Effect of the molecular weight on the lower critical solution temperature of poly(*N*,*N*-diethylacrylamide) in aqueous solutions¹

D.G. Lessard, M. Ousalem, and X.X. Zhu

Abstract: The molecular weight dependence of the lower critical solution temperature of poly(N,N)-diethylacrylamide) was studied with 11 samples of the polymer with a number-average molecular weight (M_n) ranging from 9.6×10^3 to 1.3×10^6 g mol⁻¹ and relatively narrow polydispersity indices from 1.19 and 2.60. These samples were obtained by fractional precipitation of the polymer. LCST values of polymers were measured by turbidimetry and microcalorimetry. An inverse dependence of LCST on the molar mass was found and the LCST of the samples remained more or less a constant above a critical molecular weight of ca. 2×10^5 g mol⁻¹. The enthalpy and the entropy changes as well as the LCST of the polymer depend strongly on the molar mass of the polymer, especially in low molecular weight range.

Key words: poly(N,N-diethylacrylamide), LCST, thermosensitive, phase diagram, effect of molecular weight.

Résumé : L'effet de la masse molaire sur la température critique de dissolution inférieure (LCST) du poly(*N*,*N*-diéthylacrylamide) a été étudié sur 11 fractions de masses molaires moyennes en nombre (M_n) variant entre 9.6 × 10³ à 1.3×10^6 g mol⁻¹ et ayant un indice de polydispersité situé entre 1.19 et 2.60. Ces échantillons ont été obtenus par précipitation fractionée. La LCST des solutions aqueuses du polymère a été mesurée par turbidimétrie et par microcalorimétrie. Il a été constaté que la LCST diminue avec la masse molaire de l'échantillon. Les valeurs de la LCST demeurent cependant relativement constantes pour des masses molaires supérieures à 2×10^5 g mol⁻¹. L'enthalpie et l'entropie associées aux changements de phases diminuent de la même façon avec l'augmentation de la masse molaire.

Mots clés : poly(N,N-diéthylacrylamide), température critique de dissolution inférieure, thermosensible, diagramme de phase, effet de la masse molaire.

Introduction

Thermosensitive polymers are known to undergo changes in their physical properties when the temperature is varied. Many *N*-substituted polyacrylamides in water exhibit reversible-phase separation upon heating. The temperature at which precipitation of the polymer occurs is called the lower critical solution temperature (LCST). Materials which show this behavior in water are of a great interest for medical (1) and industrial (2) applications. The most extensively studied polymer in this family is probably poly(*N*-isopropylacrylamide) (PNIPAM). Our research focuses on the effect of the molar mass on the LCST of aqueous solutions of poly(*N*,*N*-diethylacrylmide) (PDEA), which behaves similarly as PNIPAM.

Different researchers have explained the LCST phenomenon of polymers in water. It was ascribed to the greater entropy in the two-phase system than in a homogeneous

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¹This paper is dedicated to Professor G.R. Brown, who passed away on June 19, 2001.

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solution (3, 4), the formation of hydrogen bonds between the polymer and water (3, 5), the hydrophobic interactions between the polymer side chain groups (3, 6), and the disruption of specific hydrogen-bonded cyclic structure in alkyl amide units and hydroxyl functions of water (7).

Only a few studies were conducted on PDEA even though this polymer behaves similarly as PNIPAM without the ability to form hydrogen bridges with a proton on the amide group and the solvent. This polymer may be synthesized by anionic polymerization (8, 9), group transfer polymerization (8, 10), or free radical polymerization (7, 8, 10–14). It was observed that for PDEA of low molar masses ($M_n < 5000 \text{ g mol}^{-1}$) the transition temperature is 10°C higher for isotactic polymers than for their syndiotactic homologues. Different initiators were used for these tactic samples and the difference in the end-group was attributed as the origin of the discrepancy in their LCST values (8).

The aqueous solutions of PDEA can undergo precipitation between 25 and 36°C as determined by means of turbidimetry (8, 11, 15–17), differential scanning calorimetry (7, 8, 11, 17, 18), small angle neutron scattering (20), dynamic and static light scattering (10), IR spectroscopy (7), and rheology (10, 14). Early research focused on the parameters such as the addition of salts (11, 15, 17) and surfactant (11), co-monomer content (13, 14, 17, 19), and concentration of the polymer (8, 11, 16). The self-diffusion coefficients of small molecules in PDEA aqueous solutions and gels were also determined by the use of pulsed-gradient spin-echo NMR techniques (12). Most of these studies dealt with polydisperse PDEA samples, and none of them addressed clearly the question of the molecular weight effect on the LCST of the polymers.

In the present work, using fractional precipitation, we prepared 11 PDEA fractions with molar masses ranging from 9.6×10^3 to 1.3×10^6 g mol⁻¹. Turbidimetry, also called cloud point technique, and microcalorimetry were used to study the effect of molecular weight on the LCST of these fractions in aqueous solutions.

A number of parameters have been reported to influence the LCST of thermosensitive polymers. It was shown that the presence of salts in the solution generally decrease the LCST of the solution (5, 20) and added surfactants improve the solubility of the polymer, thereby raising the LCST (20-22). Also, phase separations were studied as functions of the amount of cosolvent (23), polymer concentration (24), and pressure (25). Investigations of molecular weight influence on the LCST, however, showed a large discrepancy in the results obtained. Some authors reported an inverse dependence of the LCST on the molar mass (5, 24), while others claimed the opposite (26). Several studies also reported that the molecular weight had no influence on the LCST (6, 27). It is worthwhile to mention that the fractionation of this kind of polymers is quite difficult due to the amphiphilicity of the macromolecule.

Experimental section

All chemicals were purchased from Sigma (St. Louis, Missouri, U.S.A.) and Aldrich (Milwaukee, Wisconsin, U.S.A.) and were used as received. Ammonium persulfate was recrystallized before use.

Polymer synthesis

N,*N*-Diethylacrylamide (DEA) was prepared, as reported previously (11), by reacting acryloyl chloride (97%) with an excess of diethylamine (98%) in methylene chloride at 0°C. The salt was filtered off and the solvent was evaporated. Distillation of the liquid under 0.5 mmHg (1 mmHg = 133.322 Pa) vacuum at 40–50°C in the presence of hydro-quinone yielded a clear liquid, which was kept in a freezer until use.

PDEA was obtained by radical solution polymerization of DEA using ammonium persulfate as the initiator and N, N, N', N'-tetramethylethylenediamine as the accelerator. Purified water was degassed with nitrogen and was used as the solvent. The reaction was carried out at room temperature for 4 h. The solvent was then evaporated and PDEA, after dissolution into a small amount of acetone, was purified twice by precipitation in petroleum ether, resulting in a white solid.

Fractionation and characterization

PDEA fractions were obtained by fractional precipitation using acetone as the solvent and hexane as the nonsolvent. To ensure good results, the concentration of the PDEA solution was kept low (less than 0.1 wt%) and the temperature was maintained constant at 25°C. Hexane was added until the solution turned cloudy. Then the temperature was raised by 1 or 2°C to dissolve the precipitated polymer and then allowed to cool down to the precipitation temperature. The system was kept without stirring for at least 1 day before the precipitated fraction was recovered. The remaining solution underwent further precipitation in the same way as described above. This process was repeated to obtain further fractions. In total, 11 fractions were obtained.

The molecular weight and its distribution of the polymer samples were determined by size exclusion chromatography (SEC) on a Waters system equipped with an online Waters 410 differential refractometer and a set of three Ultrastyragel columns. Tetrahydrofuran was used as the mobile phase, and polystyrene samples as the standards in the calibration of the molar masses.

Determination of LCST

The cloud point of PDEA in water was set as the temperature at the inflexion point of the curve obtained by turbidimetry. A CARY 1 BIO UV–vis spectrophotometer coupled to a temperature controller was used in the absorbance mode at a wavelength of 500 nm. A 1-cm sample cell containing ca. 80 μ L of solution was used for the measurement against deionized Milli-Q water as the reference. The cloud point of sample with higher concentration was impossible to determine with enough precision due to the saturation of the signal on the spectrophotometer.

Microcalorimetry was also used to determine the LCST of PDEA aqueous solutions. The endothermic signal at its maximum (corresponding to the LCST) was recorded for each sample on a DSC VP-microcalorimeter from Microcal Inc. A cell filled with deionized Milli-Q water was used as the reference. Heating rates of 0.1 and 1.0° C min⁻¹ were used, with both methods, to see their effect on the LCST.

The LCST values of aqueous PDEA solutions with different molecular weight were determined by means of turbidimetry and microcalorimetry at a concentration of 1 wt% to ensure an exact value of the cloud point and the LCST.

Results and discussion

The fractionated samples of PDEA have a wide range of molar masses, from 9.6×10^3 to 1.3×10^6 g mol⁻¹. The polydispersity of the fractions were lower than that of the bulk sample ($M_{\rm w}/M_{\rm n} = 3.59$) as shown in Table 1.

The LCST of a solute dissolved in a solvent can be obtained from the phase diagram of the system. The phase diagrams of two polymer samples F2 and F9 are shown in Fig. 1, where the cloud point is plotted as a function of concentrations ranging from 0.0001 to 10 wt%. The LCST is given by the lower temperature at which the phase transition occurs. It appears that the most accurate value of the LCST can be obtained for concentrations ranging from 1 to 5 wt% for low and high molecular weight samples, and no significant differences on the LCST are observed within this interval of polymer concentrations.

As shown in Fig. 2*a*, the transmittance of the 1 wt% PDEA solution decreases sharply at a certain temperature owing to the turbidity of the solutions when precipitation occurred. The exact values of the cloud point (LCST), ΔH , and ΔS are listed in Table 1. The general trend observed for this series of samples is that the LCST is lower for the higher molecular weight polymers.

Samples	$M_{\rm n}~({\rm g~mol^{-1}})$	$M_{ m w}~({ m g~mol^{-1}})$	$M_{ m w}/M_{ m n}$	$\Delta H ~(\mathrm{J}~\mathrm{g}^{-1})$	ΔS (J g ⁻¹ K ⁻¹)	LCST $(^{\circ}C)^{a}$	
						Turbidimetry	Microcalorimetry
F1	9 600	13 300	1.39	16.9	0.036	32.9	37.0
F2	19 200	40 300	2.10	26.0	0.069	31.0	34.2
F3	32 500	58 500	1.80	16.6	0.039	30.9	32.6
F4	81 600	165 700	2.03	20.1	0.016	30.1	31.0
F5	90 400	132 000	1.46	26.0	0.085	29.7	30.3
F6	96 900	252 000	2.60	22.2	0.059	29.5	30.2
F7	180 900	376 300	2.08	5.3	0.010	29.3	29.6
F8	218 000	311 700	1.43	5.7	0.018	29.1	29.2
F9	363 600	709 000	1.95	8.1	0.003	28.4	28.8
F10	593 600	890 400	1.50	2.0	0.003	28.6	28.6
F11	1 300 000	1 547 000	1.19	1.2	0.006	28.6	28.2

Table 1. Molecular weight and LCST of the PDEA fractions.

^{*a*}Heating rate at 0.1° C min⁻¹.

Fig 1. Phase diagram of the aqueous solution of PDEA of a low molar mass fraction F2 (open circles) and high molar mass fraction F9 (closed circles).



Microcalorimetric studies confirmed the general tendency of the behavior of the PDEA fractions. The endothermic phase transition occurs at lower temperatures for higher molecular weight samples as illustrated in Fig. 2b.

The inverse dependence on molar mass of the LCST was recently observed on PNIPAM (24). This phenomenon is attributed to the difference in the free volumes caused by the polymer chains and the solvent molecules. This difference is much more significant for the longer polymer chains, since they should precipitate at lower temperatures (28, 29). It was demonstrated by Patterson (28) that the LCST is proportional to the critical value of the Flory–Huggins interaction parameter (χ_c) and that the LCST decreases with the ratio of the molar volume of the polymer to that of the solvent (*r*):

[1]
$$\chi_c = 1/2(1 + r^{-1/2})^2$$

In eq. [1], if the molar volume of the polymer increases with the length of the chain, it is clear that the LCST of the polymer must decrease with the molecular weight of the polymer.

The shape of the curves presented in Fig. 3 suggests a more pronounced effect for lower molecular weight fractions. The slope is steep for values of M_n lower than 2 × 10⁵ g mol⁻¹ and becomes more gradual for higher values of

Fig. 2. LCST of 1 wt% aqueous solutions of selected PDEA fractions (see Table 1) obtained at a heating rate of 0.1° C min⁻¹ by: (*a*) turbidimetry; and (*b*) microcalorimetry.



 $M_{\rm n}$. This may explain the broadening of the transmittance curves (Fig. 2*a*) and of the endothermic peaks as $M_{\rm n}$ decreases (Fig. 2*b*). This implies a minor role of the poly-dispersity on the width of transition for heavier fractions. A critical value of $M_{\rm n}$ seems to lie at ca. 2×10^5 g mol⁻¹, after which the LCST values of the samples in water remained nearly constant.

The effect of the heating rate (1.0 and 0.1° C min⁻¹) was also investigated. At higher heating rates, the transition temperature is expected to be overestimated because of the poor heat transfer. When working with the 1.0 wt% PDEA fractions, the cloud point technique was found to be more sensitive to the heating rate as shown in Fig. 3*a*, where the LCST

Fig. 3. Effect of the molecular weight on the LCST of the PDEA fractions measured by: (*a*) spectrophotmetry (circles); and (*b*) microcalorimetry (squares) for different heating rates. Open symbols, heating at 1.0° C min⁻¹; closed symbols, 0.1° C min⁻¹.



obtained at 0.1° C min⁻¹ were 3° C lower than those measured at 1.0° C min⁻¹. Such a dependence of the LCST on the heating rate was already reported for a polydisperse sample (11). This was attributed to the poor heat transfer inherent to the method where the recorded temperature is higher than the effective temperature of the sample. Microcalorimetry has a much better heat transfer and, therefore, this effect is less pronounced as shown in Fig. 3*b*.

As seen in Fig. 4, microcalorimetry can be used also to determine the enthalpy (ΔH) and the entropy (ΔS) at the transition. These quantities seem to be strongly dependent on the molecular weight. ΔH and ΔS follow the same trend as the LCST for the samples, i.e., a hyperbolic decrease from 21.0 J g⁻¹ and 0.070 J g⁻¹ K⁻¹ for ΔH and ΔS to limit values of 0.6 J g⁻¹ and 0.003 J g⁻¹ K⁻¹, respectively. In each case, the final plateau corresponds to a sample with a molar mass of 2×10^5 g mol⁻¹. The value obtained here for ΔH is consistent with that reported by Idziak et al. (11) for a PDEA sample ($\Delta H = 22.9$ J g⁻¹ for $M_n = 2.0 \times 10^4$ g mol⁻¹).

It is understandable that the entropy change is smaller for the longer polymer chains. The ΔS values decrease as a function of the average molar mass of the polymer and remain constant after a critical point at $M_n = 2 \times 10^5$ g mol⁻¹. When a hydrophobic solute such as PDEA is dissolved in water, the surrounding molecules tend to organize themselves in an ice-like structure (3). The order created decreases the entropy of the solution. The LCST phenomenon for polymer in aqueous media is possible only if the dissolution is exothermic and the entropy of the mixture is negative

Fig. 4. Effect of the molecular weight on: (a) ΔH ; and (b) ΔS for the PDEA fractions obtained by microcalorimetry at a heating rate of 0.1°C min⁻¹.



(28). A low molar mass polymer at a given weight concentration needs to interact with more water molecules to be solvated, creating more order in the system. This increased order decreases the overall entropy of the solution. The ΔS of the transition is therefore greater.

It can also be demonstrated mathematically that lower molecular weight polymers correspond to higher the ΔH values. It is known that χ_c decrease with the molecular weight of the polymer (28) because the lower molar volume of the polymer gives a lower value of the ratio (*r*) in eq. [1]. Since χ_c is proportional to the energy required to break the contact between the polymer and the solvent (28), the energy needed to induce the phase separation (ΔH) will be greater for shorter polymer chains.

Conclusion

PDEA fractions were prepared by fractional precipitation despite the amphiphilicity of the polymer. The phase diagrams showed that the changes of the LCSTs of the PDEA aqueous solutions are not significant in the concentration range from 1 to 5 wt%. Low heating rates provide more reliable results with turbidimetry, but this effect is negligible for microcalorimetric measurements. Turbidimetric and microcalorimetric measurements have shown a sharp decrease in their LCST, ΔH , and ΔS values as a function of the molar mass of PDEA. The values become constant after a critical molar mass at ca. $M_n = 2 \times 10^5$ g mol⁻¹. Polydispersity of the polymer seems to plays a minor role for the heavier PDEA fractions.

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