

A Study on Solution Properties of Poly(*N,N*-diethylacrylamide-*co*-acrylic acid)

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ABSTRACT: Poly(*N,N*-diethylacrylamide) (PDEA), poly(acrylic acid) (PAA), and a series of (*N,N*-diethylacrylamide-*co*-acrylic acid) (DEA-AA) random copolymers were synthesized by the method of radical polymerization. The measurement of turbidity showed that the phase behaviors of the brine solutions of the copolymers changed dramatically with the mole fraction of DEA (x) in these copolymers. Copolymers cop6 ($x = 0.06$) and cop11 ($x = 0.11$) in which acrylic acid content was higher presented the upper critical solution temperature (UCST) phase behaviors similar to PAA. Copolymer cop27 ($x = 0.27$) presented the lower critical solution temperature (LCST) behavior similar to PDEA. While copolymer cop18 ($x =$

0.18) in which acrylic acid content was moderate presented both UCST and LCST behaviors. The solution properties of the polymers were investigated by measurements of viscosity, fluorescence, and pH. It is reasonable to suggest that the sharp change of the phase behavior may be attributed to the interaction between acrylamide group and carboxylic group in the (DEA-AA) copolymers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3373–3378, 2008

Key words: phase behavior; solution properties; poly(acrylic acid); poly(*N,N*-diethylacrylamide); water-soluble polymers

INTRODUCTION

Poly(*N,N*-diethylacrylamide) (PDEA) and poly(*N*-isopropyl acrylamide) (PNIPA) are temperature-sensitive polymers, whose aqueous solutions separate into two phases when temperature exceeds the lower critical solution temperatures (LCST), with the collapse of the chains.^{1,2} The crosslinked form of the polymer (hydrogel) undergoes analogous collapse transition in aqueous solution, and the process is reversible. Such phase-transition properties can be used in drug delivery systems, temperature-sensitive coatings, and smart catalysts.^{3–5}

The properties of a polymer solution, such as the phase transition temperature, the response to other stimuli like pH, the concentration of salt, etc, and even the type of phase behavior, can be changed by copolymerization of the polymer.^{6–9} It is generally believed that LCST of a polymer solution can be changed significantly through copolymerizing with ionic comonomer such as acrylic acid (AA)^{10–12},

moreover, the higher the ionic composition, the higher the LCST of the copolymer solution. But studies have shown^{13,14} that under acidic condition, LCST of the (*N*-isopropyl acrylamide-*co*-acrylic acid) copolymer (P(NIPA-AA)) is lower than that of NIPA homopolymer and its copolymer with nonionic comonomer. The acrylic acid unit does not dissociate under acidic conditions, which effectively result in a nonionic polymer, moreover the intramolecular hydrogen bonds formed between NIPA and AA, in which the acrylamide group acts as a proton acceptor and the carboxylic group acts as a proton donor^{15–20} lead to the further decrease of the LCST of the copolymer.

The LCST phase behaviors of the aqueous solutions of DEA-AA copolymers with AA content being varied between 0.059 and 0.201 have been previously studied by differential scanning calorimetry and spectrophotometry,²¹ the results showed that the LCST of the copolymer varied with the AA content, and the copolymers formed smaller aggregates above LCST compared with that of PDEA. As DEA-AA copolymer consist of two component units, therefore, not only the phase behavior of PDEA but also the phase behavior of poly(acrylic acid) (PAA) should be taken into account. Unlike PDEA and PNIPA, PAA shows upper critical solution temperature (UCST) in a brine solution,^{22,23} i.e., it undergoes phase separation at low temperature, but turns homogeneous upon heating. It is supposed that if DEA copolymerizes with appropriate content of AA, the

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TABLE I
The Compositions, Molecular Weights, and Polydispersity of PAA, PDEA,
and Copolymers

| Sample | $n_{\text{DEA}}/n_{\text{AA}}$ Molar ratio in feed | $n_{\text{DEA}}/n_{\text{AA}}$ Molar ratio in polymer ^a | $M_w \times 10^{-4}$ (g mol ⁻¹) ^b | M_w/M_n ^b |
|--------|--|--|--|------------------------|
| PAA | 0/1 | 0/1 | 5.45 | 2.10 |
| cop6 | 0.06/0.94 | 0.06/0.94 | 5.21 | 1.82 |
| cop11 | 0.12/0.88 | 0.11/0.89 | 5.47 | 1.77 |
| cop18 | 0.20/0.80 | 0.18/0.82 | 7.90 | 1.79 |
| cop27 | 0.32/0.68 | 0.27/0.73 | 5.85 | 1.82 |
| PDEA | 1/0 | 1/0 | 4.31 | 1.74 |

^a Determined by elemental analysis for nitrogen.

^b Determined by laser light scattering in methanol at 25°C.

copolymer will probably show phase behaviors of both PDEA and PAA.

In this work, the copolymers of DEA-AA with the contents of AA units being varied between 0.73 and 0.94 were synthesized. The different types of phase behavior were achieved by copolymerization of appropriate content AA with DEA. The solution properties of DEA-AA copolymers were also studied by measurements of viscosity, fluorescence, and pH.

EXPERIMENTAL

Materials

Benzoyl chloride, diethylamine, magnesium sulfate, *p*-benzenediol, methanol, dichloromethane, diethyl ether, acetone, and hexane in this study were used as received (analytical grade). Acrylic acid was distilled under reduced pressure prior to use. Azodiisobutyronitrile (AIBN) was recrystallized from 95% ethanol prior to use. Double-distilled water was used throughout.

Synthesis of *N,N*-diethylacrylamide

A solution of 46.7 mL acryloyl chloride dissolved in 30 mL dichloromethane was gradually added to another solution of 208 mL diethylamine previously dissolved in 450 mL dichloromethane at 0°C under nitrogen atmosphere. The mixture was stirred for 4 h at 0°C. The precipitated salt was removed by filtration and washed with double-distilled water to remove traces of the filtered solution. After drying over magnesium sulfate, the solvent was removed under reduced pressure. The crude product was distilled in the presence of hydroquinone at 86–88°C and under vacuum of 68 mmHg, to yield a colorless liquid product. The ¹H-NMR (CDCl₃, δ ppm) of DEA were: 6.5(1H, =CH–), 6.3(1H, CH₂=), 5.6(1H, CH₂=), 3.4(4H, –CH₂–), 1.1(6H, –CH₃).

Synthesis of polymers

PAA was synthesized by the method of radical polymerization.¹⁵ Three milliliters of acrylic acid, 0.0716 g

of AIBN, and 33 mL of methanol were mixed in a dry reaction flask. The mixture was allowed to react at 60°C for 1.5 h in the atmosphere of nitrogen. The solvent was evaporated and the polymer was dissolved in methanol, precipitated in ethyl ether, and dried under vacuum for 24 h. The precipitation-dryness step was repeated for three times. The product was undissociated acrylic acid polymer.

PDEA was synthesized according to the procedure described in Ref. 24. A solution of 1.27 g (0.01 mol) DEA dissolved in 1.5 mL methanol was stirred with 8 mg (0.0488 mmol) AIBN under nitrogen atmosphere at 60°C. Stirring was discontinued after 30 min, heating was continued for 6 h. The polymer was cooled to room temperature and then dissolved in 5 mL acetone and precipitated from 80 mL hexane. The polymer was purified by multiple dissolution (×3) in acetone, followed by precipitation into hexane, and then dried at room temperature under vacuum.

Random DEA-AA copolymers were synthesized by the method of radical polymerization, which was similar to that used for the preparation of PAA. Appropriate amount of DEA, AA, AIBN, and methanol were mixed in a dry reaction flask and allowed to react at 60°C for 1.5 h in the atmosphere of nitrogen. After the solvent was removed by distillation, the crude product was dissolved in methanol and precipitated from ethyl ether. The polymer was dried under vacuum for 24 h. The precipitation-dryness step was repeated for three times, and the purified polymer was stored in a desiccator. The molar ratios ($n_{\text{DEA}} : n_{\text{AA}}$ in monomer units) in the resultant copolymers determined by elemental analysis for nitrogen which were measured through Elementar vario EL are listed in Table I.

Characteristics of polymers

Static and dynamic light scattering measurements were performed by means of Brookhaven laser light scattering equipment consisting of a BI-200SM goniometer and a BI-9000AT digital correlator. Molecular

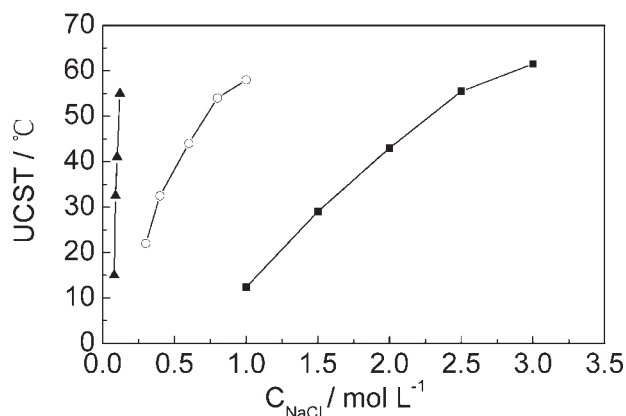


Figure 1 The influence of the concentration of NaCl on UCST of PAA, cop6, and cop11 (■: PAA; ○: cop6; ▲: cop11; concentration is 0.2% (w/v)).

weights were determined by Zimm plot based on static light scattering data and the polydispersity indices are determined by dynamics light scattering data as described in Ref. 25. The results are listed in Table I. The molecular weight of cop18 is relative larger than that of other synthesized polymer.

Measurement of phase behavior

Turbidity of the polymer solution was measured at the wavelength of 500 nm with a HP-8453 UV-visible spectrophotometer equipped with a thermostat. The concentration of the polymers solution was 0.2% (w/v).

Measurement of viscosity

Viscosity measurements were carried out with an Ubbelohde viscometer in a water bath and thermostated at 25°C ± 0.1°C.

Measurement of fluorescence

Fluorescence measurements were conducted with a Shimadzu RF-540 spectrofluorophotometer at 25°C. The excitation wave length was 336.0 nm. Pyrene was used as a polarity-sensitive probe at a concentration of 1.0×10^{-6} mol L⁻¹. The concentration of the polymers was 0.2% (w/v), and was prepared according to the method described in Ref. 13.

Measurement of pH

pH was measured with a PHS-10C pH meter at 25°C.

RESULTS AND DISCUSSION

Phase behavior

The influence of NaCl on the phase behavior of PAA, cop6, and cop11 were shown in Figure 1. The

copolymers cop6 and cop11, containing a larger fraction of AA unit, exhibit UCST phase behaviors, as shown in Figure 1. The sensitivity of UCST to NaCl concentration increases dramatically as the content of DEA increases. In the phase separation process, the polymer molecules first undergo an intrachain collapse followed by interchain aggregation. NaCl has two effects in this process. First, it can screen the electrostatic repulsion among the ionized carboxylic acid groups, which could have prevented the polymer chains to aggregate. As the mole fraction of ionizable AA unit in PAA, cop6, and cop11 are 1.0, 0.94, and 0.89, respectively, this effect is not much different for PAA, cop6, and cop11. The difference of sensitivity mainly comes from the second effect of the salt; The salt could influence the solubility of polymer by enhancing or breaking the structure of water. NaCl, as a structure breaking salt, could enhance the hydrophobic polymer-polymer interaction by breaking up the order structure of water and disrupting the hydrogen bond of carboxylic group with water molecule.²¹ Dramatically increasing the sensitivity of UCST to NaCl concentration means that the hydrophobicity of the polymer increases sharply as the content of DEA increases. The introduction of the relative hydrophobic unit DEA can not bring so much change in hydrophobicity, the hydrogen bond formed in P(DEA-co-AA) must be taken into account. It has been proved that hydrogen bond formed between acrylamide group and carboxylic group in PDEA aqueous solution when PAA or poly methyl acryl acid (PMAA) is added.^{15,26}

Cop18 copolymer shows both LCST and UCST behaviors in NaCl aqueous solution (Fig. 2). The similar behavior was found in NIPA-AA copolymer.¹⁹ Cop18 is soluble in the whole temperature range when the NaCl concentration is below 0.06 mol L⁻¹, however, it shows both LCST and UCST when the NaCl concentration is between 0.06 and 0.1 mol L⁻¹, and the two-phase region extends with

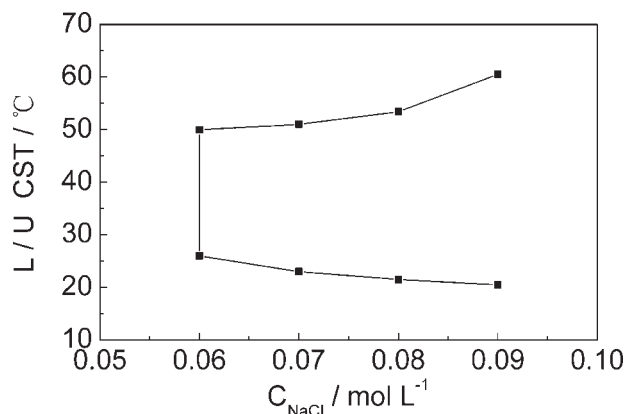


Figure 2 The influence of the concentration of NaCl on L/UCST of cop18 [concentration is 0.2% (w/v)].

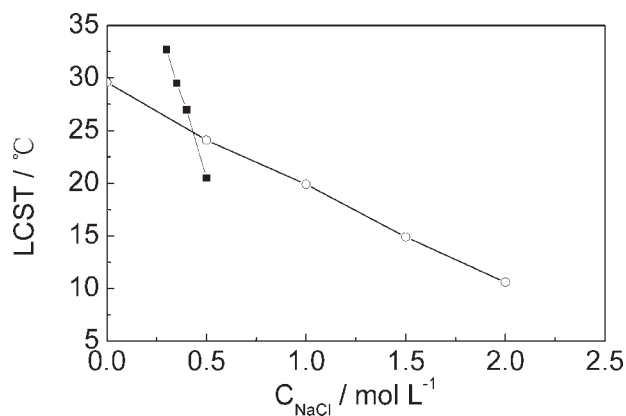


Figure 3 The influence of the concentration of NaCl on LCST of PDEA, cop27 (○: PDEA; ■: cop27; concentration is 0.2% (w/v)).

the NaCl concentration. When the NaCl concentration reaches 0.1 mol L^{-1} , the copolymer solution becomes unhomogeneous in the whole temperature range. Despite more detailed studies are needed to understand the details of this behavior, it is obvious from the present study that the phase behaviors of these copolymer solutions are resulted from a delicate balance between several contributions, such as intrachain hydrogen bonding, polymer hydration, and electrostatic effects,¹⁹ i.e. (1) below the LCST, the cop18 molecules exist in solution as extended coils, surrounded by ordered water molecules. This shell of hydration causes a decrease in the entropy of the system. Thus, the free energy of solution is lowered by the formation of hydrogen bonds but is raised by the loss of entropy; (2) at temperature above the LCST the entropy term dominates, and the solution phase is separated; (3) at temperature above the UCST, the dissociation degree of carboxylic units increase and the association of the polymer decrease, the strong interaction between ionized AA unit and water make the polymer soluble again. In spite of the relatively larger molecular weight of cop18 than other polymers, we did not consider it as the factor which led to the special phase behavior of cop18; the molecular weight difference of cop18 with other polymers only brought less than 0.3°C alternation to LCST of PDEA, refer to the study of Lesard,²⁷ and the similar phase behavior investigated in NIPA-AA copolymer solution is attributed to the copolymer composition.¹⁹

Cop27 exhibit LCST phase behavior as PDEA (Fig. 3). The addition of NaCl lowers the LCST of the polymer. Moreover LCST of cop27 is more sensitive to the NaCl concentration than that of PDEA, which indicates once again that the interaction between acrylamide group and carboxylic acid group enhances the hydrophobicity of the copolymers.

Gan et al. shows that when AA content is less than 0.201, the copolymers of DEA and AA exhibit the LCST phase behavior,²¹ the LCST varied with the content of AA in the copolymer, which is attributed to the intrachain hydrogen bond and the partially ionized AA group. Present work shows, in other end of the scale of copolymer content (AA content larger than 0.73), the phase behavior type of copolymer quickly transfer from LCST, both LCST and UCST, UCST with the AA content. It is reasonable to consider that the partially ionized AA group and the intrachain hydrogen bond are also the main cause of this change.

Solution property

The intrinsic viscosity characterizes the hydrodynamic property of single polymer chain in solution, and therefore it may provide the information of single chain, like shape, radius, and solvability. It is well known that the viscosity property of PAA aqueous solution is quite different from that of nonpolyelectrolytes. Its reduced viscosity (η_{sp}/c) does not linearly relate with concentration (c). Being a weak polyelectrolyte, the carboxylic group of the PAA has dissociation equilibrium in the aqueous solution. The degree of dissociation increases upon diluting, and intrachain repulsion caused by the charge of the polymer stretches the molecules. To avoid the stretch induced by increasing dissociation, isoionic dilution was applied in this study.^{28–30} To maintain a constant effective ionic strength, polyelectrolyte/water solution was diluted with a salt solution of the appropriate concentration in our measurements so that η_{sp}/c increased linearly with c , which allowed us to obtain the intrinsic viscosity $[\eta]$ by extrapolating the value of η_{sp}/c to $c = 0$.

The intrinsic viscosity of the copolymers at the fully ionized form and at $\text{pH} = 3$ were shown in

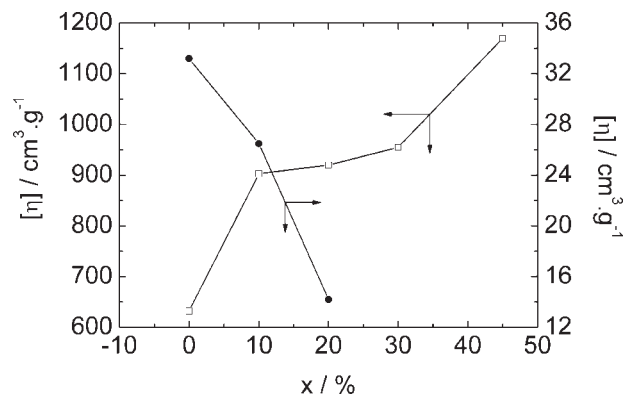


Figure 4 The variation of intrinsic viscosity $[\eta]$ with the copolymer composition x (□: polymer is fully ionized; ●: $\text{pH} = 3.00$; $T = 25^\circ\text{C}$).

Figure 4. When the copolymers are fully ionized, the value of $[\eta]$ is much higher and increases with DEA content gradually. This is caused by the complete dissociation of AA units that strengthens the repulsion between ion groups. As DEA content increases in copolymer, PAA were diluted, as a result, molecular chain extends. When the copolymers are slightly charged (pH = 3), the value of $[\eta]$ is lower and decreases substantially as DEA content increases, and one phase region is simultaneously reduced. Therefore the homogeneous aqueous solutions of cop18 and cop27 at pH = 3 cannot be prepared. The intrinsic viscosity of copolymers are even lower than that of PDEA, which is $41 \text{ cm}^3 \text{ g}^{-1}$ at 25°C in aqueous solution, indicating an especially compact structure for the copolymers, such a structure is probably caused by strong intramolecular interactions, i.e., the formation of intrachain hydrogen bonds between DEA units and AA units.

Is there extra increase of hydrophobicity generated by copolymerization of DEA units to PAA as the phase behavior shows? To make it clear, the changes in the hydrophobicity of the PAA, PDEA, and DEA-AA copolymers are monitored by the fluorescence emission spectrum of pyrene, a microenvironment polarity-sensitive probe. As it is known, pyrene is more soluble in a lower polarity microenvironment,³¹ the ratio of the intensities of the first vibronic peak to the third one (I_1/I_3) of the fluorescence emission spectrum of pyrene gives information on the existence of hydrophobic domains in the investigated solution.^{32,33} The values of I_1/I_3 of the polymers solutions at 25°C were listed in Table II. The I_1/I_3 value for the PAA solution, 1.77, shows that there are no hydrophobic domains in PAA solution. However, for PDEA solution, I_1/I_3 is 1.67 that shows some hydrophobic character because of the nonpolar ethyl groups in the PDEA. The value of I_1/I_3 of DEA-AA copolymer decreases as DEA content increases, indicating an increase of hydrophobic degree. Cop18 and cop27 even have a higher hydrophobic character than that of PDEA. The association of the polar groups in copolymer makes the reduction of contact between polar group and water, and the increase of contact between nonpolar groups and water. The hydrophobicity of nonpolar groups drives the chains of copolymer to more compact

TABLE II
The Values of I_1/I_3 of the Fluorescence Emission Spectrum of Pyrene in PAA, PDEA, and DEA-AA Copolymer Aqueous Solutions

| Sample | PAA | cop6 | cop11 | cop18 | cop27 | PDEA |
|-----------|------|------|-------|-------|-------|------|
| I_1/I_3 | 1.77 | 1.72 | 1.69 | 1.59 | 1.58 | 1.67 |

Polymer concentration: 0.2% (w/v), $I_1 = 373.0 \text{ nm}$, $I_3 = 383.9 \text{ nm}$; $T = 25^\circ\text{C}$.

TABLE III
The Apparent Dissociation Degree (a) of PAA and DEA/AA Copolymers at pH = 3

| Sample | a |
|--------|-------|
| PAA | 0.036 |
| cop6 | 0.028 |
| cop11 | 0.022 |

structure, resulting in the more hydrophobicity of the copolymer.

pH measurements provide further evidence of the intrachain hydrogen bonds in the copolymer aqueous solution. The apparent dissociation degrees (a) of the carboxylic units were listed in Table III.¹⁹

$$a = [\text{H}^+]/[\text{AA}] \quad (1)$$

where $[\text{H}^+]$ is the molar concentration of H^+ and $[\text{AA}]$ is the total molar concentration of the AA repeating units. The solutions have been prepared by using appropriate polymer concentrations so that the pH is kept at 3. It can be seen from Table III that a decreases as the DEA content in the copolymers increases. The degree of dissociation a , as obtained from eq. (1), is an apparent one, since it was calculated by assuming that all AA units were able to freely dissociate. However, the associations between two carboxylic acid groups of AA units, and between carboxylic acid and amide groups reduce the interaction between carboxylic acid groups and water, and result in the reduction of hydration of carboxylic acid groups, therefore the dissociation degree of AA decreases gradually with the increase of the contents of DEA as it is showed in P(NIPA-AA) aqueous solution.²⁰

CONCLUSIONS

A series of DEA-AA copolymers were synthesized in this study and were named as cop6, cop11, cop18, and cop27 corresponding to the DEA molar fraction in the copolymers. In spite of the possible disturbance brought out by the difference of molecular weight between cop18 and other polymer, the influence of AA content in copolymer to the phase behaviors was much more obvious. Copolymers cop6 and cop11 in which acrylic acid content was higher presented UCST behaviors; copolymer cop27 in which acrylic acid content was lower presented LCST behaviors; while copolymer cop18 in which acrylic acid content is moderate presented the behaviors of both UCST and LCST. The various phase behaviors might be attributed to the intrachain hydrogen bonding in the DEA-AA copolymer solutions. This intrachain hydrogen bonding was also supported by the measurements of viscosity,

fluorescence, and pH, which showed more compact structure, extra hydrophobicity, and less interaction with water for DEA-AA copolymers.

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