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Interpolymer Complex between Poly(*N*-acetylacrylamide) and Poly(acrylamide) in Ethanol-Water System

Norihiro KATO,[†] Masamichi TAKEDA, Yasuzo SAKAI, and Tadao UYEHARA

[†] *Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya 321-8585, Japan (E-mail: katon@cc.utsunomiya-u.ac.jp)*

Properties of an upper critical solution temperature (UCST) of poly(*N*-acetylacrylamide) (PNAcAAm) were examined in alcohol-water system. Formation of an interpolymer complex was determined by measuring the optical transmittance of the polymer solution with changing the temperature. PNAcAAm was easily soluble in water, while the temperature-dependent phase separation was observed in methanol-water, ethanol-water, and 1-propanol-water system. The formation of 1:1 (wt/wt) polymer complex between PNAcAAm and poly(acrylamide) (PAAm) made the UCST decreasing from 36.5℃ to 16℃ in aqueous solution of 30 wt% ethanol. The 1:1(wt/wt) polymer complex was insoluble below 17℃. However, the UCST of polymer mixture was not influenced in the presence of 1-10 times weight ratio of poly(*N*,*N*-dimethylacrylamide) (PDMAAm) against PNAcAAm. These results were speculated as following: The insoluble 1:1 (wt/wt) polymer complex was formed due to hydrogen bonding between the acetylamide groups of PNAcAAm and the amide groups of PAAm. On the other hand, the interpolymer complex becomes soluble in the case of the hydrogen bonding between the acetylamide groups of PNAcAAm and the *N*,*N*-dimethylamide group of PDMAAm, because the PDMAAm has a strong affinity to water.

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There are many papers reported on the thermosensitive polymer and hydrogel due to the interest in systems of the polymer performing the stimuli-responsive properties.[1-3] A typical temperature-sensitive polymer, poly(*N*-isopropylacryl-amide) (PNIPAAm) has a porperty of a lower critical solution temperature (LCST) and has been utilized to construct a variety of intelligent systems.[4,5] One of the authors has reported physicochemical studies on PNIPAAm to enhance deswelling rates of the PNIPAAm gel at higher temperature than the LCST.[6,7] Magneto-driven hydrogel was also prepared by using the fast-responsive PNIPAAm gel containing the ferromagnetic powder.[8,9] The hydrogel is activated magnetically to perform the volume phase transition of PNIPAAm by heating generated under the alternating magnetic field. It is possible to apply this magnetic induction heating to other kinds of temperature-sensitive polymers or gels. Accordingly, the accomplishment of constructing a new type of magnetically activated gels brought us following motivations to investigate the other temperature-sensitive polymers.

Katono et al. reported the interpolymer complex between poly(acrylamide) (PAAm) and poly(acrylic acid) (PAA) in the preparation of an interpenetrating polymer network (IPN).[10,11] It was described that the hydrogen bonds between the amide groups and the carboxylic acid groups in the IPN gel were scissored with raising the temperature, and then the gel swelled caused by hydration of the polymers. This gel can swell and deswell repeatedly in response to the temperature change. Interpolymer complexes are structured generally by the formation of hydrogen bonds between a polyacid and a proton-acceptor polymer such as poly(acrylamide), poly(ethylene glycol), and so on.[12,13] It is plausible that the formation and cleavage of hydrogen bonds may be related with properties of an upper critical solution temperature (UCST) of polymers in aqueous solutions. As compared with the LCST polymer, there are only a few reports concerning UCST polymers in aqueous solutions. Therefore, it is worthwhile to investigate their UCST's and the thermal properties of the UCST polymers.

In recent years, keen interests are paid for a phase separation of UCST polymers or amphoteric polymers as zwitterions.[14,15] We have studied poly(*N*-acetylacrylamide) (PNAcAAm) in connection with the thermal properties of the interpolymer complex. PNAcAAm has acetylamide groups which can play a role as both proton-donors and -acceptors in aqueous solution. The formation of the interpolymer compex was also surveyed using PAAm, poly(*N*, *N*-dimethylacrylamide) (PDMAAm) to shed light on the properties concerning the hydrogen bond formation of acetylamide groups.

The purpose of this research is to make the UCST behavior of PNAcAAm in alcohol-water system clear. The formation of interpolymer complexes due to the hydrogen bonds will be discussed in connection with the interaction between acetylamide groups of PNAcAAm and amide groups of PAAm, or dimethylamide groups of PDMAAm.

Experimental

Materials *N*-Acetylacrylamide was synthesized by the reaction between acrylamide and *N*, *N*-dimethylacetamide dimethyl acetal, and then the hydrolysis in aqueous solution of 70 % acetic acid according to the previous report.[14] The yield of *N*-acetylacrylamide for two step synthesis was 40%.

All other chemicals were of guaranteed grade or the best commercially available.

Polymer preparation *N*-Acetylacrylamide was dissolved in distilled water to adjust to 1 mol dm^{-3} solution. Nitrogen gas was bubbled into the solution to remove dissolved oxygen. Polymerization was carried out by adding ammonium peroxodisulfate at 5°C. After that, the polymer solution was dialyzed in distilled water and then freeze-dried. The molecular weight of the PNAcAAm was determined to be (85,000) by the size exclusion chromatography. In the same way as described above, PAAm (molecular weight 52,000) and PDMAAm (molecular weight 55,000) were synthesized by radical polymerization.

Turbidity measurement The desired amount of PNAcAAm was dissolved into the aqueous solutions of methanol, ethanol, or 1-propanol to adjust to 0.2 wt% polymer solutions. Similarly, 0.2 wt% solutions of PAAm or PDMAAm were prepared in aqueous solution of 30 wt% ethanol. The formation of interpolymer complex was determined by measuring the turbidity of aqueous alcohol solutions containing polymers at 500 nm using UV-VIS spectrophotometer (UV-2400PC, Shimadzu). The temperature of the cell can be controlled by the water-flowing system using the heating and cooling unit (Uni-cool UC-55N, Tokyo Rikakikai). The temperature was determined by a thermocouple inserted to the polymer solution in the cell. The polymer solution in the cell was stirred during the measurement to avoid the sedimentation of the polymer complex separated from the solution with an electromagnet controlled by a function generator (FG-273, Kenwood) and a galvanostat (HA-211, Hokuto Denko). The drastic change of the turbidity was recorded with temperature due to heating up and cooling down (0.1°C / min).

The mixtures were prepared as 0.2 wt% PNAcAAm solution containing the PNAcAAm and PDMAAm [PNAcAAm /PDMAAm = 1/1, 1/10 (wt/wt)], PAAm and PDMAAm [PAAm/PDMAAm = 1/1, 1/10 (wt/wt)], and PNAcAAm and PAAm [PNAcAAm /PAAm = 1/1, 10/1 (wt/wt)]. Temperature dependency of the turbidity was also measured to examine the interpolymer complex between different polymers.

Determination of ΔT_r The optical transmittance of the polymer solution depends on the temperature. The maximum change of the optical transmittance between the soluble and insoluble polymer solutions (e.g., between 40 and 5°C) are defined as ΔT_r. The UCST (T_c) was determined as the critical temperature, where the transmittance got to 100% during the heating process.

Results and discussion

Interpolymer complex of PNAcAAm due to self-association
Temperature dependency of the turbidity was measured in water, and in aqueous solutions of 30 wt% methanol, 30 wt% ethanol, and 30 wt% 1-propanol containing 0.2 wt% PNAcAAm. The insoluble polymer complex appeared below 36.5°C in alcohol-water system, except that the polymer complex was always soluble in water between 5 and 45°C. Figure 1 shows the result of the turbidity profiles due to the heating up process. No hysteresis was observed for any solutions in the cooling down process after heating up (data not shown). Every aqueous alcohol solution was opaque at lower than 36.5°C. These solutions became transparent above 36.5°C. It is explained in the similar way as the interpolymer complex between PAAm and PAA[10,11] that the hydrogen bonds between acetylamide groups due to self-association make the insoluble interpolymer complex below 36.5°C. After dissociation of the interpolymer complex, polymer chains bind water molecules to make hydration, and the polymer solution becomes soluble. In the case of the aqueous solution of 30 wt% alcohol, the optical transmittance change (ΔT_r) decreased with increasing the hydrophobicity of the alcohol. The optical transmittances for the solution of methanol, ethanol, and 1-propanol were 22, 51, and 98%, respectively, at around 10°C. The solubility of the interpolymer complex of PNAcAAm increased with increasing the alkyl group numbers in the alcohol. It seems, however, that the hydrogen bonds between acetylamide groups are formed in all of alcohols used.

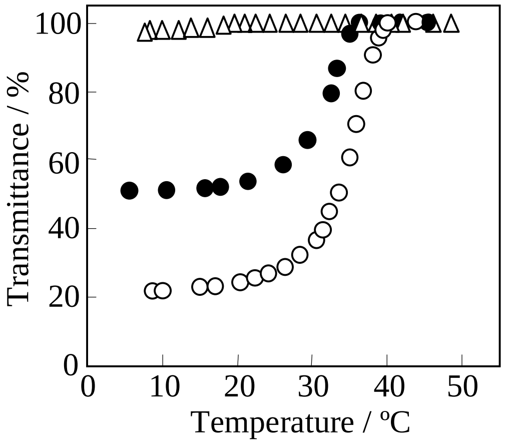

Fig. 1 Effect of temperature on the optical transmittance of the aqueous alcohol solution of PNAcAAm. Transmittance was measured at 500 nm in the heating up process: (○) 30 wt% methanol, (●) 30 wt% ethanol, (△) 30 wt% 1-propanol.

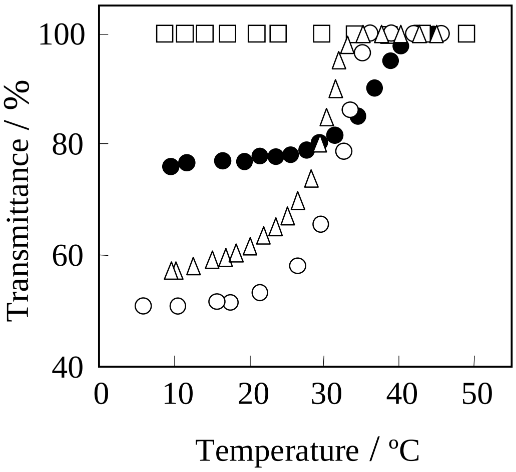

Fig. 2 Effect of ethanol concentration on the optical transmittance of the PNAcAAm solution in ethanol-water system. Transmittance was measured at 500 nm in the heating up process: (□) water, (△) aqueous 20 wt%, (○) 30 wt%, and (●) 50 wt% ethanol.

Effects of the ethanol concentration were surveyed on the turbidity. The results on the optical transmittance were shown in Fig. 2. These results show that ΔT_r increased with increasing the ethanol concentration in the range of 0 - 30 wt%. The relationship between the alcohol concentration and the optical transmittance of polymer solutions was investigated in methanol, ethanol, and 1-propanol solutions (Fig. 3).

Every alcohol solution gained the turbidity with increasing the alcohol concentration. The measurement of turbidity was not possible in the concentration of higher than 50 wt% ethanol, 70 wt% methanol, and 80 wt% 1-propanol due to precipitation of polymers during the measurement. Each minimum in the transmittance-alcohol concentration curve appeared as shown in Fig. 3. The optical transmittance increased at higher than 30 wt% ethanol, 50 wt% methanol and 50 wt% 1-propanol. Since the optical transmittance of the turbid solution was around 50%

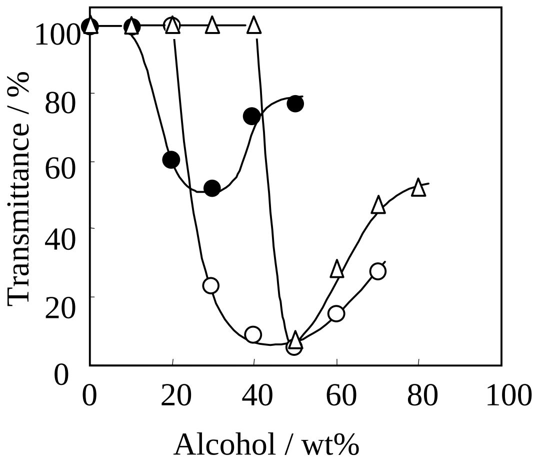

Fig. 3 Effect of alcohol concentration on the optical transmittance of the PNAcAAm solution in alcohol-water system. Transmittance (500 nm) was measured at 20°C with 0.2 wt% polymer of aqueous methanol (○), ethanol (●), and 1-propanol (△).

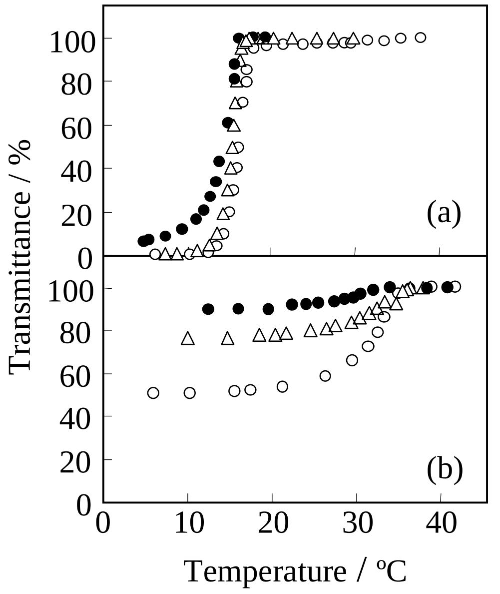

Fig. 4 (a) Effect of temperature on the optical transmittance of the solution containing PDMAAm and PAAm: (●) PAAm, (△) PAAm / PDMAAm = 1 / 1, (○) PAAm / PDMAAm = 1 / 10. (b) Effect of temperature on the optical transmittance of the solution containing PNAcAAm and PDMAAm: (○) PNAcAAm, (△) PNAcAAm / PDMAAm = 1 / 1, (●) PNAcAAm / PDMAAm = 1 / 10. Transmittance was measured with 30 wt% ethanol -70 wt% water system at 500 nm in the heating up process.

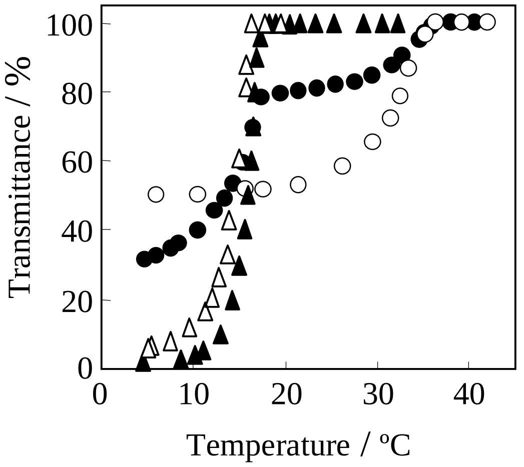

Fig. 5 Effect of temperature on the optical transmittance of the aqueous ethanol solution containing PNAcAAm and PAAm. Transmittance was measured with 30 wt% ethanol solution at 500 nm in the heating up process: (○) PNAcAAm, (△) PAAm, (▲) PNAcAAm / PAAm = 1 / 1, (●) PNAcAAm / PAAm = 10 / 1.

according to Fig. 3, 30 wt% ethanol solution was selected for carrying out following experiments in order to estimate the formation of interpolymer complex.

Comparison of PNAcAAm and PAAm Figure 4 shows the turbidity change of aqueous solution of 30 wt% ethanol containing PAAm or PNAcAAm. The T_c for PAAm and PNAcAAm were 16 and 36.5°C, respectively. Aoki et al. reported that the turbidity change was considered to be as an index of the dissociation of the hydrogen bonds between polymer chains in order to study the thermal properties of the polymers.[18] Therefore, the difference of T_c was discussed with the stability of the hydrogen bonds. The mutual association between acetylamide groups in PNAcAAm are more stable than those between amide groups in PAAm. Judging from the difference of T_c, PNAcAAm is more hydrophilic than PAAm. Because the hydrophilic PNAcAAm is possible to turn soluble with the presence of interpolymer complex.

As compared with PNAcAAm, PAAm solution gave larger ΔT_r in smaller temperature change (Fig. 4a). An acetylamide group in PNAcAAm includes two C=O groups as proton acceptors and one NH hydrogen as a proton donor. On the other hand, an amide group in PAAm includes one C=O group as a proton acceptor and two NH hydrogens as proton-donors. Therefore, it is plausible that the amide groups in PAAm as the proton donor can bind easier to dimethyl amide groups of PDMAAm as the proton acceptor than the acetylamide groups of PNAcAAm.

Interpolymer complex of PDMAAm to PAAm or PNAcAAm PDMAAm in aqueous solution of 30 wt% ethanol was transparent between 5 and 50°C (data not shown). This is because PDMAAm can not form hydrogen bonds between dimethylamide groups, which can not serve as the proton donor. Accordingly, interpolymer complex for PDMAAm was considered not to be observed in the range of 5 - 50°C.

As shown in Fig. 4a, addition of PDMAAm into PAAm made a slight shift of T_c to higher temperature. On the contrary, T_c's of PNAcAAm can not be affected in the presence of PDMAAm (Fig. 4b), and ΔT_r decreased with increasing the PDMAAm concentration. Since dimethylamide groups of PDMAAm can serve as only the proton-acceptor, this result demonstrates that the hydrogen bond formation between the amino group of PAAm and the carbonyl group of PDMAAm was responsible for the insoluble polymer complex.

It is known that PDMAAm is one of the LCST polymer, of which two methyl groups covalent bonded to nitrogen atom in a dimethylamide group can play a role as the hydrophobic region, in which the hydrophobic hydration occurs.[16-18] PDMAAm has the strong affinity for water below 60°C. The de-hydrated PDMAAm precipitates above 60°C. It is also known that the PDMAAm gel deswells gradually with increasing temperature.

Figure 4a shows that the interpolymer complex between PNAcAAm and PDMAAm is soluble in aqueous solution of 30% ethanol due to the strong affinity of the PDMAAm for water. Acetylamide groups of PNAcAAm may form the hydrogen bonds with dimethylamide groups of PDMAAm. The optical transmittance increased with increasing the PDMAAm concentraion. The NH hydrogen of acetylamide group in PNAcAAm is the only proton-donor in this system. It is obvious that the self-association of PNAcAAm decreases caused by the substitution to hydrogen bonds with increasing PDMAAm as a proton acceptor. It seems that the self-association of PAAm is stronger than that of PNAcAAm. Therefore, the profile of PAAm do not show larger change as compared with that of PNAcAAm at low temperature.

Interpolymer complex between PNAcAAm and PAAm Formation of the interpolymer complex between PAAm and PNAcAAm was investigated in aqueous solution of 30 wt% ethanol (Fig. 5). Addition of PAAm to PNAcAAm (PNAcAAm /AAm = 1/1) lowered T_c of PNAcAAm from 36.5 to 19°C. The transmittance–temperature curve of 1/1 PNAcAAm-AAm was almost overlapped with that of PAAm. This result indicates that the hydrogen bonds between the amide group of PAAm and the acetylamide group of PNAcAAm are stronger than the self-association between the acetylamide groups.

In the case of the PNAcAAm/PAAm = 10/1, two-stage profile was observed as shown in Fig. 5. This result means that a part of acetylamide groups form hydrogen bonds with the amide groups and the rest of acetylamide groups form self-association each other. When the opaque solution containing polymers was heated up from 5°C, the hydrogen bonds between the acetylamide groups and the amide groups was scissored with increasing the optical transmittance drastically, which meets the curve of PNAcAAm /PAAm = 1/1. The second-stage of the curve started at around 17°C. Two-stage profile is evident that diffenrent kinds of polymer complexes are present independently in the solution, and the self-associated PNAcAAm is dissociated to become soluble due to the hydration of the polymer.

It is concluded that PNAcAAm forms the insoluble interpolymer complex in alcohol-water system. The critical temperature for the dissociation of the complex is controlled by the nature and the concentration of alcohol. The solubility of interpolymer complex between PNAcAAm and PAAm changes from soluble to insoluble and vice versa reversibly at the narrow range of the temperature.

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