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ORIGINAL CONTRIBUTION

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Phase transition of aqueous solutions of poly(*N,N*-diethylacrylamide-*co*-acrylic acid) by differential scanning calorimetric and spectrophotometric methods

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Abstract The phase transition of aqueous solutions of poly(*N*,*N*-diethylacrylamide-*co*-acrylic acid) (DEAAm–AA) is studied by differential scanning calorimetry (DSC) and UV–vis spectrophotometry. The copolymer aqueous solutions are shown to have well-defined lower critical solution temperatures (LCSTs). The LCST values obtained from the maximum of the first derivatives of the DSC and optical transition curves agree well. DSC can be used to measure the phase-transition temperature of more dilute polymer solutions. On increasing the AA composition in the copolymers, the LCST values of the copolymer increase, then decrease at higher AA composition. For the aqueous solution of the copolymers, the transition curve obtained by the spectrophotometric method is highly wavelength dependent. The LCST values are found to be concentration-dependent. The changes in the heat of the phase transition of the copolymer solutions measured from DSC are lower than that of the homopolymer PDEAAm solution. This is consistent with the suggestion that the polymer chains of the copolymers collapsed only partially at temperatures above the LCST. The added salt (sodium chloride) decreases the transition temperature of the polymer solution.

Key words Phase transition · *N*,*N*-Diethylacrylamide · Acrylic acid · Differential scanning calorimetry

Introduction

The volume-phase transitions of polymer aqueous solution and polymer gels have attracted much attention in recent years [1–7]. Remarkable progress has been made in the understanding of the phase transitions and critical phenomena in polymer solutions. Most of the studies have focused on poly(*N*-isopropylacrylamide) (PNIPAAm) and its copolymers [8–16]. PNIPAAm exhibits a well-defined lower critical solution temperature (LCST) in water around 32 °C [17]. The cross-linked PNIPAAm gel undergoes an analogous collapse transition temperature in aqueous solvent [18]. It is commonly accepted that this phase transition and the accompanying changes in polymer conformation are the results of a delicate balance between the hydrophobic interactions and hydrogen bonding. The phase transition is a process of extended coil to compacted globule collapse of the polymer chain, and then it aggregates to precipitate from solution [6].

Apart from PNIPAAm, several other N-substituted polyacrylamides also exhibit phase-transition behaviour. The LCST values of homopolymers of *N*-ethylacrylamide and *N*-cyclopropylacrylamide have been reported [19–21]. Recently, attention has been paid to poly(*N*,*N*-diethylacrylamide) (PDEAAm) as an alternative thermosensitive water-soluble polymer to PNIPAAm [22–24]. Idziak et al. [22] reported that the LCST of PDEAAm is around 33 °C, while Itakura et al. [23] have demonstrated that PDEAAm is not molecularly dissolved in water but forms molecular aggregates below the cloud point in a one-phase region. On the other hand, although the structure of the alkyl group of acrylamide is most important to determine the solution behaviour, the LCST of the thermosensitive polymers can be varied by copolymerizing with hydrophilic or hydrophobic monomers or by the addition of salts and surfactants in the aqueous solutions [25, 26]. A better understanding of the properties of these copolymers should help in developing new thermosensitive polymers or hydrogels. In this work, hydrophilic monomer acrylic acid (AA) was copolymerized with DEAAm. Differential scanning calorimetry (DSC) and UV–vis spectrophotometry were used to measure the phase-transition temperatures. The effect of AA contents in the copolymer on the phase-transition temperature were studied. The variation of the molecular conformation of the copolymer in aqueous solution with transition temperature are also discussed.

Experimental

Materials

Acryloyl chloride, diethylamine, triethylamine, sodium chloride and sodium hydroxide were used as received from Aldrich Chemical Co. 2,2′-Azobis(isobutyronirile) (AIBN) was recystalized from ethanol. AA was distilled under vacuum at 60 °C to remove inhibitor. Tetrahydrofuran (THF), acetone and hexane were all reagent grade and were used as received.

Monomer synthesis

A mixture of acryloyl chloride (36 ml) in 100 ml THF was added slowly to a mixture of diethyamine (67.5 ml), triethylamine (96 ml) and THF (200 ml). The reaction temperature was kept at 0–5 °C. After all the acryloyl chloride had been added, the solution was left at room temperature overnight. The salt which precipitated was removed by filtration. The filtrate was stripped off the solvent using a rotary evaporator. The crude product was then distilled in the presence of hydrochinondiemethylaether (inhibitor) under vacuum at 80 °C, to yield a colourless liquid product (35 g, 70%). The ^{1}H NMR ($CDCl_3$, δ ppm) data were 1.1 (tt, 6H, $J = 7$ Hz, $-CH_3$), 3.4 (qq, 4H, $J = 7$ Hz, $-CH_2$), 5.7 (d, 1H, $J = 12$ Hz, $CH_2=$), 6.1(d, 1H, $J = 17$ Hz, $CH_2=$), 6.6 (dd, $J = 11$, 6 Hz, 1H, $=CH$). The assignment of the ^{13}C-NMR of DEAAm is 12.55 and 13.99 ppm, 2($-CH_3$); 41.81, 47.07 ppm, 2($-CH_2-$); 128.53, 128.23 ppm, ($CH_2=$ and $CH=$); 168.44 ppm, ($=O$).

Polymer synthesis

PDEAAm and P(DEAAm–AA) were prepared by solution radical polymerization. The polymerization was carried out in a 50-ml round-bottomed flask with stirring. Both DEAAm and AA were dissolved in methanol and the final solution contained 30% (w/w) of total monomers. After AIBN (0.5 wt% of total monomer) had been added, the solution was purged with nitrogen gas for 15 min. The reaction was carried out at 55 °C for 8 h. The products were diluted with acetone before precipitation in hexane. After filtration, the product was finally dried at room temperature under vacuum. The compositions of the copolymers were determined by potentiometric titration conducted with a ABU93 triburette titration system. The molecular weights of the copolymers were determined using a Brookhaven BI-200SM goniometer laser light scattering instrument, which is equipped with a 532-nm channel BI9000AT digital multiple-τ correlator. The solvent for dissolving the samples was methanol.

Spectrum measurements

The NMR measurements and the IR measurements were recorded using a Bruker ACF-400 (400 MHz) Fourier transform (FT) spectrometer and a Perkin-Elmer FTIR spectrometer (model 1725X), respectively.

Spectrophotometer measurements

The percentage transmittance of the polymer solution was measured using a Lambda 2 (Perkin Elmer) spectrophotometer which was connected to a programmable temperature scanning water bath controller and a Pantinum II computer for data acquisition. The sample temperature was monitored by an external sensor. The heating rates were manually controlled at 0.5 °C/min for all runs. The LCST values were determined from the maxima of the first derivatives of the transmittance against temperature curves.

Calorimetric measurements

Scanning calorimetric measurements were made by using a MicroCal Mc-2 high-sensitivity differential scanning calorimeter (MicroCal, Northampton, Mass., USA). The origin^{TM} software supplied by manufacturer was used for DSC data collection and analysis. Samples were run against the appropriate reference samples. The sample and the reference solutions (distilled water) were degassed to remove bubbles and were transferred to the respective cells with a syringe. Reference solutions in both cells were run to obtain the baseline, which was subsequently subtracted from the sample scans. All the solutions within the cells were kept under nitrogen to suppress bubble formation. Data acquisition and analysis was carried out using the Micro DSC software package. The excess heat capacity, $C_{p,\mathrm{ex}}$, of the sample solution was calculated from the difference between the sample and the reference traces. The enthalpy change for the transition, ΔH, was calculated from the area under the peak. The LCST value was determined from the maximum of the first derivative of the heat capacity versus temperature plot.

Results and discussion

Wavelength dependence of optical transition curve

The compositions and molecular weights of the copolymers DEAAm–AA and PDEAAm are shown in Table 1. The percentage transmittance versus temperature curves for 0.5 wt% aqueous solution of DEAAm–AA-6 are shown in Fig. 1. It can be seen that the longer the wavelength, the broader the transition curves. At shorter wavelength (400 nm), when the temperature is raised to 34.3 °C, the percentage transmittance decreases from 97 to 0.1%. For longer wavelengths, at 720 nm, even when the temperature has risen to 36 °C, the percentage transmittance is still 36.4%.

Table 1 The compositions of *N*,*N*-diethylacrylamide (*DEAAm*) copolymers. Acrylic acid (*AA*)

Samples	Feed ratio in monomer DEAAm/AA (mol/mol)	Composition in copolymers DEAAm/AA (mol/mol)	Molecular weight in methanol ($\times 10^{-5}$ mol/g)
Poly(DEAAm)	100/0	100/0	4.12
DEAAm–AA-6	94.01/5.98	94.02/5.98	3.19
DEAAm–AA-13	89.78/10.22	86.77/13.22	3.06
DEAAm–AA-20	79.87/20.13	79.36/20.64	3.08

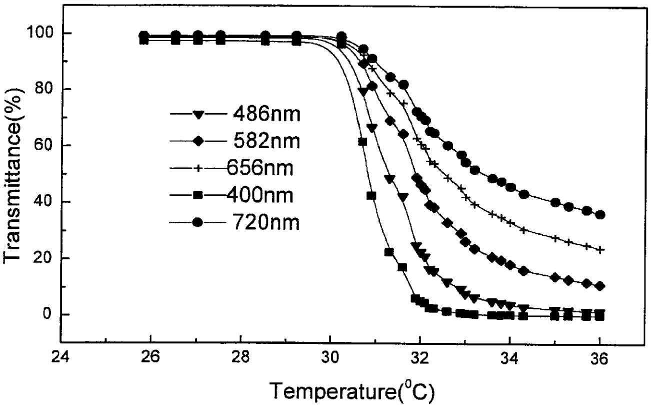

Fig. 1 The percentage transmittance curves of 0.5 wt% aqueous solution of *N*,*N*-diethylacrylamide–acrylic acid (*DEAAm–AA-6*) at different wavelengths

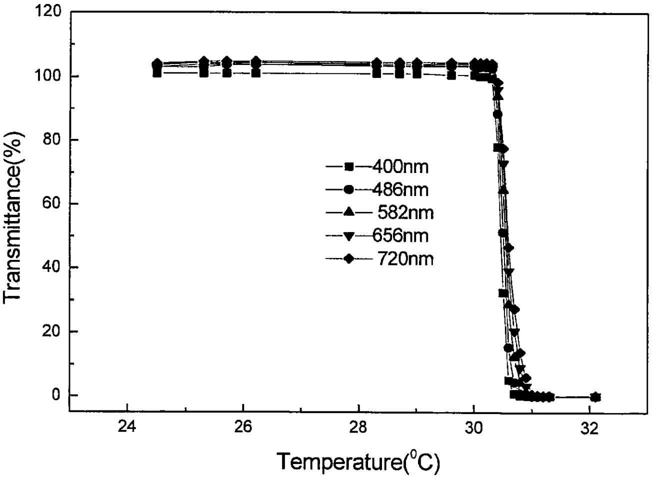

Fig. 2 The percentage transmittance curves of 0.5 wt% aqueous solution of poly(DEAAm) at different wavelengths

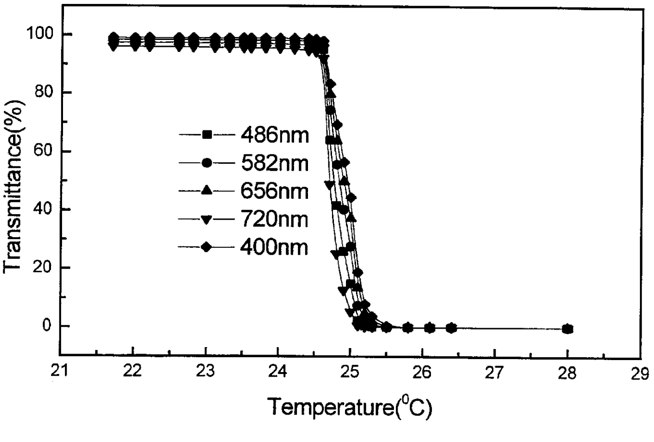

Fig. 3 The percentage transmittance curves of 0.5 wt% aqueous solution of DEAAm–AA-6 with 0.05 M NaCl at different wavelengths

On the other hand, the PDEAAm aqueous solution with the same concentration shows a much sharper transition at the range of wavelengths studied, from 400–720 nm as shown in Fig. 2. When the temperature is raised from 30.3 to 30.7 °C, the percentage transmittance reduces from 100 to 0%. The transition temperature range is only 0.4 °C. When NaCl salt is added to the aqueous solution of the DEAAm–AA copolymer, the percentage transmittance–temperature curves become sharper (Fig. 3). Compared with the nonsalt aqueous solution, the LCST decreases by 3 °C. Carey and Ferguson [27] indicated that the temperature dependence of the thermosensitive polymer is due to the delicate balance between enthalpy and entropy which determines the concentrations of hydrophobic and hydrophilic groups present at the polymer/water interface. In the PDEAAm aqueous solution, when the water temperature increases, the polymer surface become more hydrophobic, the PDEAAm molecular chains aggregate to form bigger particles and they finally phase-separate from solution. This process is fast and the percentage transmittance changes sharply with temperature. The broader optical transmittance transition of DEAAm–AA-6 aqueous solution is believed to be due to the presence of the hydrophilic AA group in the copolymer. The partially ionized carboxylic acid groups make the copolymer chains more difficult to collapse because of the electrostatic repulsions when the temperature is raised. The added salt has the effect of enhancing the hydrophobic polymer–polymer interaction by breaking up the order structure of water and disrupting the hydrogen bonds of the carboxyl groups with water molecules [22]. The polymer chain in the salt solution is less extended than that in nonsalt solution; hence, a shaper phase-transition curve is observed.

From the percentage transmittance versus temperature curve, the LCST value can be obtained by using two different methods: one is to take the temperature corresponding to a 10% reduction in the percentage transmittance change; the other is to take the temperature at which the differential of the percentage transmittance with respect to temperature is a maximum [8]. We find that the peak of the first derivative of the percentage transmittance versus temperature is sharper than that of the percentage transmittance–temperature plot, so we define here the maximum of the first derivative of the percentage transmittance–temperature plot as the LCST of the polymer solution. The LCST values of 0.5 wt% aqueous solutions of DEAAm–AA and PDEAAm are presented in Table 2. It is found that the LCST value is wavelength-dependent for aqueous solution of DEAAm–AA-6. The LCST value decreases with increasing wavelength. A 1.4 °C difference is observed for the transitions measured at 400 and 720 nm; however, for the copolymer solution with added NaCl and the nonsalt homopolymer PDEAAm solution, the transitions are very sharp and no wavelength dependence is observed.

Effect of heating–cooling process on the phase transition

The percentage transmittance versus temperature curve of a 0.5 wt% DEAAM–AA-13 aqueous solution at 582 nm, for both the heating and cooling cycles, is shown in Fig. 4. There is a slight shift in the transition curve, suggesting that the phase transition is not completely reversible and that some hysteresis has taken place in this system. This indicates that the transition is macroscopically kinetically limited. Compared with the heating process, the speed of dissociation of the aggregated particles is slower when cooling. This is consistent with the result from light scattering experiments that PDEAAm can form fairly stable larger aggregates in water at high temperature which are hard to decompose by cooling and further repeated heating [23].

Table 2 The lower critical solution temperature values of solutions of DEAAm polymers. All solution concentrations are 0.5 wt%, the salt concentration in the DEAAm–AA-6-S is 0.5 M NaCl

Wavelength(nm)	400	480	582	656	720
DEAAm–AA-6	30.7	31.8	31.9	31.9	32.1
Poly(DEAAm)	30.5	30.5	30.5	30.5	30.5
DEAAm–AA-6-S	28.1	28.1	28.1	28.1	28.1

Effect of polymer concentration

DSC curves of DEAAm–AA-13 with different polymer solution concentrations are shown in Fig. 5. All the DSC curves are asymmetrical with a steep leading region before approaching the maximum of excess heat capacity ($C_{p,\mathrm{max}}$). We take the maxima of the first derivatives of the curves as the LCST values of the solutions (inset of Fig. 5). The LCST values, determined by both the DSC and the spectrophotometric methods at different concentrations, for the two copolymers and the homopolymer of DEAAm are

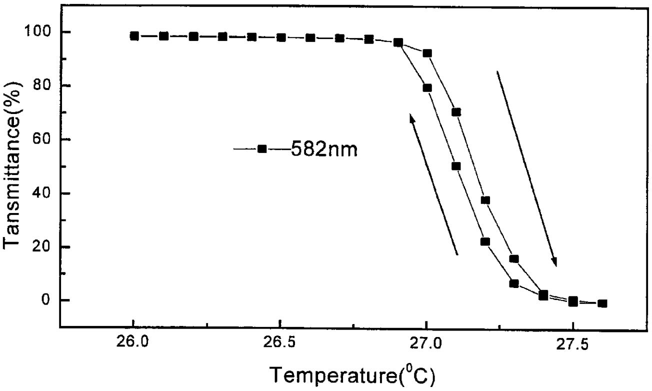

Fig. 4 The percentage transmittance versus temperature curves of 1 wt% DEAAm–AA-13 aqueous solution at 582 nm through the heating and cooling circles

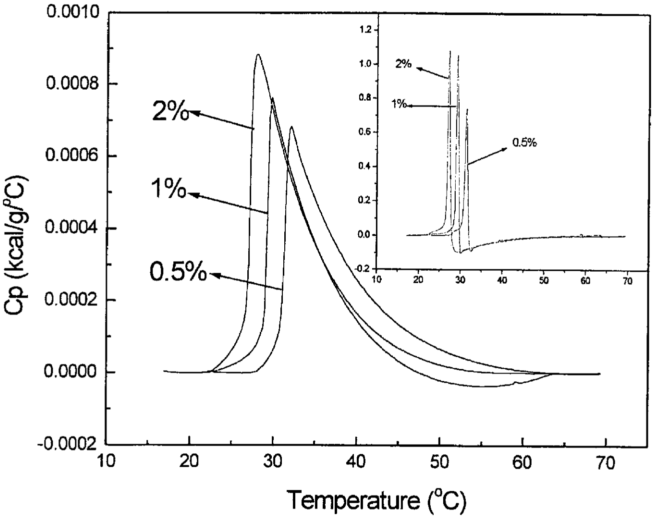

Fig. 5 The differential scanning calorimetry (*DSC*) curves of DEAAm–AA-13 aqueous solution with concentrations of 0.5, 1 and 2 wt%. The heating rate is 60 K/h. The first derivatives of the curves are shown in the *inset*

shown in Fig. 6. It can be clearly seen that as the concentration increases, the LCST decreases. For a dilute solution of 0.1 wt%, the copolymer samples DEAAM–AA-6 and DEAAm–AA-13 show no transition by the spectrophotometric method. At the same concentration, a phase transition can be detected for the PDEAAm homopolymer. This should be due to the fact that by copolymerization with AA, the copolymer can form stabler nanoparticles than PDEAAm, which just forms molecular aggregates in the one-phase region [23, 28]. In these aggregated particles, the carboxylic groups may lie outside the coils and they repel each other. The electrostatic repulsion renders the polymer particles stabler even at high temperature, and they do not aggregate further and precipitate. In dilute solution (0.1 wt%), these ionic particles are too small compared to the wavelength setting of the spectrophotometric measurement to be detected. In PDEAAm solution, owing to there being no electrostatic repulsion, the polymer particles are less stable and aggregate more easily to form bigger particles and they precipitate at low solution concentrations. This is the main reason why the phase transition could be observed at low concentrations by spectrophotometric methods for PDEAAm. The results in Fig. 6 suggest that DSC is more sensitive than the spetrophotometric method for the study of the phase transition of polymer solutions.

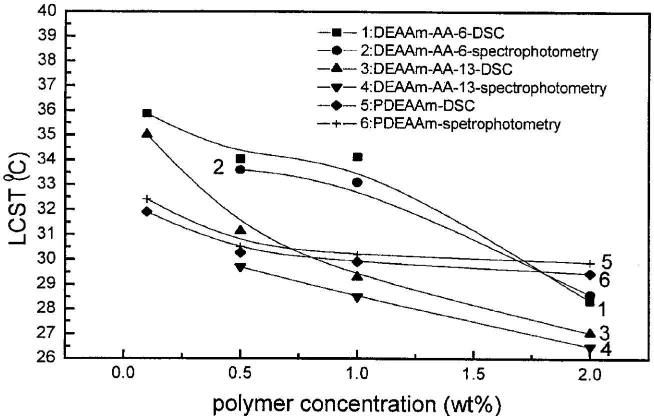

Fig. 6 The lower critical solution temperature (*LCST*) values obtained by calorimetric measurement and the spectrophotometric method at 582 nm

Thermodynamic results by DSC

The thermodynamic parameters of DEAAm–AA copolymers at different concentrations obtained by the DSC method are presented in Table 3. When the concentrations of DEAAM–AA-6 and DEAAM–AA-13 increase from 0.1 to 0.5 wt%, the ΔH values increase by a factor of approximately 2.2 and 5.2, respectively. After the initial increase, the ΔH values do not change much on further increase in the polymer concentration from 0.5 to 2 wt%. In the phase-transition process, it is believed that the polymer molecules first undergo an intrachain collapse, followed by interchain aggregation [28]. In very dilute solution (0.1 wt%), the interchain aggregation may not be complete, giving rise to lower ΔH values. These phenomena are more evident for the two copolymers DEAAm–AA-6 and DEAAm–AA-13 compared to the PDEAAm homopolymer. The electrostatic repulsion of the carboxylic groups in the copolymers could have prevented the complete collapse of the polymer chains. For the same reason, it can be seen that even at higher concentrations, the ΔH values of the two copolymers are substantially lower than that of the PDEAAM homopolymer.

Table 3 Thermodynamic parameters of aqueous solutions of DEAAm polymers at different concentration. ΔH_{cal}: the calorimetric enthalpy of the transition; T_{m}: the temperature at which the excess heat capacity of the transition is a maximum; $\Delta T_{1/2}$: the width of the transition in degrees at half the maximum of the excess heat capacity; T_0: the point at which the baseline intercepts with the onset temperature

Sample	Concentration (% w/w)	Scan rate (K/h)	ΔH (J/g ±0.01)	$C_{p,\mathrm{max}}$ (J/g/K ±0.001)	T_{m} (°C ±0.01)	$\Delta T_{1/2}$ (°C±0.01)	T_0 (°C ±0.01)
PDEAAmC1	0.1	60	34.20	4.778	33.13	7.02	31.74
PDEAAmC2	0.5	60	53.26	5.325	31.81	9.27	30.13
PDEAAmC3	1	60	47.99	4.780	31.12	8.53	29.40
PDEAAmC4	2	60	47.74	4.657	30.79	9.02	28.67
DEAAm–AA-6-C1	0.1	60	14.30	1.994	36.11	6.41	32.28
DEAAm–AA-6-C2	0.5	60	31.14	3.344	36.52	7.28	35.76
DEAAm–AA-6-C3	1	60	34.49	3.494	34.71	6.27	33.98
DEAAm–AA-6-C4	2	60	37.33	5.229	28.95	5.53	28.23
DEAAm-AA-13C1	0.1	45	4.68	0.890	36.45	6.22	34.43
DEAAm–AA-13C2	0.5	45	24.37	2.867	32.01	6.60	30.94
DEAAm–AA-13-C3	1	60	23.24	3.076	29.68	5.53	28.53
DEAAm–AA-13-C4	2	60	30.18	3.670	27.98	5.86	26.95

Influence of AA content on the LCST of DEAAm–AA copolymer

The effect of AA content in the copolymer on the LCST values is shown in Fig. 7. With increasing AA content, it is found that the LCST values first increase slightly, after reaching a maximum at 7 mol%, then decrease to lower temperatures than that of PDEAAm. Wu and Zhou [29] have reported the transition temperatures of the copolymers NIPAAm-*co*-AA using a laser light scattering technique. The transition temperatures are found to increase with AA contents up to 6.2 mol%; however, transition temperatures arenot reported for samples with AA content higher than 6.2 mol%. The effect of AA composition on the LCST of DEAAm–AA copolymer solution can be explained as follows. By incorporating a small amount of AA, the hydrophilicity of the copolymer is enhanced through hydrogen bonding with water, causing the LCST value to increase initially. As the AA content in the copolymer increases further, the extent of the hydrogen bonding between the carboxylic groups (intramolecular and intermolecular) also increases, causing the polymer chain to collapse at a lower temperature. In our experiments, it is found that when the AA content is more than 25 mol% in the feed, the copolymers obtained are not soluble in water; however, these copolymers become soluble after being titrated to basic pH with sodium hydroxide. The hydrogen bonding interaction between the carboxylic acid groups is then destroyed in basic conditions; hence, the solubility of the copolymers increases.

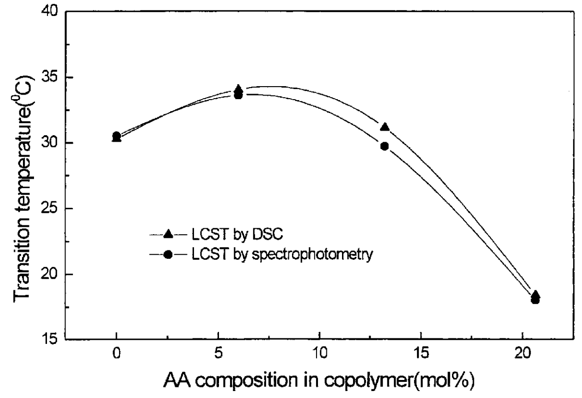

Fig. 7 Effect of AA content on the LCST values of copolymer aqueous solutions at 0.5 wt% concentration

Effect of heating rate of DSC on the LCST

The effect of the experimental heating rate on the DSC thermogram is illustrated in Fig. 8. It is found that different heating rates of 35, 45 and 60 K/h have an insignificant effect on the values of T_m and $C_{p,\max}$; however, there is a very slight increase in the ΔH value with increasing heating rate (Table 4).

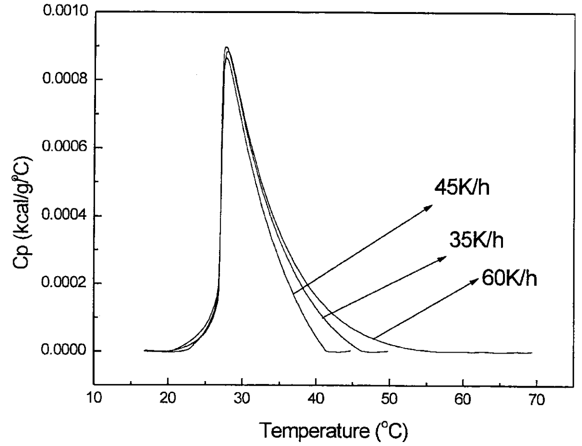

Fig. 8 Effect of DSC scanning rate on the transition of DEAAm–AA-13 aqueous solution, with a concentration of 2 wt%

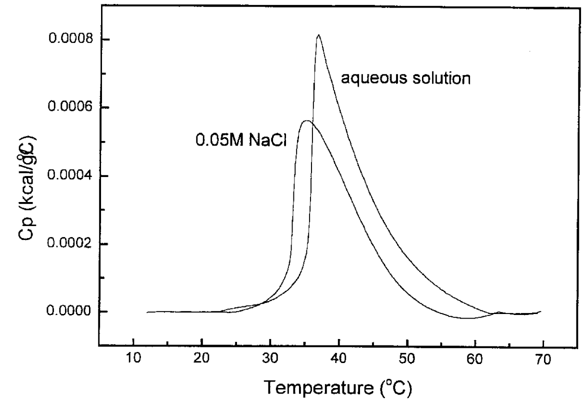

Fig. 9 The DSC thermograms of 0.5 wt% aqueous solution of DEAAm-AA-6 with salt and without salt at a scanning rate of 60 K/h

Table 4 Calorimetrically recorded parameters for 2 wt% DEAAm–AA-13 aqueous solution. The meanings of all parameters are same as in Table 3

Scan rate (K/h)	ΔH (J/g, ±0.01)	$C_{p,\max}$ (J/g/K ±0.001)	T_m (°C ±0.01)	$\Delta T_{1/2}$ (°C ±0.01)	T_0 (°C ±0.01)
35	25.96	3.666	27.78	5.65	27.1
45	27.00	3.666	27.73	5.86	27.1
60	30.18	3.670	27.98	6.23	27.1

Effect of salt on the phase transition

The micro DSC thermograms of DEAAM–AA-6 solutions without and with salt are shown in Fig. 9. The added NaCl weakens the hydrogen bond interaction between the polymer chain and water, making the polymer chains collapse at a lower temperature. The LCST value of the salt solution is lower by 1.58 °C compared to that of the nonsalt solution.

Conclusions

Solution polymerization of DEAAm with AA produces thermosensitive copolymers in solution. The AA composition in the copolymer affects the LCST values of the copolymer solution. The LCST value increases initially with increasing AA content then decreases as the AA content increases further. The phase-transition temperatures of the copolymers were obtained by both spectrophtometric and calorimetric methods, but DSC can be used to detect the transition temperature of more dilute polymer solutions. As the polymer concentration increases, the LCST values decrease. It is interesting to note that in the spectrophotometric method, the percentage transmittance–temperature curves are wavelength-dependent for aqueous solutions of the copolymers. This was explained as being due to the high stability of the collapsed polymer chain because of the electrostatic repulsion of the partially ionized AA group in the copolymers. The particles do not aggregate to a bigger size, as in the case of PDEAAm homopolymer. In the PDEAAm aqueous solution and the DEAAm–AA aqueous solution with salt, there is no wavelength dependence for the percentage transmittance–temperature curves, owing to the lack of electrostatic repulsion interactions.

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