Thermosensitive Phase-Separation Behavior of Poly(acrylic acid)-*graft*-poly(*N*,*N*-dimethylacrylamide) Aqueous Solution

Tetsuo Shibanuma,[†] Takashi Aoki,[*,†,||] Kohei Sanui,[†] Naoya Ogata,[†,§]
Akihiko Kikuchi,[‡] Yasuhisa Sakurai,[‡] and Teruo Okano[*,‡,⊥]

Department of Chemistry, Sophia University, 7-1 Kioi-cho, Chiyoda, Tokyo 102-8554, Japan;
and Institute of Biomedical Engineering, Tokyo Women's Medical University, 8−1 Kawada-cho,
Shinjuku, Tokyo 162-8666, Japan

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ABSTRACT: To investigate the influence of molecular architecture of poly(acrylic acid) (PAAc)-*graft*-poly(*N*,*N*-dimethylacrylamide) (PDMAAm) (PAAc-*g*-PDMAAm) on its solution properties in aqueous media, graft copolymers were synthesized by free radical copolymerization of AAc with PDMAAm macromonomer. PAAc-*g*-PDMAAms were water-soluble at lower temperatures, while they showed a liquid−liquid phase separation from water above the characteristic transition temperatures. The phase transition behavior was affected by the copolymer compositions and pH of the solution. Below the transition temperature, hydrogen-bonding formation between AAc and DMAAm units was observed in the PAAc-*g*-PDMAAm aqueous solution by FT-IR−ATR measurement. Graft copolymers were thus formed spherical associates with a diameter of ca. 150 nm estimated from the dynamic light scattering measurement. At higher temperatures, the dehydrated regions and the weak dehydration of the PDMAAm chains induced cooperatively the hydrophobic aggregation, resulting in thermosensitive phase separation from water. Randomly copolymerized poly(AAc-*co*-DMAAm) was a water-soluble polymer which demonstrated no phase transition. The mixture of two linear polymeric chains, PAAc and PDMAAm, strongly resulted in interpolymer complexes via hydrogen bonding in aqueous solution, causing precipitation independent of temperatures. The graft-type copolymers demonstrate characteristic solution properties in an aqueous milieu, despite the fact that all polymer systems in this study had AAc and DMAAm units.

Introduction

Attractive research reports concerning the graft-type polymers that demonstrated characteristic phase transition behavior in aqueous milieu have recently appeared. Okano et al.[1] prepared a novel graft-type poly(*N*-isopropylacrylamide) (PIPAAm) hydrogel having PIPAAm grafts on a PIPAAm backbone network which showed a more rapid response to temperature changes as compared with the conventional PIPAAm hydrogel. PIPAAm is a well-known water-soluble polymer which exhibits a lower critical solution temperature (LCST) near 32 °C.[2,3] PIPAAm hydrogels in aqueous milieu also exhibit reversible swollen−shrunken changes in response to temperature changes. In the case of the graft-type hydrogel, when the temperature was raised above its LCST, the freely mobile grafted chains readily caused hydrophobic aggregation and subsequently triggered dehydration of the whole network, resulting in drastic shrunken changes.[1] Hoffman et al.[4] reported that a poly(acrylic acid)-*graft*-PIPAAm (PAAc-*g*-PIPAAm) aqueous solution demonstrated different temperature- and pH-sensitivities of the phase transition from those of a randomly copolymerized poly(AAc-*co*-IPAAm) aqueous solution. PAAc-*g*-PIPAAm showed constant phase transition behavior that was independent of AAc contents in the graft copolymer, while the transition temperature of the random copolymer increased drastically with increasing AAc contents in the random copolymer and eventually disappeared above an AAc content of 40 mol %. They concluded that the main and graft-side chains of the graft copolymer functioned separately as the pH- and temperature-sensitive segments, respectively.

Peppas et al.[5] reported swollen−shrunken behavior of a graft-type hydrogel having a poly(methacrylic acid) (PMAAc) main chain and poly(ethylene glycol) (PEG) graft chains in response to solution pH changes. PMAAc and PEG form interpolymer complexes via hydrogen bonding at low pH.[6] The pH-sensitive interpolymer complex affected the swelling behavior of the PMAAc-*g*-PEG hydrogel. Furthermore, this behavior depended on both copolymer composition and molecular weight of the graft-side chain. The main and graft chains, those that are capable to form the interpolymer complexes in response to pH, are utilized for pH-responsive hydrogels in drug delivery applications.[7]

We already investigated hydrogen-bonded interpolymer complexes between PAAc and polyacrylamide (PAAm) derivatives and constructed temperature-responsive interpenetrating polymer network (IPNs) hydrogels.[8−11] These polymers in distilled water form interpolymer complexes via hydrogen bonding and precipitate at low temperatures, while the complexes dissociate at higher temperatures, dissolving in hot water. Temperature-induced formation/dissociation of the polymer complexes governs swelling behavior of the IPN hydrogel, which shrinks at low temperatures and swells at high temperatures. Among the previous studies, PAAc and poly(*N*,*N*-dimethylacrylamide) (PDMAAm) were found to form stable interpolymer complexes via hydrogen bonding at even 70 °C in distilled water.[11] Additionally, dissociation of complexes between PAAc and poly(DMAAm-*co*-AAm) was observed

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* To whom correspondence should be addressed.
[†] Sophia University.
[‡] Tokyo Women's Medical University.
[§] Present address: Faculty of Photonics Science and Technology, Chitose Institute of Science and Technology, 858-65, Bibi, Chitose, Hokkaido 066-8655, Japan
[||] E-mail: a-takasi@hoffman.cc.sophia.ac.jp.
[⊥] E-mail: tokano@lab.twmu.ac.jp.

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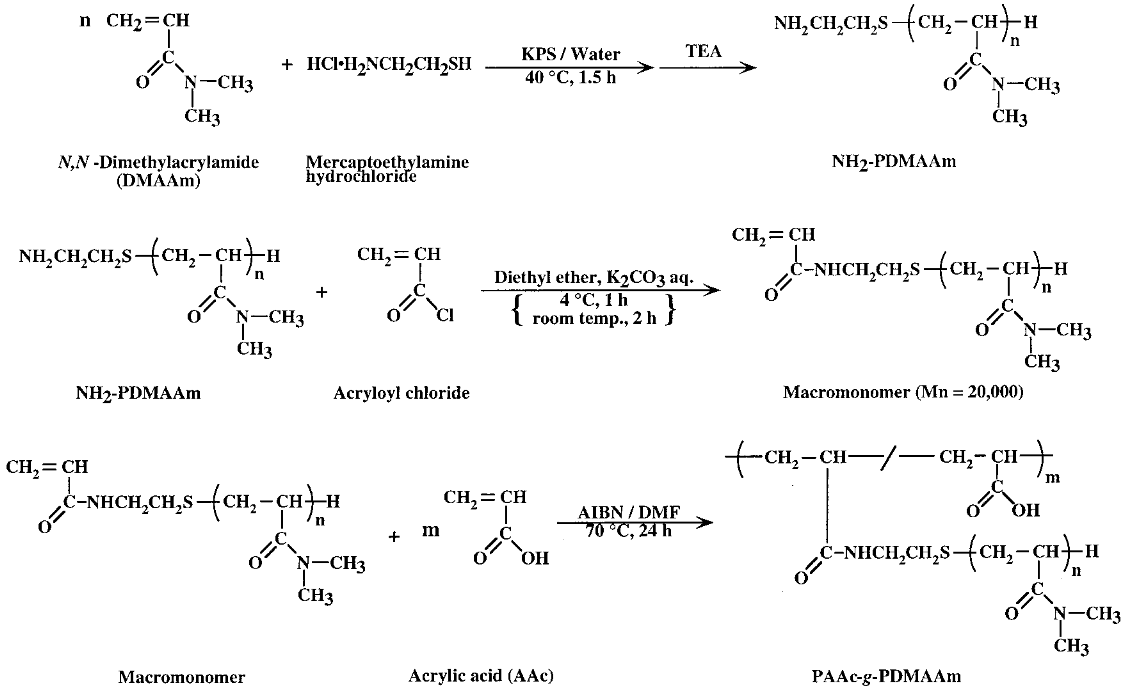
Scheme 1. Syntheses of H_2N−PDMAAm, Its Macromonomer, and the Graft Copolymer (PAAc-*g*-PDMAAm)



at higher temperatures with increasing DMAAm contents. DMAAm worked as a strong hydrogen-bonded acceptor, forming stable interpolymer complexes with PAAc.[11,12] PAAc/poly(DMAAm-*co*-AAm) IPN hydrogels showed a phase-transition behavior between shrunken and swollen states near living body temperature, achieving reversible and pulsatile solute release.[11]

In this study, we have extended our previous polymer−complex study from the blend systems to graft-type copolymer systems and investigated the effect of molecular architecture of PAAc-*g*-PDMAAm on solution properties of the polymer in aqueous solution. The graft-type copolymer showed a different solution behavior from PAAc/PDMAAm blend and random copolymer, poly(AAc-*co*-DMAAm), in terms of phase transition and aggregate formation.

Experimental Section

Materials. *N*,*N*-Dimethylacrylamide (DMAAm) was supplied from Kohjin Co., Ltd (Tokyo, Japan). Poly(acrylic acid) (PAAc) (M_w = 20 000) and mercaptoethylamine hydrochloride (MEAH) were purchased from Aldrich Co. (Milwaukee, WI) and Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan), respectively. Other reagents were purchased from Wako Pure Industries, Ltd. (Osaka, Japan). DMAAm (bp 50.0 °C/5.5 mmHg), AAc (bp 48.0 °C/20.0 mmHg), acryloyl chloride (bp 73.0 °C), and *N*,*N*-dimethylformamide (DMF, bp 40.0 °C/8.0 mmHg) were distilled before use. Potassium persulfate (KPS) and 2,2′-azobis-(isobutyronitrile) (AIBN) were purified by recrystallization from distilled water and methanol, respectively. Diethyl ether (bp 35.5 °C) was distilled after being treated with sodium wire. Other reagents were used as received.

Table 1. Feed and Polymer Compositions of the Graft and Random Copolymers

code	feed composition (mol %)		polymer composition (mol %)[a]		yield (%)
	AAc	DMAAm[b]	AAc	DMAAm[b]	
PAAc-*g*-PDMAAm/45	66.7	33.3	54.7	45.3	78.1
PAAc-*g*-PDMAAm/56	50.0	50.0	44.4	55.6	87.5
PAAc-*g*-PDMAAm/65	40.0	60.0	34.6	65.4	40.1
PAAc-*g*-PDMAAm/75	25.0	75.0	24.8	75.2	24.5
poly(AAc-*co*-DMAAm)	50.0	50.0	52.5	47.5	79.5

[a] Determined by elemental analysis and ^{1}H NMR. [b] Denoted with units of mol %.

Synthesis of NH_2−PDMAAm. A semitelechelic PDMAAm with a terminal amino end group was synthesized by a radical telomerization of DMAAm using MEAH as a chain transfer agent, as shown in Scheme 1. DMAAm (0.24 M), MEAH (7.0 mM), and KPS (1.2 mM) as an initiator were dissolved in distilled water. The solution was degassed by nitrogen gas bubbling, and telomerization was carried out at 40 °C for 90 min under nitrogen gas atmosphere. After the reaction, triethylamine was added to the reaction mixture for neutralization, and then the solution was dialyzed against distilled water for 3 days using a dialysis membrane (Spectra Por; molecular weight cutoff size, 1000). NH_2−PDMAAm was obtained by lyophilization (yield 58.7%). The number-average molecular weight (M_n) of the product was determined by titration of terminal amine groups. The sample (0.2 g) was dissolved in 10 mL of DMF, and the solution was titrated with 0.05 N perchloric acid in acetic acid solution.

Synthesis of Macromonomer. A macromonomer was synthesized by a condensation reaction of an amino group of NH_2−PDMAAm with an excess amount of acryloyl chloride. NH_2−PDMAAm (2.58 g, 0.13 mmol) was suspended in 100 mL of diethyl ether containing acryloyl chloride (3.3 g, 36.5 mmol). To the vigorously stirred diethyl ether solution was added an aqueous solution of potassium carbonate (5.5 g/50 mL) dropwise over a 1-h period at approximately 4 °C on an ice bath. The reaction mixture was stirred for a further 2 h at room temperature. After the reaction, the aqueous phase was extracted and then was dialyzed against distilled water with the dialysis tube (Spectra Por, molecular weight cutoff size, 1000) for 3 days. The purified macromonomer was obtained by the lyophilization (yield 58.2%).

Synthesis of the Graft and Random Copolymers Constructed with AAc and DMAAm. Graft copolymers were prepared by copolymerization of AAc with the DMAAm macromonomer in degassed DMF at 70 °C for 24 h under nitrogen gas atmosphere, using AIBN as an initiator, as shown at the bottom of Scheme 1. Feed compositions for the copolymers were summarized in Table 1. The designation X in PAAc-*g*-PDMAAm/X denotes the DMAAm unit mole percentage in the graft copolymer. After the copolymerization, the reaction solutions were poured into ethyl acetate for reprecipitation of the polymers and dried in vacuo to remove the solvent. The random copolymer of AAc with DMAAm was synthesized in a similar manner.

Analyses. ^{1}H NMR spectra were obtained using deuterated water with a JEOL JNM GX 270 spectrometer at 270 MHz (JEOL, Tokyo, Japan). A phase contrast microscope (IX70, Olympus, Tokyo, Japan) was used for observation of graft copolymer aqueous solution at 54 °C. Fourier transform-infrared (FT-IR) spectra of the various polymer systems in aqueous solutions were recorded on a Shimadzu FT-IR 8600PC (Shimadzu, Kyoto, Japan) with an ATR equipment (Micro Circle, Spectra Tech, Inc., CT) using 200 average scans at a resolution of 4 cm^{-1}. IR spectra for 2.0 wt % of the polymer aqueous solutions were measured at room temperature. A light-scattering spectrophotometer (DLS-7000 Photal, Otsuka Electronics, Osaka, Japan) with a He−Ne laser ($\lambda_0 = 632.8$ nm) was used for dynamic light scattering measurement. A 0.2 wt % sample of the polymer aqueous solution was measured at 20.5 °C with a temperature controller. A dialysis against distilled water with dialysis tube (Spectra Por; molecular weight cutoff size, 50 000) was carried out to prepare the sample solution for measuring temperature dependence of cumulant diameter of graft copolymer. Optical transmittance of the polymer aqueous solutions at various temperatures was monitored at 500 nm by means of a spectrophotometer (UV-1200, Shimadzu). The quartz cell was thermostated with a circulating water jacket equipped with a temperature controller (RTE−211, NESLAB, NH). Each polymer concentration was 2.0 wt %. NH_2−PDMAAm synthesized in this study was used as a linear PDMAAm to investigate the transmittance of polymer mixture solutions. Transition temperature is defined as temperature at 50% of transmittance for each polymer solution.

Results and Discussion

Characterizations of Materials. The number-average molecular weight (M_n) of the NH2−PDMAAm was calculated to be approximately 20 000 by acid−base titration. From the ratio of protons of the vinyl end groups (5−6 ppm) to those for the methyl groups (2.9 ppm) of DMAAm units in ^{1}H NMR spectrum, the M_n of the macromonomer was estimated to be approximately 21 000. The functionality of the terminal end group of PDMAAm was considered to be almost one from the results of acid−base titration and ^{1}H NMR measurements. As shown in Table 1, yields of the graft copolymers decreased with increasing DMAAm contents. Ethyl acetate, which was used for reprecipitation purification, might not be a poor solvent for PDMAAm graft side chains. Recoveries of the graft copolymers with higher DMAAm contents were low.

Solution Properties of Polymers. AAc, DMAAm, and their homopolymers, PAAc and PDMAAm, are all soluble in water over the whole range of temperatures from 5 to 80 °C, although PAAc forms partial hydrogen bonding between carboxylic acid groups in aqueous media. The temperature-dependent transmittance changes of aqueous solutions containing various polymers composed of AAc and DMAAm units are shown in Figure 1. Optical transmittance for the PDMAAm and PAAc blend aqueous solutions was 0% independent of temperature. It was caused by the precipitation due to the interpolymer complexes between these polymers. The interpolymer complexes are very stable at even 80 °C in aqueous solution. This was consistent with the results of the previous study.[11] Randomly copolymerized poly(AAc-*co*-DMAAm) was water-soluble at temperatures ranging between 10 and 70 °C, since the copolymer solution was observed to be completely transparent. On the contrary, the PAAc-*g*-PDMAAm aqueous solution was transparent at lower temperatures, while the transmittance of the solution changed drastically from transparent to turbid above characteristic temperatures. The PAAc-*g*-PDMAAm solution exhibited the temperature-induced phase transition between hydrated and dehydrated states of the polymer. The copolymer composition of PAAc-*g*-PDMAAm also affected the phase separation behavior. The solution behavior was observed at higher temperatures with increasing DMAAm contents. An aqueous solution of PAAc-*g*-PDMAAm/45 having 45.3 mol % of DMAAm content already exhibited turbidity at 10 °C, although PAAc-*g*-PDMAAm/75 with 75.2 mol % of DMAAm content was a water-soluble polymer which showed no phase separation at all temperature ranges examined. It can be noted that the graft structure of the copolymer composed of PDMAAm grafted on the PAAc backbone exhibited the characteristic phase separation from water, since other aqueous solution systems of polymer blend and random copolymer showed no phase transition behavior.

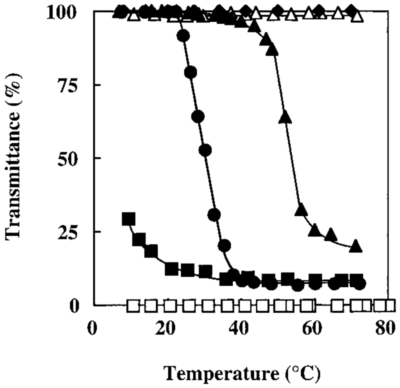


Figure 1. Temperature dependence of optical transmittance changes for the various polymer aqueous solutions: PAAc-*g*-PDMAAm/75 (◆); PAAc-*g*-PDMAAm/65 (▲); PAAc-*g*-PDMAAm/56 (●); PAAc-*g*-PDMAAm/45 (■); poly(AAc-*co*-DMAAm) (△); PAAc/PDMAAm mixture (□).

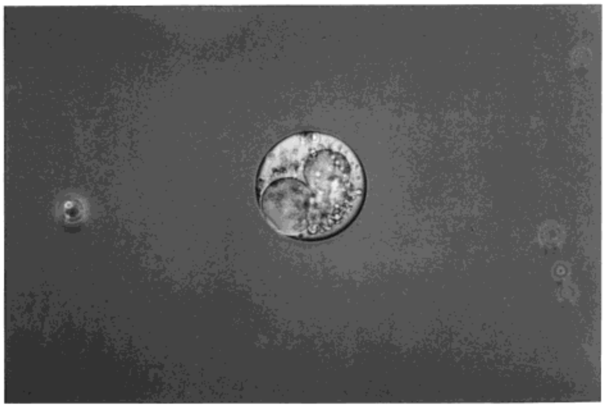


Figure 2. Phase-contrast micrograph of coacervate formed from aqueous solution of PAAc-*g*-PDMAAm/56 at 54 °C. Magnification: 40×.

As shown in Figure 1, the transmittance for the graft copolymer aqueous solutions did not reach 0% above the transition temperatures. Since small oily materials were seen in the polymer solution within the warmed quartz cell, the PAAc-*g*-PDMAAm/56 aqueous solution at 54 °C was observed by a phase-contrast microscope. The microscopic view shown in Figure 2 revealed that liquid−liquid phase separation from the hot water appeared clearly. The phase separation by coacervates with heterogeneous sizes spontaneously occurred in the polymer solution above the transition temperature without stirring. When the solution was cooled, the coacervates gradually became smaller and finally disappeared, returning to a homogeneous aqueous solution. The coacervation by the graft copolymer was considered as follows: PDMAAm shows a negative heat of dilution in water.[13] This is thought to be based on two hydrophobic methyl groups substituted on the N atom in DMAAm. Water molecules readily form hydrophobic hydration around the short alkyl groups at low temperatures and interact with the amide groups via hydrogen bonding, inducing the high hydration states of DMAAm units. When the PDMAAm aqueous solution is heated, liberation of water molecules around the methyl groups increases the entropy slightly, and PDMAAm has a weak dehydrated state. The small dehydration change is also understood from the swelling behavior of PDMAAm hydrogel as a function of temperature.[14] However, hydrophobicities of the short alkyl groups in DMAAm units are insufficient to change drastically the polymer solubility and to give hydrophobic aggregation in water, while the isopropyl groups in PIPAAm have such a hydrophobic property as to result in precipitation in aqueous solution above its LCST. It is also found that introduction of hydrophobic comonomers in PDMAAm chains accelerates dehydration states of DMAAm units at higher temperatures, resulting in the phase separation of a random copolymer from water.[15,16] The similar coacervate formation was observed in a hot aqueous solution of a DMAAm copolymer having hydrophobic comonomers.[16] In the PAAc-*g*-PDMAAm aqueous solution system, the interpolymer complexes between the main and graft-side chains might work as hydrophobic segments to assist the dehydration of DMAAm units at high temperatures, causing the coacervation.

We have used the FT-IR-ATR method to confirm the interaction between the PAAc main chain and PDMAAm grafts in water. Figure 3 showed FT-IR spectra for carbonyl stretching regions for PDMAAm, PAAc, PDMAAm/PAAc blend, and PAAc-*g*-PDMAAm in distilled water at room temperature. The FT-IR spectra for PDMAAm and PAAc showed the bonds for amide (1618 cm^{-1}) and carboxyl (1716 cm^{-1}) groups, respectively. In the spectrum for the PDMAAm/PAAc blend solution, the new carbonyl stretching bonds for PDMAAm and PAAc were observed at lower (1608 cm^{-1}) and higher wavenumbers (1735 cm^{-1}), respectively. This revealed that PDMAAm and PAAc acted as a hydrogen-bonding acceptor and a hydrogen-bonding donor, respectively, for the complex formation. In other words, these appearances of new bonds demonstrated the existence of a hydrogen-bonding interaction between PDMAAm and PAAc. The FT-IR spectrum for the PAAc-*g*-PDMAAm aqueous solution was almost same as that for the PDMAAm/PAAc blend solution. There existed hydrogen bonding in the water-soluble PAAc-*g*-PDMAAm molecules. It is conceivable that PAAc-*g*-PDMAAm in aqueous milieu has two regions: one is the dehydrated region composed of the hydrogen-bonded interpolymer complexes between main and graft-side chains and the other is the hydrated region of both chains which did not participate in the complex formation. Therefore, the change in the polymer composition might govern the balance of the hydrophobic and hydrophilic properties, varying the phase separation behavior, as shown in Figure 1.

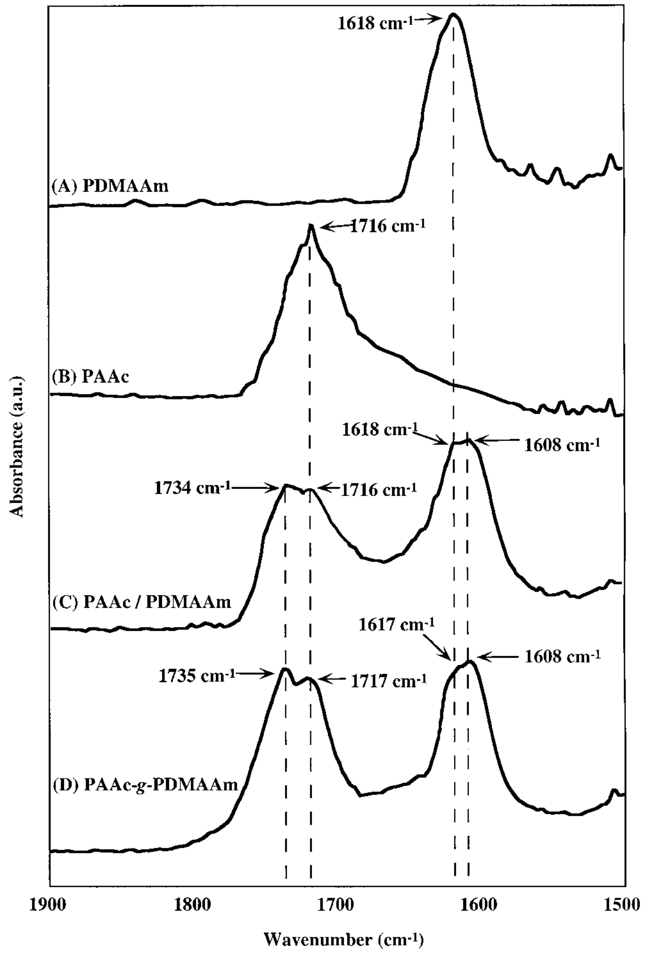


Figure 3. FT-IR–ATR spectra in the regions between 1900 and 1500 cm^{-1} of the polymer aqueous solutions containing (A) PDMAAm, (B) PAAc, (C) PDMAAm/PAAc mixture, and (D) PAAc-*g*-PDMAAm/56.

The results of the dynamic light scattering measurements gave us more detail consideration on the soluble states of the graft copolymer in aqueous milieu. Figure 4a showed a γ-fraction of the diameter for PAAc-*g*-PDMAAm/56 in distilled water at 20.5 °C. The graft polymers had bimodal size distribution in the aqueous solution and were found to form large polymeric associates with a diameter of 141.3 nm. The temperature dependence of the cumulant diameter of the graft copolymer was investigated, since small size materials could be removed and the large associates stably existed in the solution after dialysis. As shown in Figure 4b, the diameter was maintained to be approximately 150 nm within the temperature ranges from 20 to 27 °C. It increased drastically above 27 °C. The change in the diameter was in good accordance with that in the optical transmittance for the copolymer aqueous solution (Figure 1). Furthermore, the associates at 20 °C were the spherical forms, since their diameters showed the constant values independent of the detection angles (data not shown). It is clear that the water-soluble graft copolymer forms 150 nm size spherical associates and that the hydrophobic aggregation between the associates occurred above 27 °C, showing the turbidity of the copolymer solution. Some investigators already reported that amphiphilic graft copolymers similarly formed large aggregates in water.[17–20] The balance between hydrophobic and hydrophilic properties in graft copolymers governs to form such polymeric associates or

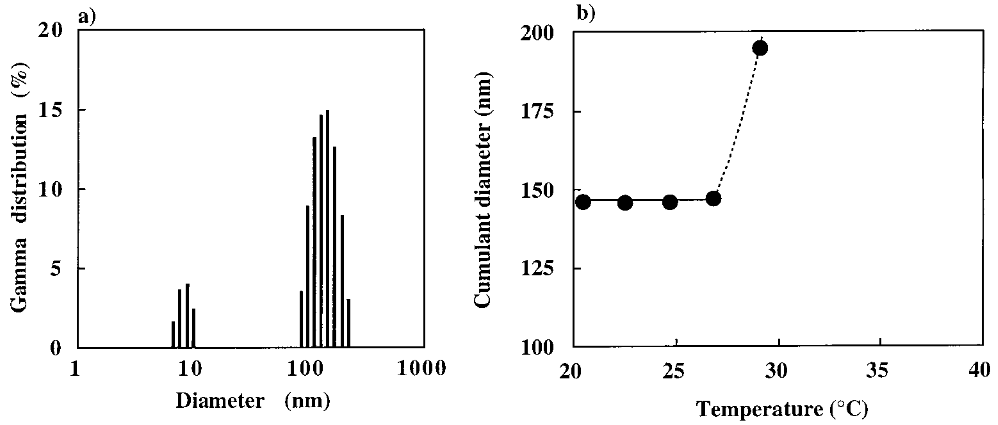
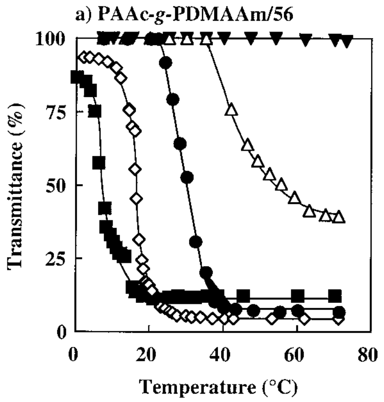


Figure 4. γ fraction of the PAAc-*g*-PDMAAm/56 in distilled water at 20.5 °C (a) and the temperature dependence of cumulant diameter (b). Polymer concentration: 0.2 wt %.



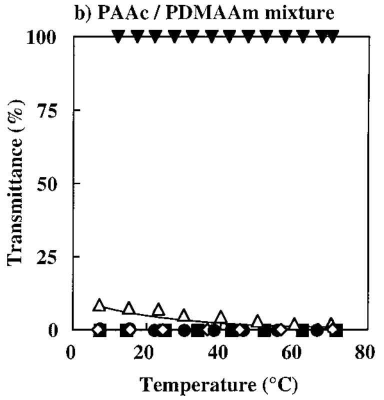


Figure 5. Effect of pH conditions on optical transmittance changes for the PAAc-*g*-PDMAAm/56 (a) and PDMAAm/PAAc (b) aqueous solutions. pH conditions: pH 2.5 (■); pH 2.8 (◇); pH 3.0 (●); pH 3.6 (△); pH 3.8 (▼).

micelles in their water-soluble states. In the case of PAAc-*g*-PDMAAm having AAc and DMAAm units, hydrogen-bonded polymer complexes between the PAAc main and the PDMAAm side chains acted as hydrophobic segments, resulting in formation of the large polymeric associates.

The pH conditions of the polymer aqueous solutions govern ionic dissociation of the AAc carboxyl groups of the main chains. The effect of the pH on the temperature-dependent transmittance change for the polymer aqueous solutions is shown in Figure 5. The phase separation behavior of PAAc-*g*-PDMAAm/56 was observed at higher temperatures with increasing pH values. At pH 3.8, the transmittance for the polymer solution maintained 100% independent of temperature, indicating no phase separation. The higher pH values of the solution prompted more ionic dissociation of the carboxylic acid groups, causing the formation of less hydrogen bonded polymer complexes between AAc and DMAAm units of the graft copolymers. On the contrary, the transmittance for the PDMAAm/PAAc blend aqueous solution was 0% independent of temperature under pH ranges from 2.5 to 3.6, while it was observed to be 100% at pH 3.8. This revealed that PDMAAm and PAAc in aqueous media below pH 3.6 formed the hydrogen-bonded complexes that did not dissociate at even high temperatures. pH 3.8 was not a suitable condition for the formation of the hydrogen-bonded polymer complex in water. These results are in good agreement with the previous study.[21] The paper also includes the point that the polymer mixture shows LCST in an aqueous milieu at pH 3.7.

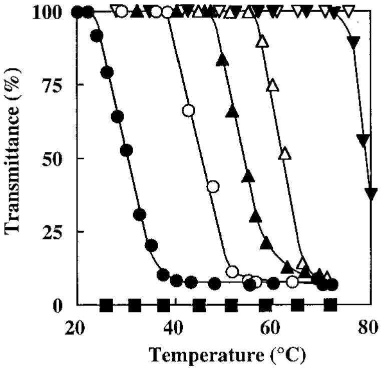


Figure 6. Effect of PDMAAm or PAAc addition on transmittance changes for PAAc-*g*-PDMAAm/56 aqueous solution. PDMAAm concentrations: 0 wt % (●); 0.2 wt % (○); 0.5 wt % (▲); 1.0 wt % (△); 1.5 wt % (▼); 2.0 wt % (▽). PAAc concentration: 0.1 wt % (■).

Moreover, the PDMAAm/PAAc blend systems form a solid precipitate out of the solution. The dehydration states were quite different from the liquid–liquid phase separation of the PAAc-*g*-PDMAAm, despite that both polymer mixture and graft-type copolymer systems contained AAc and DMAAm units. The differences of the dehydrated states between these two systems might be attributed to the difference in the complexation between AAc and DMAAm units. In the PDMAAm/PAAc blend systems which were composed of the linear polymers, the initial hydrogen-bonded complex formation between AAc and DMAAm units of each polymeric chain might trigger the cooperative formation of the adjacent complexes between the neighboring AAc and

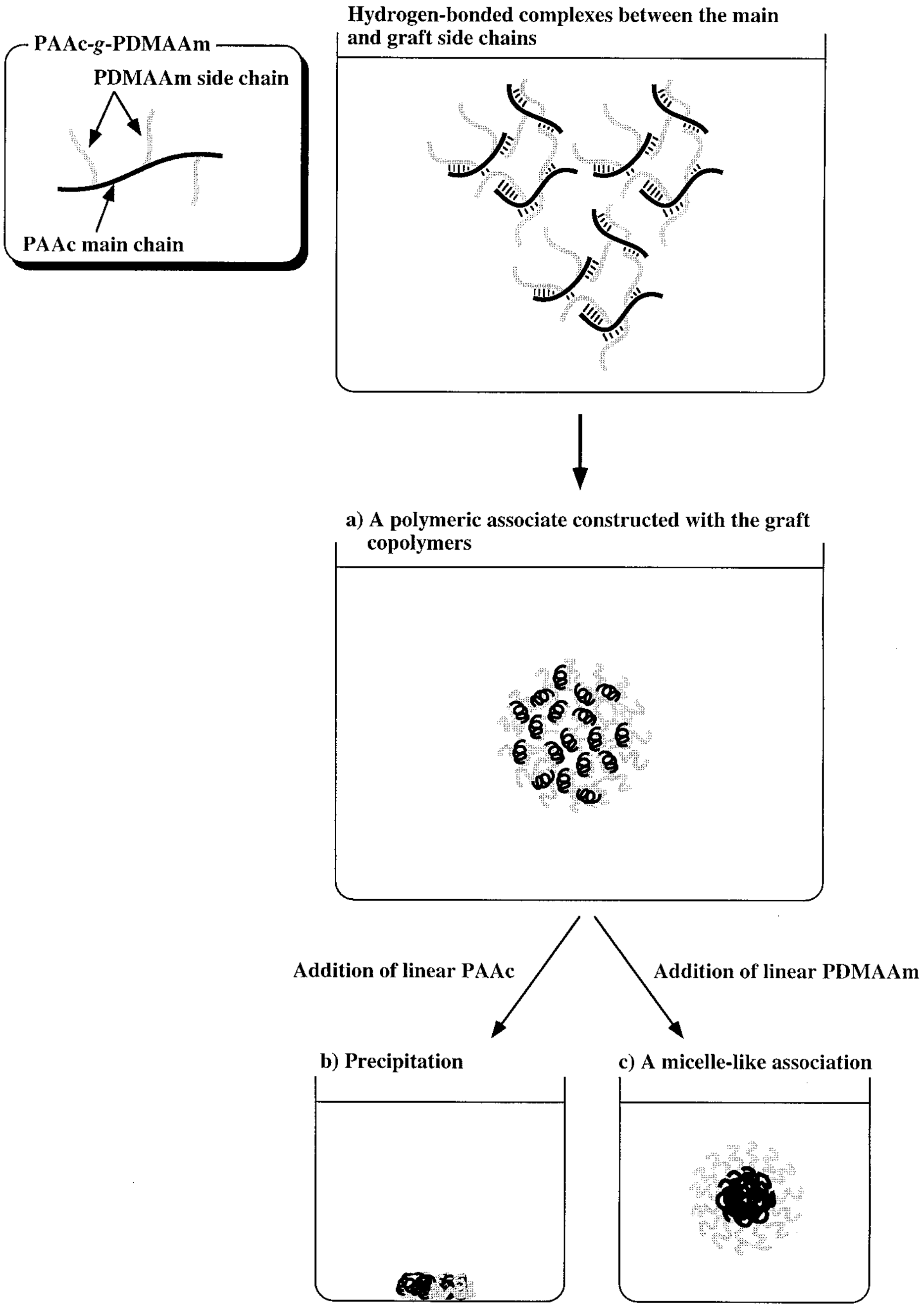


Figure 7. Conceptional representation for hydrogen-bonded association of PAAc-*g*-PDMAAm with or without linear PAAc or PDMAAm in aqueous media.

DMAAm units. The effective complex formation between the polymeric chains resulted in only the completely dehydrated state. In the PAAc-*g*-PDMAAm system, since one end of the PDMAAm chains was bound covalently to the PAAc backbone chains, the PDMAAm and PAAc chains have limited motions. The complexes between two polymeric chains formed ineffectively. Therefore, there are the hydrated main and graft chains which formed no complexes in the addition of the hydrophobic region composed of the hydrogen-bonded interpolymer complexes. The intra- and interpolymer complexes of the graft copolymer that formed partially did not dissociate at 70 °C in water. They acted as hydrophobic segments to cooperatively result in hydrophobic aggregation, enhancing the thermo-induced dehydration behavior of DMAAm units that did not participate in complex formation at high temperatures. The molecular architecture of the graft-type copolymer governed the polymer complexation for the associates and caused the liquid−liquid phase separation above the transition temperatures.

Effect of the Linear Polymer Addition on Solution Behavior of PAAc-*g*-PDMAAm. Linear PDMAAm and PAAc were independently dissolved in the PAAc-*g*-PDMAAm/56 aqueous solution to investigate the change in the phase-separation behavior of the graft copolymer. As shown in Figure 6, the solution turbidity change occurred at higher temperatures with increasing linear PDMAAm concentrations. At a PDMAAm concentration of 2.0 wt %, the phase separation of the graft copolymer is not optically observed. On the contrary, when 0.1 wt % of PAAc was added into the graft copolymer solution, the transmittance was 0% and the precipitate was formed even at room temperature. The results indicated that additions of PDMAAm and PAAc, which could work as a hydrogen-bonding acceptor and a hydrogen-bonding donor, respectively, into the copolymer solutions, resulted in the opposite solution property changes. A random copolymer of DMAAm with hydrophobic comonomers also shows coacervate above its transition temperature.[15,16] The PAAc-*g*-PDMAAm molecules themselves might randomly contain two regions: one was based on hydrophobic polymer complexes between main and side chains, and the other was hydrophilic polymer chains without any complexations (Figure 7a). In other words, the partially formed hydrogen-bonded complexes and the hydrated chains were poorly segregated in the associates. When the solution temperature was elevated, the associates aggregated hydrophobically to show the liquid−liquid phase separation from water.

On the other hand, the hydrated PDMAAm graft chains of the associates were consumed to form the polymer complexes by the addition of the linear PAAc, causing totally dehydrated precipitation of the graft copolymer associates (Figure 7b). In the mixed systems of PAAc-*g*-PDMAAm and the linear PDMAAm, as the linear PDMAAm chains had a relatively higher mobility than the graft chains, they might interact selectively with the PAAc main chains of the graft copolymers, creating the completely dehydrated regions. The dehydrated PAAc/linear PDMAAm complexes hydrophobically aggregated in the graft copolymer solution and functioned as hydrophobic core segments. Additionally, the hydrated PDMAAm graft chains worked as hydrophilic shell segments, which surrounded the dehydrated polymer complexes. Since the polymer complexes and the graft chains were segregated in the graft/linear polymeric associate systems, the graft copolymers did not show phase separation from water and were solubilized (Figure 7c). Moreover, the graft/linear polymeric associates are stabilized in aqueous milieu by utilizing a dialysis method from DMSO to water. They have a relatively smaller diameter of approximately 120 nm, as compared with that of the graft copolymers. Interestingly, the graft/linear polymeric associates maintain spherical form in physiological buffer solution at even pH 7.4, while associates composed of only graft copolymers break readily into smaller materials in the same solution. It can be also noted that the hydration of the graft chains prevents the breaking of hydrogen bonding between the polymer chains under physiological conditions. A more detailed investigation about the polymeric associations constructed with PAAc-*g*-PDMAAm and linear PDMAAm will be reported in the next paper.

Conclusion

PAAc-*g*-PDMAAms were synthesized by free radical copolymerization of AAc with PDMAAm macromonomer. The graft copolymers showed liquid−liquid phase separation above characteristic transition temperatures, although they were water-soluble below these temperatures. On the contrary, the PDMAAm/PAAc blend produced a solid precipitate and poly(DMAAm-*co*-AAc) was water-soluble independent of temperatures. Clearly, the molecular architecture of the graft copolymers governed the different solubility behavior of the polymer in aqueous solution as compared with those of the blend and random polymers. FT-IR-ATR spectra and DLS analyses supported the point that the graft copolymers below the transition temperature contained partially formed polymer complexes between PAAc main and PDMAAm side chains via hydrogen bonding, forming polymeric associates with diameters of approximately 150 nm. The liquid−liquid phase separation from water was observed in the graft copolymer aqueous solution above the transition temperature, since the dehydrated behavior of DMAAm units and hydrophobic segments based on the polymer complexes cooperatively formed hydrophobic aggregation of the polymeric associates.

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