# Synthesis and Characterization of Temperature- and pH-Sensitive Poly(*N,N*-diethylacrylamide-*co*-methacrylic acid)

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**ABSTRACT:** A series of pH- and temperature-responsive (*N,N*-diethylacrylamide-*co*-methacrylic acid) (DEAM–MAA) random copolymers were synthesized by free-radical copolymerization techniques, and their lower critical solution temperatures (LCSTs) at different pH values and their critical phase-transition pH values at different temperatures were determined by transmittance measurements, respectively. The LCSTs of DEAM–MAA copolymers depend on the MAA content in the copolymers and are significantly affected by the pH of the aqueous solution. Similarly, the critical phase-transition pH values also depend on the MAA content of the DEAM–MAA copolymers and are significantly affected by the temperature of the aqueous solution. The LCST of DEAM–MAA copolymers increases with an increase in the MAA content. The critical phase-transition pH increases with increasing MAA content in the copolymer and also increases with increasing aqueous solution temperature. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3563–3568, 2003

**Key words:** transmittance; lower critical solution temperatures (LCST); copolymerization; phase behavior; radical polymerization

## INTRODUCTION

The unique and novel properties of intelligent polymeric materials, which exhibit large property changes in response to small changes in external conditions such as, for example, temperature,[1–3] pH,[4–6] electric fields,[7,8] and chemicals,[9] offer an unlimited amount of potential applications relevant to industry, the environment, and the biomedical field.[10,11] These applications include drug delivery systems,[12,13] temperature-sensitive coatings,[14] smart catalysts,[15,16] and pervasive membranes,[17] to name but a few.

Poly(*N*-isopropylacrylamide) (PNIPAM) is a temperature-sensitive polymer that exhibits a well-defined lower critical solution temperature (LCST) in water at around 32°C.[18–20] At present, most studies have been focused on PNIPAM and its copolymers.[21–24] The crosslinked PNIPAM gel undergoes analogous collapse transition temperature in aqueous media.[25,26] It is known that the phase-transition and accompanying polymer conformation changes result from a delicate balance between the hydrophobic interaction and hydrogen bonding. Recently there has been considerable interest in the use of materials that respond to two stimuli, either mutually or independently in specific environments, with particular emphasis on pH/temperature-responsive polymers that

have been prepared by copolymerizing the temperature-sensitive NIPAM with monomers containing base or carboxylic acid groups, such as methacrylic acid (MAA), to give a pH-dependent LCST.[27–29]

Besides PNIPAM, several other N-substituted polyacrylamides such as poly(*N,N*-diethylacrylamide) (PDEAM), poly(*N*-ethylacrylamide) (PEAM), and poly(*N*-cyclopropylacrylamide) (PCPAM) also exhibit the phase-transition behavior.[30,31] These thermosensitive polymers can also be made to respond to other stimuli such as light,[32] pH,[28] and both electric field and magnetic field[33] by copolymerization or grafting with other specific monomers, such as acrylic acid (AA), which renders the copolymer to be sensitive to pH/temperature changes.[28,34]

Unlike other polyacids, poly(methacrylic acid) (PMAA) behaves differently. It adopts hypercoiled conformation at low pH because of the hydrophobic interactions introduced by the methyl groups along the polymer backbone. However, on addition of base to solution, the carboxyl groups ionize and acquire negative charges. The increase in coulombic repulsive forces results in a nonuniform sudden conformational transition from the hypercoiled to expanded form. This conformational change is reversible.[35,36] It is expected that the smart behavior of PMAA may be introduced into a temperature-sensitive polymer, such as PDEAM, to form a copolymer, and properties of this copolymer could be customized to be doubly sensitive to external temperature and pH stimulus. This copolymer may form the basis of new intelligent

separation materials, drug delivery materials, and intelligent support of various catalysts. In view of this possibility, we investigated the synthesis and characterization of DEAM–MAA copolymer. The main aim of this study was to investigate the effects of pH and MAA contents on the copolymer phase-transition temperatures, and the effects of temperature and MAA contents on the copolymer critical phase-transition pH values.

## EXPERIMENTAL

### Materials

Diethylamine, dichloromethane, magnesium sulfate, sodium hydroxide, acetone, methanol, diethyl ether, and hexane were used as received (analytical grade). 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. MAA was distilled under vacuum before use. Double-distilled water was used throughout. The solution pH was adjusted using $0.5M$ NaOH solution and/or $0.5M$ HCl solution.

### Preparation of acryloyl chloride

A mixture of 70 g (0.97 mol) acrylic acid, 234 g (1.66 mol) benzoyl chloride, and 0.5 g (0.0045 mol) hydroquinone was distilled at a fairly rapid rate through an efficient 25-cm distilling column. The distillate was collected in a receiver containing 0.5 g (0.0045 mol) hydroquinone, immersed in ice. When the temperature at the top of the column, which remained between 60 and 70°C for most of the distillation, had reached 85°C, the distillation was discontinued. The crude product was redistilled through the same column and the fraction boiling at 72–74°C at 740 mmHg was collected.

### Preparation of DEAM

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 $N_2$ atmosphere. The reaction 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 85–88°C under vacuum at 68 mmHg, to yield a colorless liquid product. $^1$H-NMR (CDCl$_3$, δ ppm): 6.5 (1H, $=$CH–), 6.3 (1H, CH$_2=$), 5.6 (1H, CH$_2=$), 3.4 (4H, –CH$_2$–), 1.1 (6H, –CH$_3$).

### Preparation of PDEAM

PDEAM was prepared by free-radical polymerization, according to literature procedures.[31] A solution of 1.27 g (0.01 mol) DEAM dissolved in 1.5 mL methanol was stirred with 8 mg (0.0488 mmol) AIBN under $N_2$ at 62°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 ($\times3$) in acetone, followed by precipitation into hexane, and then dried at room temperature under vacuum.

### Preparation of DEAM–MAA copolymers

Five DEAM–MAA random copolymers were prepared by copolymerization of the two monomers in methanol using AIBN as an initiator. The polymerization method used was similar to that used for the preparation of PDEAM. The molar ratios ($n_{DEAM} : n_{MAA}$ in monomer units) in the feed of five copolymers DEAM–MAA-1, DEAM–MAA-2, DEAM–MAA-3, DEAM–MAA-4 and DEAM–MAA-5 were 0.95 : 0.05; 0.90 : 0.10; 0.85 : 0.15; 0.80 : 0.20, and 0.70 : 0.30, respectively. The resultant copolymers were purified by multiple dissolution ($\times3$) in methanol, followed by precipitation into diethyl ether and then dried at room temperature under vacuum. The molar ratios ($n_{DEAM} : n_{MAA}$ in monomer units) in the resultant copolymers DEAM–MAA-1, DEAM–MAA-2, DEAM–MAA-3, DEAM–MAA-4, and DEAM–MAA-5 determined by elemental analysis for nitrogen were 88.25 : 11.75, 84.18 : 15.82, 81.07 : 19.93, 68.09 : 31.91, and 57.74 : 42.26, respectively.

### Polymer characterization

Molecular weights were determined by laser light scattering (LLS) techniques (Brookhaven BI-2000SM, USA) using methanol as solvent. The weight-average molecular weights $[M_w/(g\ mol^{-1})]$ of the five copolymers DEAM–MAA-1, DEAM–MAA-2, DEAM–MAA-3, DEAM–MAA-4, and DEAM–MAA-5 were as follows (all values $\times 10^5$): 1.67, 1.23, 0.921, 0.744, and 0.383, respectively, and the weight-average molecular weight $[M_w/(g\ mol^{-1})]$ of homopolymer PDEAM was $1.24 \times 10^5$. $^1$H-NMR measurements were recorded on an NMR spectrometer (Bruker AM-400, Billerica, MA). Elemental analysis was conducted on the Elementar Vario EL (Germany). Transmittances of the solutions were determined on a UV–vis spectrophotometer (Shimadzu UV-240; Kyoto, Japan) and pH measurements were conducted on a PHS-1 acidimeter.

### Spectrophotometric phase-transition measurements

Concentration of the polymeric solution used for the determination of phase transition was 0.2 wt %. Because of its sensitivity to the changes in the turbidity of the solution, 550 nm was selected as the analyzing

wavelength. The sample solution was put in a sample holder that was connected to a programmable temperature controller. Double-distilled water was adopted as reference for the measurement. The temperature range of the measurement was from 20 to 70°C. The temperature was increased 2°C for every 10 min. The LCSTs were determined from the maximum transition point of transmittance against temperature curves.

The pH-responsive behavior of the polymeric solution (0.2 wt %) was determined by studying the turbidity of the solution over a wide pH range. The critical phase-transition pH was determined from the maximum transition point of transmittance against pH curves.

## RESULTS AND DISCUSSION

For convenience in the discussion, the signs $1^{\#}$, $2^{\#}$, $3^{\#}$, $4^{\#}$, and $5^{\#}$ identify five random copolymers DEAM–MAA-1, DEAM–MAA-2, DEAM–MAA-3, DEAM–MAA-4, and DEAM–MAA-5, respectively.

Because the transmittance percentage of temperature/pH-sensitive polymer solutions would decrease at LCST and critical phase-transition pH, our approach to determine the characterizations of homopolymer and copolymers was to focus on the transmittance percentage measurements.

The LCST of PDEAM was determined by light-absorbance experiment and was observed at around 29°C. The thermal reversible phase transition in aqueous solutions is a consequence of the macromolecular transition from a hydrophilic to a hydrophobic structure at this temperature. The variation in pH of PDEAM aqueous solution had no significant effect on its LCST. The copolymerization of the temperature-responsive DEAM with pH-responsive MAA monomers results in a dually sensitive polymeric material, that is, sensitive to both temperature and pH.

Five random copolymers prepared by radical polymerization were used to investigate how their LCST values vary with MAA contents in copolymers and solution pH and how the critical pH values vary with MAA contents in the copolymers and solution temperature.

### Effect of MAA content and pH on the LCST of DEAM–MAA copolymers

Figures 1–3, the polymeric solution transmittance percentage versus temperature curves, show the variation of polymeric LCST values with MAA contents at pH 7.00, 6.40, and 5.80, respectively. LCST values of all five copolymers were significantly affected by aqueous solution pH.

Interestingly, the phase transition studied by spectrophotometry revealed that the copolymers exhibited a rather different characteristic from that of the ho-
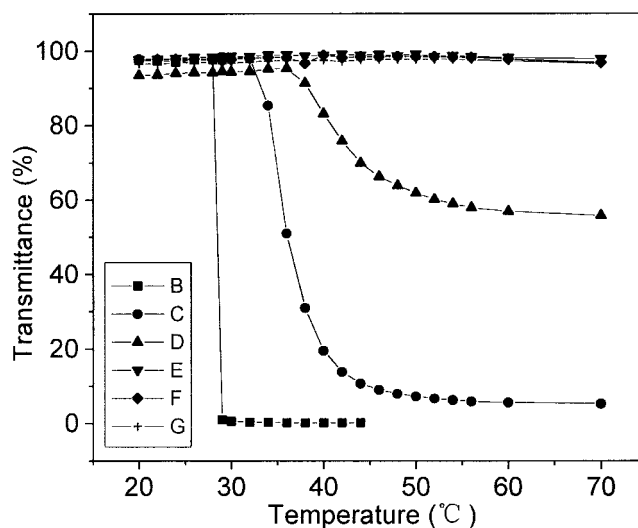


**Figure 1** Curves of 0.2 wt % polymeric aqueous solution transmittance versus temperature at pH 7.00 (B: PDEAM; C: $1^{\#}$; D: $2^{\#}$; E: $3^{\#}$; F: $4^{\#}$; G: $5^{\#}$).

mopolymer PDEAM. The transmittances of PDEAM and copolymers were measured as a function of temperature at certain pH values. The results, shown in Figure 1, indicated the transmittance versus temperature curves for 0.2 wt % aqueous solutions at pH 7.00. The copolymer transition curves were very much broader, in contrast with the PDEAM transition curve, which was significantly sharper. In addition, the copolymer transition curves became increasingly smoother with increasing MAA contents. It can be seen that transmittance of $1^{\#}$ drastically decreased at 32°C and the transmittance of $2^{\#}$ decreased slowly, whereas the transmittances of $3^{\#}$, $4^{\#}$, and $5^{\#}$ basically did not change with progressively increasing temperature. The main reasons for the preceding results are as follows:

1. *The polymer dilution effect.* That is, the PDEAM segments in the copolymer are separated and diluted by the PMAA segments, and this polymer dilution effect is further strengthened with increasing MAA content. The polymer dilution effect inhibited the intrachain hydrophobic interaction of the thermally responsive polymer and, as a result, the copolymer LCSTs would not become evident—in fact, would not even exist—with increasing MAA content.

2. *The static electricity repulsive effect.* Because most of the carboxyl groups were ionized into carboxyl anions at pH 7.00,[36–39] after the copolymer acquired negative charges, the coulombic repulsive forces among these carboxyl anions also caused the intramolecular hydrophobic interaction to diminish.
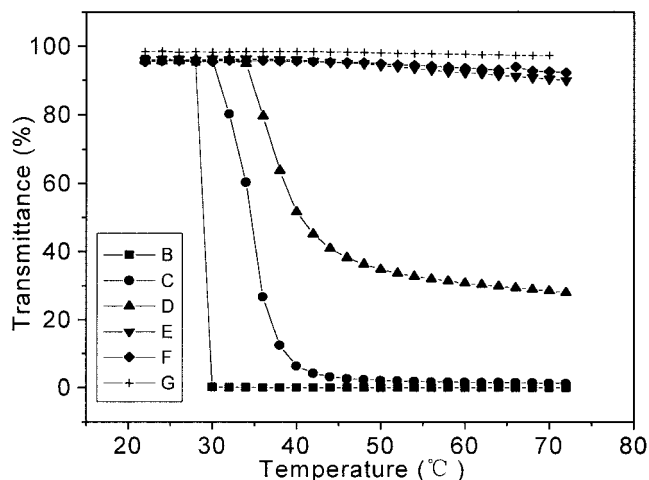
**Figure 2** Curves of 0.2 wt % polymeric aqueous solution transmittance versus temperature at pH 6.40 (B: PDEAM; C: 1[#]; D: 2[#]; E: 3[#]; F: 4[#]; G: 5[#]).



**Figure 3** Curves of 0.2 wt % polymeric aqueous solution transmittance versus temperature at pH 5.80 (B: PDEAM; C: 1[#]; D: 2[#]; E: 3[#]; F: 4[#]; G: 5[#]).

Results of transmittance at pH 6.40 are shown in Figure 2. The transmittance versus temperature curve for PDEAM almost did not have any change: its LCST was still 29°C, but the copolymer transmittances had some changes compared against those shown in Figure 1. The transition points of transmittance versus temperature curves for 1[#] and 2[#] were at 32 and 35°C, respectively, and the transmittances curves for 3[#] and 4[#] also had slight changes compared against those in Figure 1. The above results can be understood by considering the fact that the carboxyl groups in the copolymers were partially ionized into carboxyl anions at pH 6.40, so the coulombic repulsive forces in the copolymer chains were weaker. Although the polymer dilution effect to every corresponding copolymer does not have any changes, the weakness of the coulombic repulsive forces means that the hydrophobic interaction would become stronger, so the pH variations would have some effects on the copolymer transmittances.

Results of transmittance at pH 5.80 are shown in Figure 3. The transmittance versus temperature curve for PDEAM did not have any changes and variations in the pH values did not have any effect on the LCST of PDEAM, but the copolymer transmittances had some remarkable changes compared with those shown in Figures 1 and 2. At pH 5.80, the transmittances for 1[#] and 2[#] obviously decreased at 32 and 34°C, so their LCSTs were about 32 and 34°C, respectively; transmittances for 3[#], 4[#], and even 5[#] also evidently decreased with gradually increasing temperature. The above results can be understood by considering the fact that most of carboxyl groups almost did not ionize at lower pH (pH < 6.00), in addition to the existence of methyl groups; these two factors strengthened the intermolecular H-bonding between carboxyl
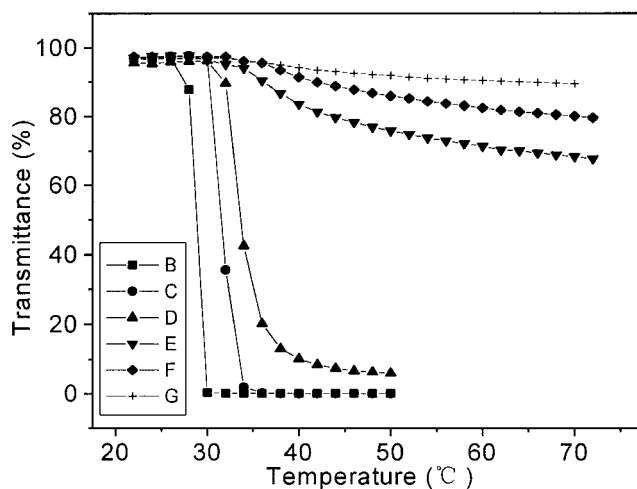
groups and amide groups (Fig. 7) and the intramolecular hydrophobic interaction, and allowed easier separation of the copolymer from the solution with gradually increasing temperature.

## Effect of the MAA contents and temperature on the copolymer critical phase-transition pH

Figures 4–6, the transmittance percentage versus pH curves for the copolymer solutions, show copolymer critical phase-transition pH variations with MAA contents in the copolymers at 24, 27, and 30°C, respectively. The cloud points at critical phase-transition pH values were believed to result from the formation of inter- and intramolecular H-bonding complexes between the acid moieties of the carboxylic acid and the amide groups (Fig. 7).
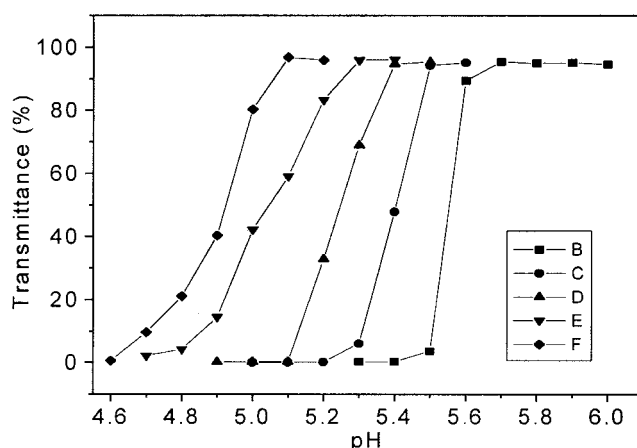


**Figure 4** Curves of 0.2 wt % DEAM–MAA copolymer aqueous solution transmittance versus pH at 24°C (B: 5[#]; C: 4[#]; D: 3[#]; E: 2[#]; F: 1[#]).
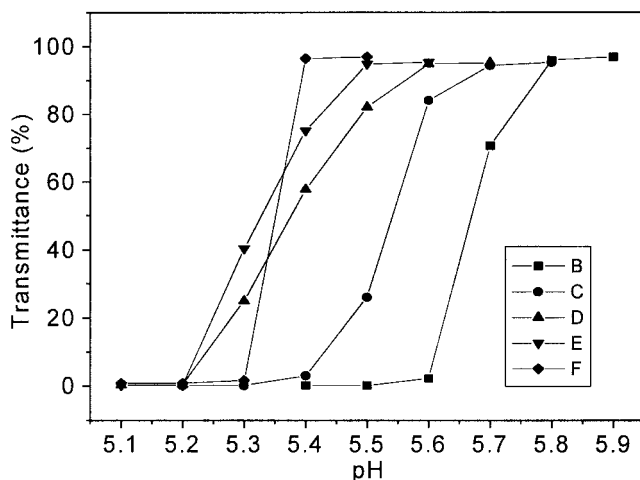
**Figure 5** Curves of 0.2 wt % DEAM–MAA copolymer aqueous solution transmittance versus pH at 27°C (B: 5[#]; C: 4[#]; D: 3[#]; E: 2[#]; F: 1[#]).
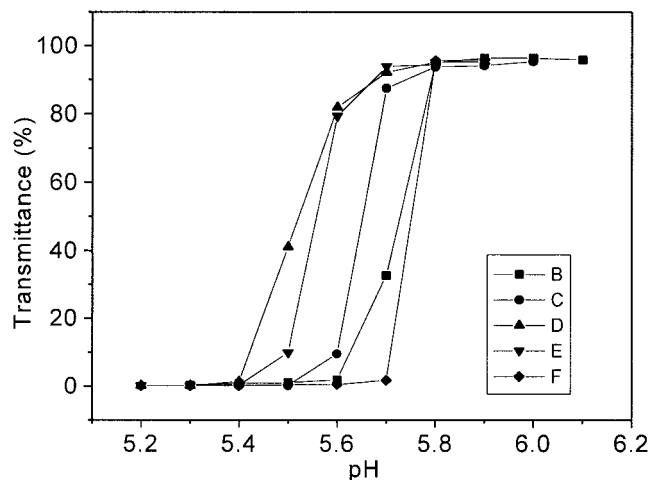


**Figure 6** Curves of 0.2 wt % DEAM–MAA copolymer aqueous solution transmittance versus pH at 30°C (B: 5[#]; C: 4[#]; D: 3[#]; E: 2[#]; F: 1[#]).

Results of transmittance at 24°C are shown in Figure 4. As one may observe, the transmittance decreased rapidly as the pH reached the critical value, dependent on the copolymer composition and structure. Below the critical pH, the solution rapidly precipitated, coagulated, and formed aggregates. Interestingly, the phase transitions investigated by spectrophotometry revealed that the copolymer critical pH values gradually increased with increasing MAA contents. For example, critical pH values of 1[#] and 5[#], relative to MAA contents and MAA ionization degree, were around 4.90 and 5.55, respectively (to 5[#] because the MAA content was higher). Although most of carboxyl groups trended to be ionized into carboxyl anions at higher pH,[36,38–40] there were still sufficient free carboxyl groups to participate in forming H-bonding to produce phase separation; thus 5[#] could produce phase separation at higher pH (~ 5.60). Compared with 5[#], the MAA contents of 1[#] were lower, and although the carboxyl groups were fewer in number, they basically did not ionize and could form H-bonding only at lower pH values[36–39]; as a result, its critical pH was lower (pH ~ 4.60). Consequently, the critical pH of 5[#] was higher than that of 1[#]. Thus the copolymer critical pH depended on the MAA contents; moreover, the higher the MAA content in the copolymer, the higher the copolymer's critical pH.

Results of transmittance at 27°C are shown in Figure 5. Critical pH values of 1[#], 2[#], 3[#], 4[#], and 5[#], shown in Figure 5, were around 5.35, 5.35, 5.45, 5.55, and 5.65, respectively. Compared with Figure 4, besides 1[#], the other copolymer critical pH values increased with increasing MAA contents. The reasons were basically consistent with those of the results in Figure 4. However, there are two differences that distinguish results shown in the two figures: (1) the copolymer critical pH in Figure

5 was higher than that of the corresponding copolymer in Figure 4; and (2) the critical pH of 1[#] in Figure 5 evidently approached that of 2[#]. This was because the hydrophobic interaction increased with increasing temperature and this hydrophobic interaction, accompanied by the H-bonding interaction, caused the copolymer critical pH to be increased after the copolymer solution temperature was increased from 24 to 27°C, particularly to 1[#], because its polymer dilution effect was the weakest and its hydrophobic interaction was the strongest; thus this hydrophobic interaction accompanied by suitable H-bonding caused the critical pH of 1[#] (pH ~ 5.35) to be close to that of 2[#] (pH ~ 5.35).

Figure 6 shows that the critical pH values of 1[#], 2[#], 3[#], 4[#], and 5[#] at 30°C were around 5.75, 5.55, 5.50, 5.65, and 5.70, respectively. Compared with the results shown in Figures 4 and 5, the change tendencies of the critical pH values of 3[#], 4[#], and 5[#] were similar to those in Figures 4 and 5, although there were two points in
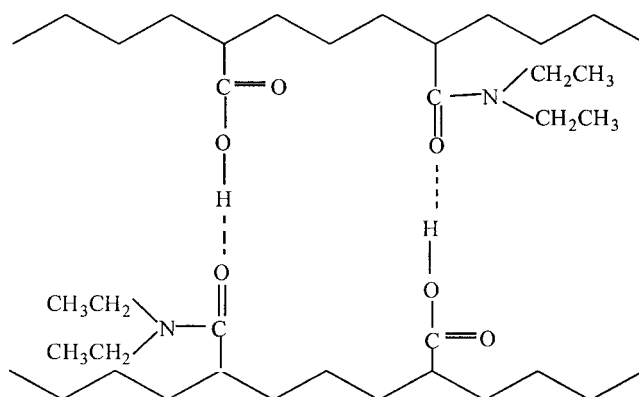


**Figure 7** Intermolecular H-bonding between the DEAM and MAA units.

Figure 6 different from results shown in Figures 4 and 5. One point was that the critical pH values of $3^\#$, $4^\#$, and $5^\#$ in Figure 6 were evidently higher than those of the corresponding copolymers in Figures 4 and 5, and the other was that the critical pH of $1^\#$ was the highest value of all the copolymers, about 5.75. Moreover, the critical pH value of $2^\#$ (pH $\sim$ 5.55) was also higher than that of $3^\#$, around pH 5.50. The reason was that the PDEAM segments in $1^\#$ occupied absolutely and the characteristics of $1^\#$ were basically similar to those of PDEAM. The hydrophobic interaction was accelerated with increasing temperature and would further accelerate inter- and intrachain H-bonding. Because the LCST of PDEAM was only 29°C and the MAA content of $1^\#$ was the lowest, the hydrophobic interaction of $1^\#$ would be the strongest of all the copolymers at 30°C and the hydrophobic interaction and H-bonding were accelerating each other. Based on the above reasons, it may be understood that the critical pH value of $1^\#$was the highest of all the copolymers at 30°C (pH $\sim$ 5.75) and the critical pH value of $2^\#$ was also higher than that of $3^\#$.

## CONCLUSIONS

DEAM–MAA copolymers have pH/temperature double sensibilities. At certain pH values, the LCSTs of DEAM–MAA copolymers depend on the MAA content in the copolymers, and the LCSTs of copolymers increase with increasing MAA content. The copolymer solution transmittance curves become sharper with decreasing pH, especially to the copolymers with lower MAA contents.

At certain temperatures, the copolymer critical phase-transition pH values also depend on the MAA content of the DEAM–MAA copolymers, and the critical phase-transition pH values increase with increasing MAA content. The copolymer critical phase-transition pH increases with increasing temperature.

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