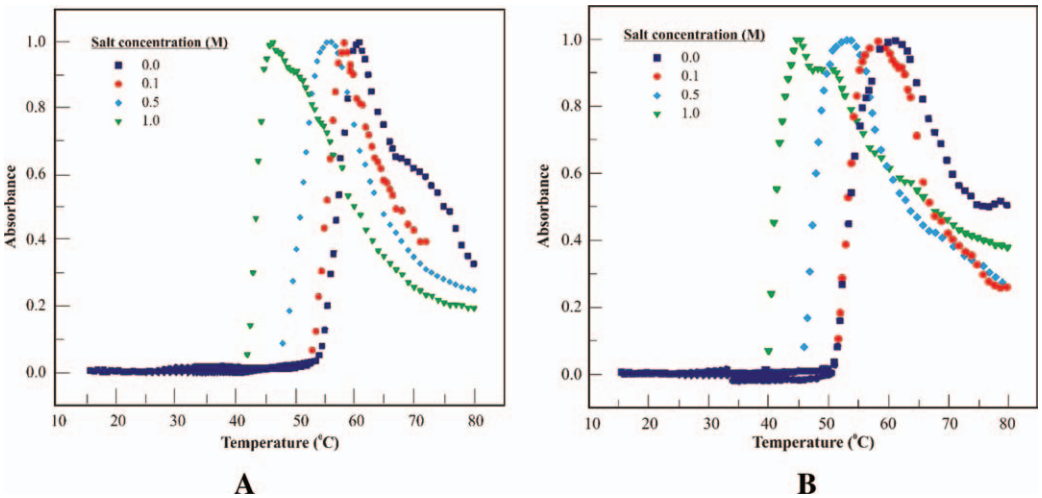

Figure 3. The curves showing the effect of salt concentration on the variation of absorbance with temperature (λ: 500 nm). PCPA concentration: (A) 0.1 wt % and (B) 1.0 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The plots showing the effect of salt (NaCl) concentration on the variation of the absorbance with temperature are given in Figure 3(A,B). These curves are utilized to determine the CFT values for PCPA. The graphs were obtained using the data from the experiments carried out with the solutions prepared at different NaCl concentrations (no salt, 0.1, 0.5, and 1.0*M* salt concentrations) for low (0.1 wt %) and high (1.0 wt %) polymer concentrations. Thermal aggregation behavior was observed in all cases studied.

In Figure 4, the effect of NaCl concentration on CFT for PCPA is seen. It is considerable here that the CFT values could be controlled by salt concentration in a wide temperature range. It can also be seen from the figure that the polymer concentration is not effective on CFT.

Figure 5(A,B) shows the effect of salt concentration on the change of absorbance with temperature and these graphs serve the purpose of determining the CFT values for PDEA. These curves were obtained using the data from the experiments carried out by utilizing the solutions prepared at different NaCl concentrations (no salt, 0.1, 0.5, and 1.0*M* salt concentrations) for low (0.1 wt %) and high (1.0 wt %) polymer concentrations. The thermoflocculation was observed in all cases except in the situation in which no salt was used with the lowest polymer concentration, as expected.

The effect of NaCl concentration on CFT for PDEA is shown in Figure 6. This behavior indicates that the CFT value is mainly controlled by salt concentration.

In Figure 7(A,B), the plots showing the effect of salt concentration on the variation of the absorbance with temperature are given and these curves are useful for determining the CFT values for PPEA. These graphs were obtained using the data from the experiments carried out by utilizing the solutions prepared at various NaCl concentrations (no salt, 0.1, 0.5, and 1.0*M* salt concentrations) for low (0.1 wt %) and high (1.0 wt %) polymer concentrations. A definite thermoaggregation occurred at all salt concentrations, although thermal aggregation behavior was not observed in the media without salt at both polymer concentrations.

In Figure 8, the effect of NaCl concentration on CFT is shown for PPEA. Here, the behavior similar to the case of temperature sensitive polymers with a relatively polar structure was observed. This means that the CFT value was controlled mainly by salt concentration, independently of polymer concentration, for PCPA having a relatively low polarity.

The addition of NaCl increases the hydrogen bonding among the water molecules and therefore decreases it among water molecules and hydrophilic chains. Subsequently, the hydrogen bonding among the hydrophilic chains becomes dominant, which results in a stronger tendency for the polymers to associate, and this situation decreases the CFT values of the

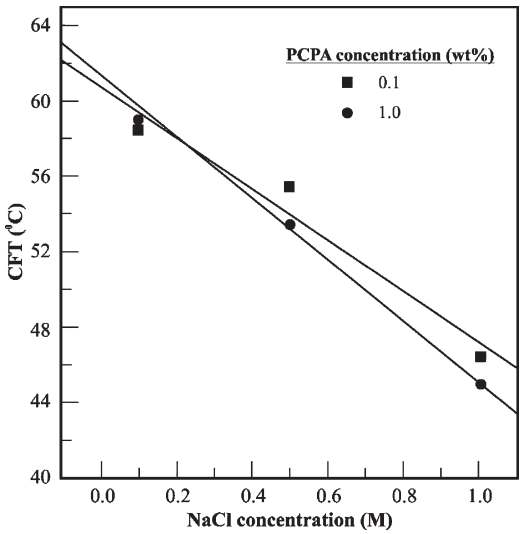

Figure 4. The effect of NaCl concentration on the CFT of PCPA.

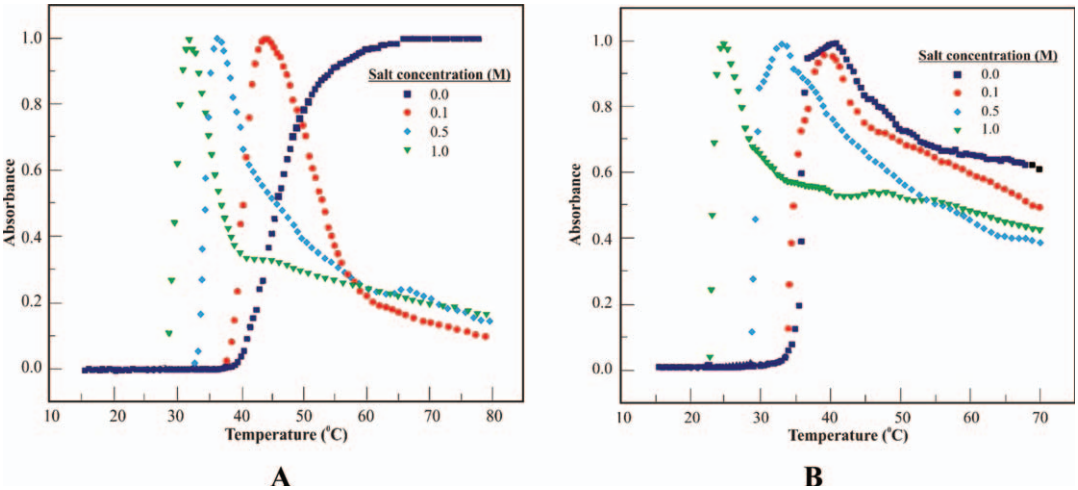

Figure 5. The curves showing the effect of salt concentration on the variation of absorbance with temperature (λ: 500 nm). PDEA concentrations: (A) 0.1 wt % and (B) 1.0 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymers.[58,59] The presence of NaCl will undoubtedly increase the polarity of the aqueous medium, thus enhancing the hydrophobic–hydrophobic interactions.[60] The stronger hydrophobic-hydrophobic interaction indicates the stronger tendency of the polymers to self-aggregation; a feature that will result in lower solubility of the polymer in water, hence a decrease will occur in CFT. Therefore, both mechanisms account for the decrease in the CFT values of the temperature sensitive polymers obtained in this study. Figures show that the lowering of CFT is a linear function of the salt concentration, supporting the observations found in the literature by different authors.[61–64] The changes in the CFT values, which are caused by the addition of sodium chloride, can be explained with salting-in effect.[64] The CFT values of the obtained temperature sensitive polymers synthesized in this and previous[26,27] studies are given in Table III.

Free energy balance involving hydrophobic, hydrophilic and H-bridge mediated interactions determines the solubility of a given polymer in water. Simple salts are generally assumed to exert their influence by acting on the water structure (salting in/salting out) and the resulting behavior can be interpreted as a consequence of the "hydrophobic effect."[52] The addition of almost all inorganic salts generally results in a decrease of the LCST which depends on the kinds of salts and their concentrations. Analyses of the salt effects on LCST for temperature sensitive polymers should also be considered for polymer–polymer, polymer–water, polymer–ion, and water–ion interactions.[50]

Ethyl alcohol was selected as solvent to investigate the effects of binary solvent mixtures on solution properties of PDEA, PCPA, and PPEA. By using ethyl alcohol, it was possible to evaluate the influence of size and shape of the hydrophobic group on the phase separation temperatures. The effect of ethyl alcohol concentration on LCST for PCPA, PDEA, and PPEA homopolymers in the ethyl alcohol/water mixtures is shown in Figure 9(A–C), respectively. The LCST values of PCPA and PPEA appear to decrease linearly with the ethyl alcohol concentration for the investigated range confirming the well-established results found in the literature on the cononsolvency phenomenon for PNIPA.[65,66] The LCST value decreases with increasing alcohol concentration in the ethyl alcohol concentration range of 0.0–20.0 % v/v for PCPA [Figure 9(A)]. However, in the aqueous ethyl alcohol, at concentrations higher than40 % v/v, the PCPA was soluble at 70°C. The similar behavior represented by polymers having hydrophobic structure was also observed in the case of PDEA after the thermal phase separation [Figure 9(B)]. The results obtained for PDEA is in accordance with those given by Panayiotou et al. for the same polymer.[51] PDEA represented temperature sensitivity in a relatively wide range of ethyl alcohol concentration (0.0–30.0 % v/v). However, thermal phase separation did not occur for alcohol concentrations higher than 40.0 % v/v. The effect of ethyl alcohol concentration on LCST for PPEA is shown in Figure 9(C). According to this figure, PPEA lost the temperature sensitivity for alcohol concentrations higher than 10.0 % v/v. This shows that PPEA has a more polar

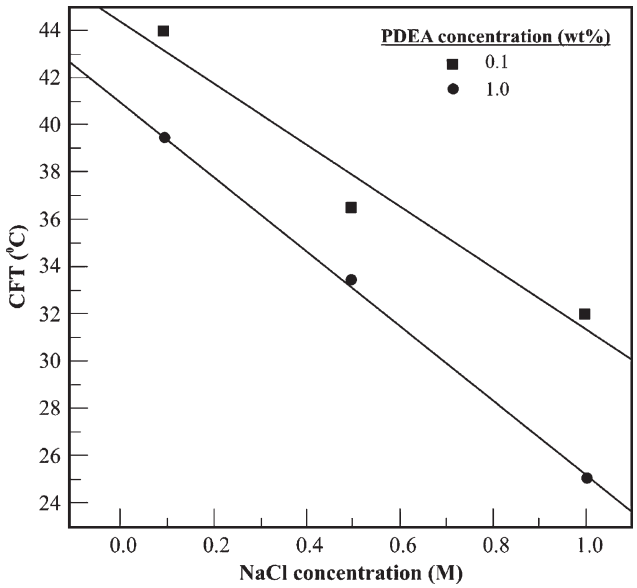

Figure 6. The effect of NaCl concentration on the CFT of PDEA.

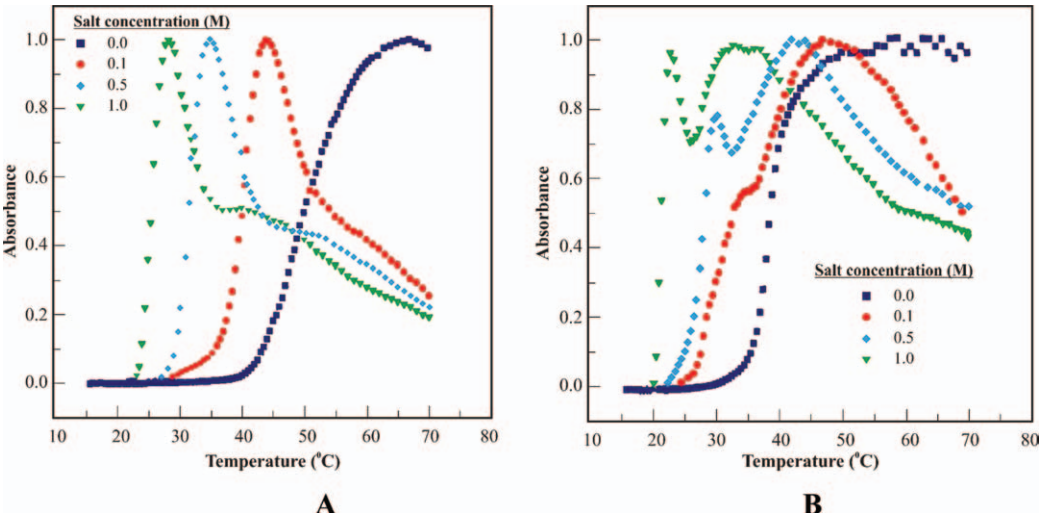

Figure 7. The curves showing the effect of salt concentration on the variation of absorbance with temperature (λ: 500 nm). PPEA concentrations: (A) 0.1 wt % and (B) 1.0 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structure with respect to the other polymers synthesized in this study. These changes in the LCST values of the PCPA, PDEA, and PPEA homopolymers may be correlated with the competition between polymer–water, water–ethyl alcohol, and polymer–ethyl alcohol interactions mediated by compositional factors.

The valuability and importance of the results on LCST and CFT were also discussed more thoroughly in our previous studies.[26,27]

Organic solvents influence the thermoprecipitation of temperature sensitive polymers from aqueous solutions. The addition of solvents may promote a drastic change in the LCST of linear poly(*N*-isopropylacrylamide) (PNIPA) molecules in solution.[65,66] For example, the addition of small amounts of a solvent like methanol to aqueous solutions of PNIPA initially decreases the transition temperature, and only a further addition of solvent promotes an increase.[66] The linear temperature sensitive polymer (i.e., PNIPA) solubility is reduced within a range of intermediate solvent concentrations in binary hydro-organic solutions, showing a rather rare phenomenon called "co-nonsolvency," which describes the situation of polymers soluble in two pure solvents but less soluble or insoluble in their mixtures, for some mixture compositions.[25] Two theories have been proposed to explain the co-nonsolvency phenomenon. Schild[25] and Schild et al.[66] supported a model based on the assumption of a preferential interaction of the organic solvent molecules (e.g., alcohol) and the polymer chains. The solubilizing effect of the hydrogen bonding between the polymer and the water molecules is much weaker in this case and solubility is reduced. Winnik et al.[67] and Asano et al.[68] suggested that the driving force for co-nonsolvency is a preferential interaction of the water with the alcohol molecules, which limits the number of solvent molecules available to solubilize the polymer.

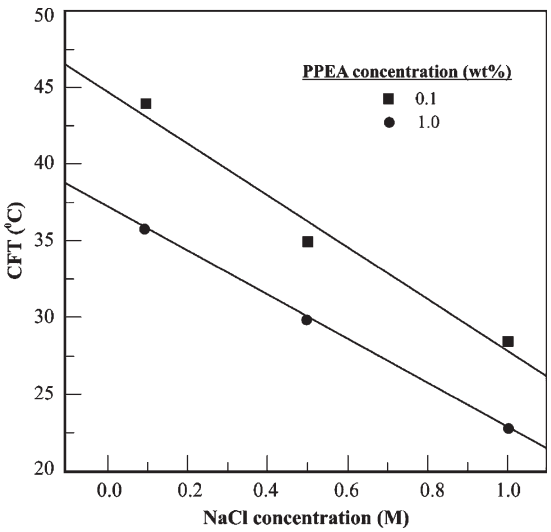

Figure 8. The effect of NaCl concentration on the CFT of PPEA.

CONCLUSION

Temperature sensitive homopolymers of polyacrylamides (PPEA, PCPA, and PDEA) with different alkyl groups have

Table III. The CFT Values of the Obtained Polymers

	CFT values (°C)				
C_{NaCl} (*M*)	PAMPA[27]	PCPA	PEPA[26]	PDEA	PPEA
C_p = 0.1 wt %					
0.1	52.5	58.5	52.5	44.0	44.0
0.5	43.0	55.5	50.0	36.5	35.0
1.0	35.0	46.5	43.5	32.0	28.5
C_p = 1.0 wt %					
0.1	47.5	59.0	37.5	39.5	36.0
0.5	37.0	53.5	34.5	33.5	30.0
1.0	28.5	45.0	32.0	25.0	23.0

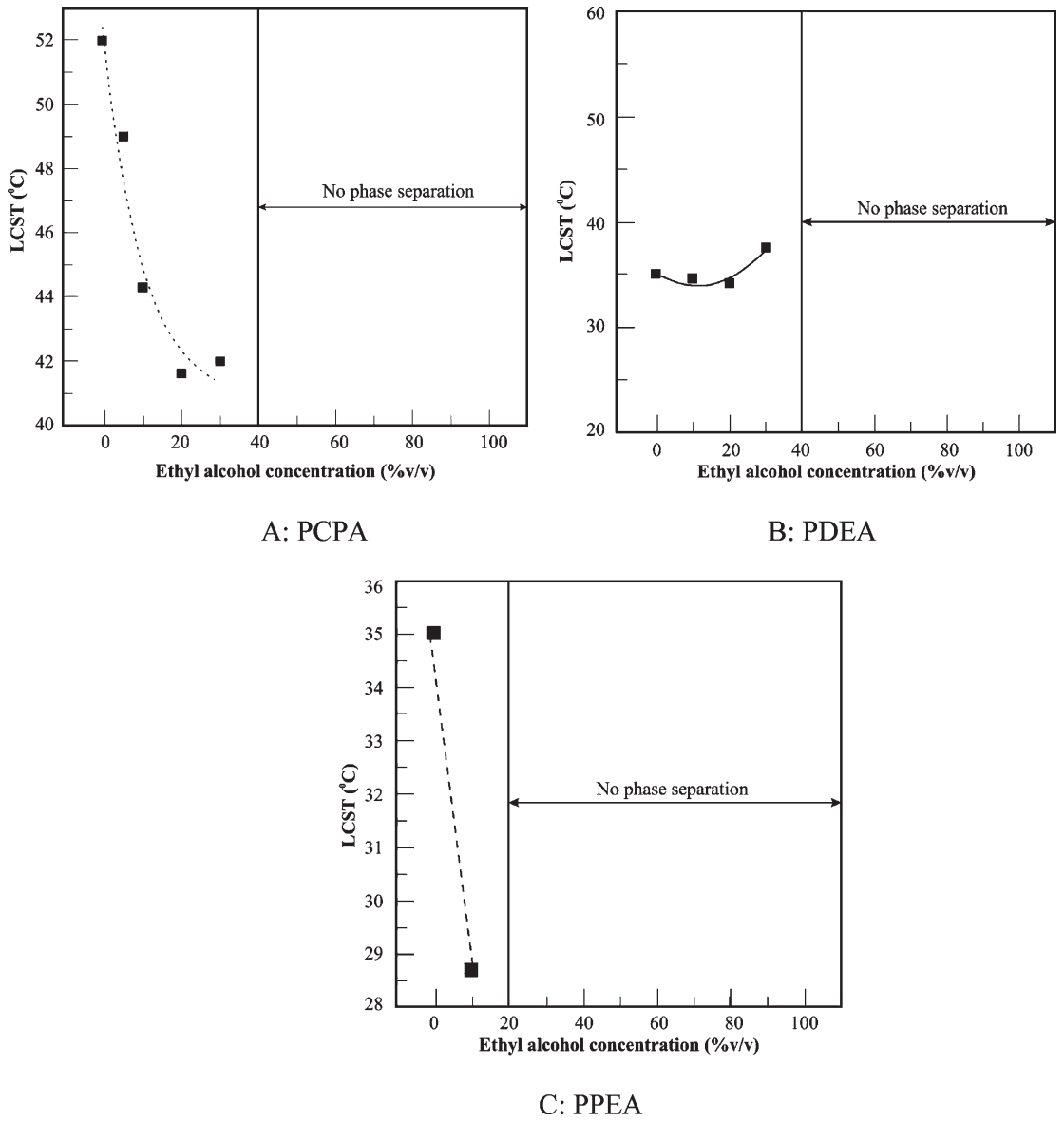

Figure 9. The variation of LCST with the ethyl alcohol concentration in the aqueous medium. PCPA (A), PDEA (B), and PPEA (C) concentrations: 1.0 wt %.

successfully prepared in the linear form by solution polymerization of the monomers, respectively, piperidineethanolacrylamide, cyclopropylacrylamide, and diethylacrylamide, which were synthesized via the nucleopylic substitution reaction of acryloyl chloride with the relevant amines. The variations of polymerization yields with the initiator concentrations were investigated for the polyacrylamides and a significant effect of the initiator concentrations on the polymerization yields was not found. The LCSTs of the homopolymers are different because the alkyl groups present in their structures are different from each other. The LCST value decreases linearly with increasing PCPA concentration and a considerable decrease is observed in the PDEA concentration range of 0.1–2.5 wt % while the LCST decreases regularly with increasing polymer concentration in the temperature range of 25–42.5°C for PPEA. The polymer concentration is not effective on CFT for PCPA while it effects the polymer concentration slightly for PDEA and PPEA. The CFT values are mainly controlled by salt concentrations for all the studied polymers due to the polarities of the polymers.

The effect of alcohol concentration on LCST for PCPA, PDEA, and PPEA was also investigated. The LCST value decreases with increasing alcohol concentration in the alcohol concentration range of 0.0–20.0 % v/v for PCPA. The similar behavior represented by polymers having hydrophobic structure was also observed in the case of PDEA after the thermal phase separation. However, the thermal phase separation did not occur for alcohol concentrations higher than 40.0 % v/v for PDEA. The PPEA lost the temperature sensitivity for alcohol concentrations higher than 10.0 % v/v since it has a more polar structure with respect to the other polymers synthesized in this study.

The novel temperature sensitive polymer, polypiperidineethanolacrylamide (PPEA), synthesized for the first time in this study, and the other polymers, PDEA and PCPA, and their temperature sensitivity behaviors, were investigated in details in the present study. The obtained polymers are all useful for further studies for various applications. Especially, the different forms of these polymers, like their hydrogel forms, should be studied. The uses of these polymers and their different forms, like hydrogels and novel copolymers, in various areas such as biotechnology, controlled drug release, advanced separation methods, gene delivery, etc. are also potential subjects for future studies.

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