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ORIGINAL ARTICLE

Thermal hysteresis of aggregation states of thermoresponsive block copolymers forming intermolecular hydrogen bonds

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Abstract

The aggregation behaviors of a diblock copolymer and a triblock copolymer of poly(2-ethyl-2-oxazoline) (PEOX) and polyethylene oxide (PEO) in aqueous solutions were investigated mainly by static and dynamic light scattering and infrared spectroscopy. PEOX is a thermoresponsive polymer that is soluble in water at room temperature, but insoluble above 60 °C, and it forms aggregates with poly(methacrylic acid) (PMAA) by using intermolecular hydrogen bonds. The structures of the aggregates of PEOX, which were formed due to the thermoresponsive interactions and intermolecular hydrogen bonds were estimated by measuring the aqueous solutions and precipitates formed by mixing solution of the block copolymers of PEOX and PEO and solution of PMAA at various mixing ratios and temperatures. The differences between the structure formed by mixing aqueous solution of the block copolymers of PEOX and PEO and that of PMAA mixed at 25 °C and measured at 65 °C and that formed in aqueous solutions mixed and measured at 65 °C were investigated to elucidate the influences of thermoresponsive interactions and intermolecular hydrogen bonds. There were no significant differences between the aggregates formed by the diblock copolymer and PMAA mixed at different temperatures, and the aggregates formed by the triblock copolymer and PMAA mixed at 65 °C had higher molar mass than that mixed at 25 °C.

Introduction

Polymer chains in solution sometimes form aggregates via interpolymer interactions such as coordinate bonds between metallic ions and ligands bound to the side chains of polymers, ionic interactions between polyanions and polycations, hydrogen bonding between proton-donating polymers and proton-accepting polymers, and interactions inducing stereocomplexes of some specific polymers. Some interactions can be canceled to dissociate the aggregates into isolated polymer chains under some specific circumstances. These switchable polymer aggregates have the potential to be applied as a drug delivery system (DDS). Polymers forming aggregates by two or more kinds of interactions can respond to even very complicated circumstances. Biopolymers are typical polymers that utilize many kinds of interactions for their functions.

Poly(2-ethyl-2-oxazoline) (PEOX) has excellent biocompatibility [1, 2] and high mixability with many other polymers. These properties enable PEOX to be applied to modify the surface of polymer materials. Hong et al. [3] prepared films of poly(methyl methylate) containing oligo (2-ethyl-2-oxazoline) grafted from poly(methyl methylate) to enhance the biocompatibility of poly(methyl methylate) films without changing bulk properties.

PEOX is also known to aggregate with poly(methacrylic acid) (PMAA) or poly(acrylic acid) (PAA) by forming hydrogen bonds among the polymer chains [4]. There have been studies on the basic solution properties of PEOX in water, alcohols [5], and tetrahydrofuran [6], and it is known that PEOX is soluble in water at room temperature, but insoluble when the temperature is increased to ~65 °C. Chen et al. [7] reported a lower critical solution temperature (LCST) type phase diagram of an aqueous solution of PEOX with weight average molecular weight M_w of 1.16×10^5. The diffusion coefficient for the faster mode, which was identified as

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molecularly dispersed PEOX chains, increased drastically above 60 °C, and excess low-angle scattering became evident above 62 °C. These results suggest that the elevation of the solution temperature suddenly induced structural changes of PEOX chains above 60 °C.

Copolymers of PEOX and biocompatible polymers such as poly(L-lactic acid) [8–10], poly(aspartic acid) [11], and poly(ε-caprolactone) [12] were synthesized and their aggregation behaviors were investigated for their potential application as DDS. The ability of some of the block copolymers of PEOX [9, 10] to carry model drug molecules was also tested.

PEOX and some poly(2-alkyl-2-oxazoline)s are soluble in water at low temperatures, and insoluble at elevated temperatures, although their phase separation temperatures depend on length of the alkyl groups in their side chains. The micellization behavior of block copolymers of poly(2-isopropyl-2-oxazoline) which have unique crystallization behaviors, has attracted the interest of many researchers [13, 14].

We have studied the aggregation behaviors of PEOX homopolymers [15] or block copolymers of PEOX and poly(ethylene oxide) (PEO) [16] and PMAA, which were formed by mixing an aqueous solution of PEOX polymers and an aqueous solution of PMAA. Infrared spectra of the aggregates formed by the PEOX homopolymer and PMAA indicated the formation of hydrogen bonds between carbonyl groups of PEOX and hydroxyl groups of PMAA. PEOX and PMAA tend to form aggregates with equimolar compositions of EOX and MAA, although they can form aggregates with nonequimolar compositions when the composition of feed polymers deviates drastically from the equimolar composition. Dynamic light scattering indicated the formation of aggregates between PEOX and PMAA, but the intrinsic viscosities of the solutions containing both PEOX and PMAA were significantly lower than those of solutions containing only PEOX or PMAA. These results suggest the formation of aggregates with very high polymer densities, that is, very small dimensions.

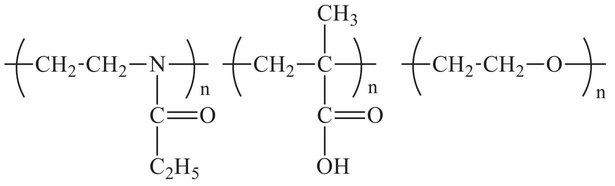
The aggregation behavior of a diblock copolymer of PEOX and PEO with PMAA was also investigated to elucidate the influence of block chains on the aggregation between PEOX and PMAA. PEO was used as the block chains copolymerized with PEOX because it is a typical hydrophilic polymer and is widely used for medical purposes and cosmetics due to its high biocompatibility. PEO was also reported to form complexes with PMAA or PAA. PEO also tends to form equimolar complexes irrespective of the molar ratio of the feed solutions [17–30]. Based on the experimental results of our previous study, PEO has a weaker tendency to form aggregates with PMAA than PEOX [16]. Although the block copolymers of PEOX and PEO also tend to form equimolar complexes with PMAA, its tendency to form equimolar complexes was weaker than the tendency of PEOX homopolymer and that of PEO homopolymer, and nonequimolar complexes were formed when the composition of feed polymers deviated drastically from the equimolar composition.

In this study, the aggregation behaviors of a PEOX-PEO diblock copolymer or a PEOX-PEO-PEOX triblock copolymer and PMAA formed by mixing their solutions at different temperatures were primary investigated by static and dynamic light scattering measurements and infrared spectroscopy. The structures of the aggreges formed by mixing the solutions at 65 °C were assessed and compared to the structures of the aggreges formed by mixing the solutions at 25 °C to elucidate the structural changes of the aggregates of the copolymers and PMAA induced by the drastic change of the structure of PEOX blocks above 60 °C. Because PEOX is insoluble in water above 65 °C, aggregates of PEOX and PMAA cannot be prepared by mixing their aqueous solutions at 65 °C. On the other hand, aggregates can be prepared by mixing an aqueous solution of PEOX-PEO block copolymer and a solution of PMAA because the PEO blocks allow the block copolymers to dissolve in water even above 65 °C. The difference in the structures of the aggregates formed by mixing the solutions at 25 °C and measured at 65 °C, and those formed by mixing and measured at 65 °C was analyzed to investigate the thermal hysteresis of the aggregates.

Experimental Procedure

Materials

A PEOX-b-PEO diblock sample and PEOX-b-PEO-b-PEOX triblock sample were purchased from Polymersource. The number average molecular weights M_n of PEOX and PEO blocks reported by the supplier, were 6,500 and 5,000, respectively both for the diblock and triblock copolymers. The ratios of weight average molecular weights M_w and M_n reported by the supplier were 1.25 and 1.27, respectively. Elemental analyses were carried out with the block copolymers to check the molar ratios of PEOX and PEO. The weight ratios of carbon and nitrogen elements measured by the elemental analyses equaled to the values calculated from the molecular weights reported by the supplier to within 1.2%. The block copolymers were first dissolved in water to obtain a 1 wt% solution and then filtered. Water was removed under vacuum, and the polymers were dissolved again in tert-butyl alcohol, and freeze-dried. The details of this procedure were described in our previous paper [16]. The PMAA used in this study was also purchased from Polymersource and used without further purification. The M_w and M_w/M_n were measured in our



PEOX PMAA PEO

Fig. 1 Chemical structures of PEOX, PEO, and PMAA

previous study [15] and found to be 2.78×10^5 and 1.59, respectively by size exclusion chromatography-on line-multi angle light scattering [15]. The chemical structures of the polymers are shown in Fig. 1.

The specific refractive index increments of the aqueous solutions of the block copolymers and PMAA, which are necessary for the analysis of static light scattering, were measured at 25, 35, and 45 °C. The details of the instrument were described in our previous paper [31]. The wavelength was fixed at 633 nm. Because our refractometer was available below 50 °C, the specific refractive index increments measured at 25, 35, and 45 °C were extrapolated to obtain the values at 65 °C. We used 0.154, 0.161, and 0.150 $\mathrm{cm}^3\ \mathrm{g}^{-1}$ as the specific refractive index increments for the diblock copolymer, the triblock copolymer, and PMAA at 25 °C and values of 0.141, 0.152, and 0.144 $\mathrm{cm}^3\ \mathrm{g}^{-1}$ were used at 65 °C.

Measurements

Elemental analyses were carried out to investigate the molar ratios of the block copolymers and PMAA in aggregates and check the molar ratios of PEOX and PEO in the block copolymers. A Flash EA manufactured by Thermo Electron, which detects carbon, nitrogen, hydrogen, and sulfur elements, was used at a temperature of 950 °C, with an oxygen flow of 200 ml/min, and a helium flow of 200 ml/min. The ratio of carbon and nitrogen which is independent of residual water in the samples was used to analyze the molar ratios. Sulfur was undetectable within experimental error for the samples in this study.

Precipitates of aggregates formed by mixing relatively concentrated solutions of the block copolymer and that of PMAA were prepared for the elemental analyses and Fourier transform infrared spectroscopy (FT-IR). The precipitates were obtained as follows. Aqueous solutions containing 35 g/L of PEOX (62 g/L for the diblock copolymer, and 51 g/L for the triblock copolymer) and 35 g/L of PMAA were prepared by stirring the solutions overnight at room temperature. Before mixing the solutions, the solutions were immersed in an NCB-1200 circulating temperature controller manufactured by Tokyo Rikakikai, which was controlled at 25 or 65 °C. After checking that the solution temperature reached the setting temperature, the PMAA solution was added to the block copolymer solution. The molar ratios of MAA to EOX and EO were controlled by changing the volumes of the added solutions. To check the influence of thermal hysteresis, the block copolymer solution and PMAA solution which were controlled at 25 °C were mixed, and then immersed in the circulating temperature controller controlled at 65 °C for 30 min. Precipitates were obtained by centrifugation at 1000 rpm for 5 min. The supernatant was removed with a pipet, water was added to wash the precipitate, and the mixture was centrifugated again. The obtained precipitates were dried under vacuum for more than 3 days.

IR spectra were measured for KBr tablets containing ~3 wt% polymer samples with an FT/IR-4100 manufactured by JASCO. The details of the instrument and measurement conditions were described in our previous paper [15].

Static and dynamic light scattering measurements were carried out for aggregate solutions without precipitates, which were prepared by mixing dilute solutions of the block copolymers and PMAA. The procedures for preparation of the dilute solutions of the block copolymers and the solution of PMAA were the same as those used for more concentrated solutions to collect the precipitates for IR measurements except the polymer concentrations differed.

After the solutions were immersed in the water bath of the circulating temperature controller, which was controlled at 25 °C or 65 °C, the PMAA solutions were added to the block copolymer solutions of the same volume and stirred for an hour to form aggregates in the solution. When the solution was mixed at 65 °C, the mixed solution was stirred on a hot-stir plate controlled at 65 °C. The molar concentration of EOX was fixed at 0.002 M (0.38 g/L for the diblock copolymer and 0.29 g/L for the triblock copolymer) and the molar concentration of MAA was fixed at 0.12 M (10.3 g/L) for solutions used for light scattering measurements. Because the polymers form precipitates very easily, we gave up measuring solutions with other mixing ratios, such as the solutions containing equimolar EOX and MAA.

The solution was poured through a disposable filter unit with a pore size of 0.45 μm into a glass tube that had been dried after washing with filtered acetone, and the tube was sealed to avoid the evaporation of water during the measurements. Static and dynamic light scattering measurements were carried out with an ALV-5000/E/EPP instrument manufactured by ALV. The wavelength of the light source was 633 nm. The temperature of the test solution was controlled by circulating water controlled with an circulating temperature controller. The detailed procedure of the filtration, measurement conditions, and analysis were described in our previous paper [15]. We introduce solution codes in this manuscript. “D” or “T” at the first letter in the solution codes indicates the aggregates formed by the

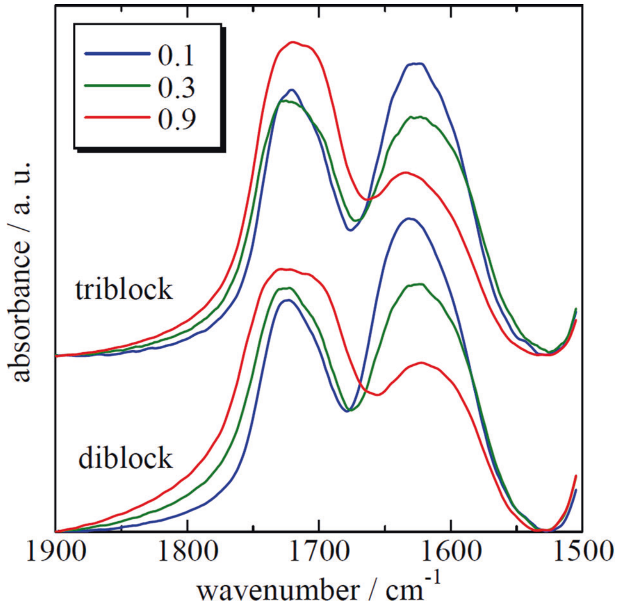


Fig. 2 Infrared spectra of the aggregates of the block copolymers of PEOX and PEO and PMAA formed by mixing their aqueous solutions with different molar ratios of PMAA at 25 °C. The numbers in the legend indicate the molar fraction of MAA relative to the total monomer contents in the solution

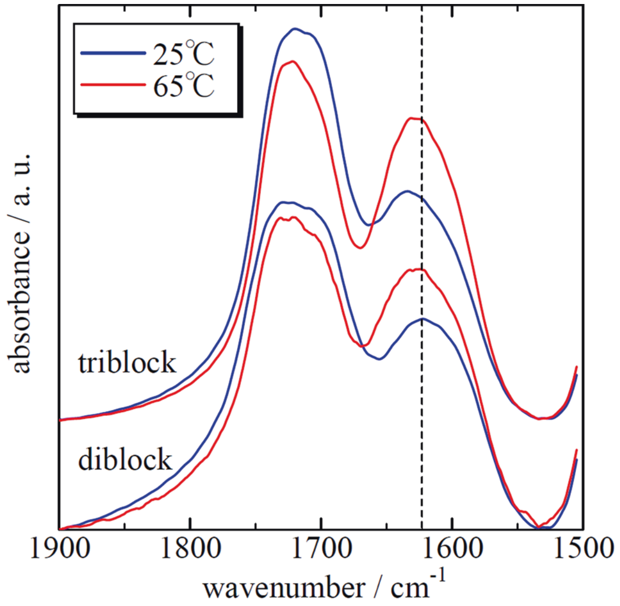


Fig. 3 Infrared spectra of the aggregates of the block copolymers of PEOX and PEO and PMAA formed by mixing their aqueous solutions at different temperatures. The molar ratios of MAA were fixed at 0.9. The vertical broken line indicates 1623 cm^{-1}

diblock copolymer or triblock copolymer. The second number is the temperature in °C when the solutions were mixed, and the last number is the temperature in °C when the measurement was carried out. For example, D65-25 indicates the solution of the diblock copolymer and PMAA, mixed at 65 °C and measured at 25 °C.

Results

Figure 2 summarizes the IR spectra of the aggregates formed by mixing block copolymer solutions and PMAA solutions with different mixing ratios at 25 °C. The numbers in the legend indicate the molar fraction of MAA relative to the total monomer contents in the solution. The peaks at 1640 and 1710 cm^{-1} were assigned to the peaks of the carbonyl groups in PEOX and PMAA, respectively [15]. The peak for PMAA increased with an increase of the molar fraction of MAA, but the change in the intensity ratio of the peak at 1640 cm^{-1} and to that at 1710 cm^{-1} was insignificant. This result suggests that the block copolymers also have a strong tendency to form equimolar aggregates with PMAA.

Figure 3 summarizes IR spectra of the aggregates of the block copolymers of PEOX and PEO and PMAA formed by mixing their aqueous solutions at different temperatures. The molar ratio of PMAA was fixed at 0.9. Because the spectra of the aggregates formed by mixing the solutions at 25 °C and then immersing them in a water bath controlled at 65 °C for 30 min showed no significant difference from the spectra of aggregates formed by mixing the solutions at 25 °C, they are not shown in the figure. The IR spectrum of the aggregates formed by mixing the solutions at 65 °C had a stronger peak assigned to PEOX. This suggests that the block copolymers also had a stronger tendency to form equimolar aggregates with PMAA when the solutions were mixed at 65 °C than when the solutions were mixed at 25 °C. The vertical broken line in the figure indicates 1623 cm^{-1}. The peak wavenumber of the carbonyl groups in the aggregates formed by the triblock copolymer (1633 cm^{-1}) was larger than that in the aggregates formed by the diblock copolymer (1623 cm^{-1}). This peak shift suggests the formation of slightly different hydrogen bonds in the aggregates formed by the diblock and triblock copolymers.

The molar fraction of MAA was investigated by performing elemental analyses of the aggregates. The molar fractions of MAA in the aggregates of the diblock copolymer and PMAA were 0.65 and 0.50 when the solutions were mixed at 25 and 65 °C. The molar fractions of MAA in the aggregates of the triblock copolymer and PMAA were 0.57 and 0.52 when the solutions were mixed at 25 °C and 65 °C, respectively. These results indicate that the block copolymers also had a stronger tendency to form equimolar aggregates with PMAA when the solutions were mixed at 65 °C than when the solutions were mixed at 25 °C.

Figure 4 shows the results of static light scattering studies for the aggregates formed when aqueous solution of the diblock copolymer of PEOX and PEO and solution of PMAA were mixed and measured at 25 °C and 65 °C. K, c, and R_0 stand for optical constant, polymer concentration (g/ml), and excess Rayleigh ratio extrapolated to zero scattering vector,

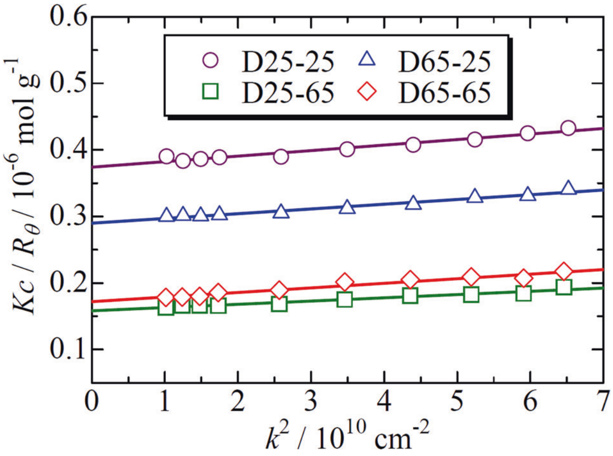


Fig. 4 Results of static light scattering studies of the aggregates formed by aqueous solution of the diblock copolymer of PEOX and PEO and that of PMAA mixed and measured at 25 and 65 °C. The first and second numbers in the sample codes indicate the temperature in °C at which the solutions were mixed and measured, respectively

Table 1 Summary of the results obtained by static and dynamic light scattering for the solutions containing the aggregates formed by the block copolymers and PMAA

	$R_{\mathrm{H,app}}$/nm	R_0/Kc/mol g^{-1} 10^6	$R_{\mathrm{g,app}}$ nm	$R_{\mathrm{g,app}}/R_{\mathrm{H,app}}$
D25-25	47	2.7	26	0.55
D65-25	53	3.5	27	0.52
D25-65	40	6.3	30	0.76
D65-65	41	5.8	35	0.85
T25-25	39	1.6	25	0.64
T65-25	62	3.4	34	0.55
T25-65	35	2.7	25	0.70
T65-65	42	4.3	36	0.86

respectively. The optical constants were calculated from the specific refractive index increments and other measurement conditions. As described in the experimental section, the molar concentration of EOX was fixed at 0.002 M (0.38 g/L for the diblock copolymer and 0.29 g/L for the triblock copolymer) and the molar concentration of MAA was fixed at 0.12 M (10.3 g/L), which shows that PMMA was the major component and that the block copolymers were the minor components in these solutions. The scattering intensities of all the solutions in Fig. 4 were much stronger than expected from the molecular weight of PMAA (2.78×10^5 g mol^{-1}, that is, 3.60×10^{-6} mol g^{-1}), which suggests the formation of aggregates in the solutions.

The value of Kc/R_θ for the solutions containing PEOX and PMAA, which were measured at 65 °C were smaller than those measured at 25 °C, which indicates the formation of aggregates with higher molar mass, that is, larger aggregation numbers at 65 °C than at 25 °C. While the value of Kc/R_θ for the solution mixed at 25 °C and measured at 65 °C was comparable to that for the solution mixed and measured at 65 °C, the value of Kc/R_θ for the solution mixed at 65 °C and measured at 25 °C was significantly smaller than that from the solution mixed and measured at 25 °C. These results suggested that the molar mass of the aggregates formed by the diblock copolymer and PMAA was mainly determined by the measurement temperature, but the aggregates formed at a higher temperature were partially dissociated after cooling to a lower temperature. The apparent radius of gyration $R_{\mathrm{g,app}}$ reflecting polymer dimensions was also investigated from the slope in this figure, and the results are summarized in Table 1.

Figure 5 shows the relaxation spectra $A(\tau)$ for the aggregates formed by aqueous solution of the diblock block copolymer of PEOX and PEO and solution of PMAA mixed and measured at 25 and 65 °C. Relaxation time is designated as τ. The autocorrelation functions obtained directly from the measurements and converted to the relaxation spectra are shown in the Supporting Information. Because the apparent hydrodynamic radius $R_{\mathrm{H,app}}$ of PMAA in the solution without PEOX was measured to be 7 nm, the peaks with $R_{\mathrm{H,app}}$ of ~10 nm, might be caused by PMAA chains without aggregation or aggregates with a very small aggregation number.

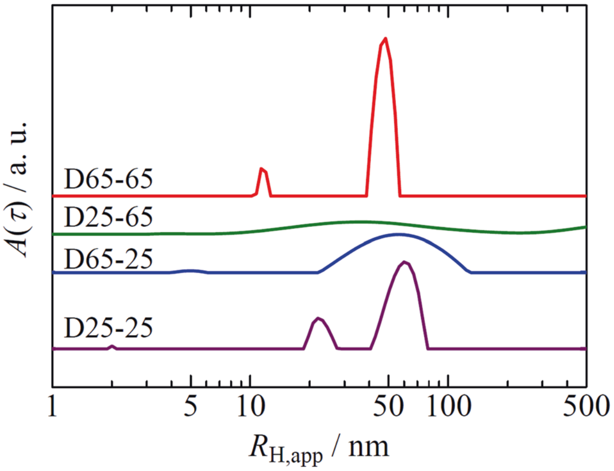


Fig. 5 Relaxation spectra for the aggregates formed from aqueous solution of the diblock block copolymer of PEOX and PEO and that of PMAA mixed and measured at 25 and 65 °C. The data obtained with a scattering angle of 60° are shown in this figure. The first and second numbers in the sample codes indicate the temperature in °C when the solutions were mixed and measured, respectively

For the solutions containing the block copolymer and PMAA, a peak always appeared at $R_{\mathrm{H,app}}$ of ~50, and it was often a very broad single mode, but sometimes there was a sharp peak with two additional peak. The shapes of the relaxation spectra were not uniform even for the same solution. We tried to estimate $R_{\mathrm{H,app}}$ for each peaks, and determine the size distribution of the aggregates from the relaxation spectra, but were unable to reach clear

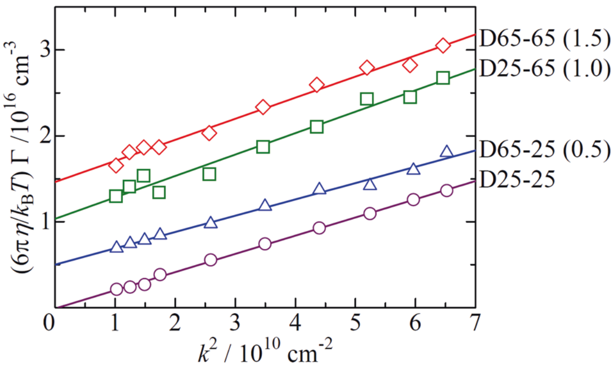


Fig. 6 Results of dynamic light scattering for the aggregates formed by aqueous solution of the block copolymer of PEOX and PEO and that of PMAA mixed and measured at 25 and 65 °C. The data points are shifted vertically by the values indicated in the parentheses. The first and second numbers in the sample codes indicate the temperature in °C when the solutions were mixed and measured, respectively

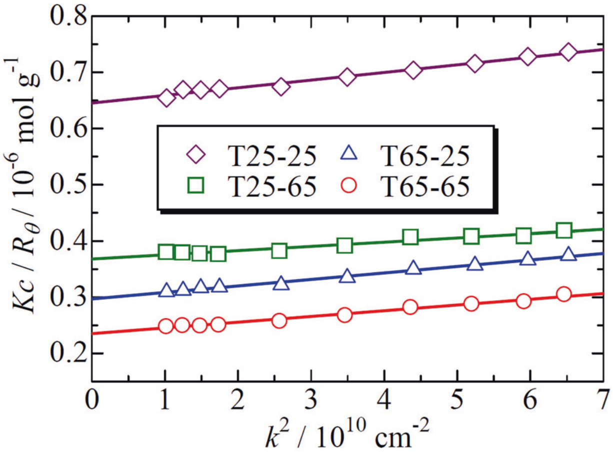


Fig. 7 Results of static light scattering for the aggregates formed by aqueous solution of the triblock copolymer of PEOX and PEO and that of PMAA mixed and measured at 25 and 65 °C. The first and second numbers in the sample codes indicate the temperature in °C when the solutions were mixed and measured, respectively

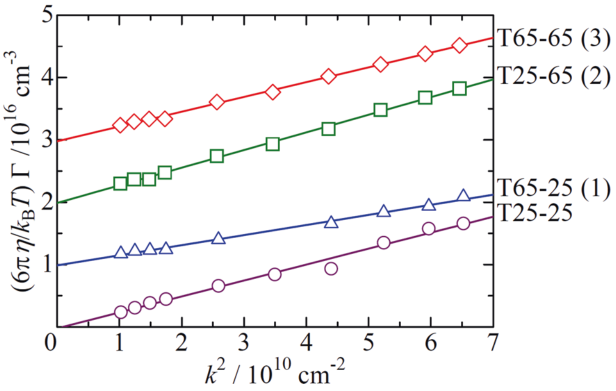


Fig. 8 Results of dynamic light scattering for the aggregates formed by aqueous solution of the triblock copolymer of PEOX and PEO and that of PMAA mixed and measured at 25 and 65 °C. The data points are shifted vertically by the values indicated in the parentheses. The first and second numbers in the sample codes indicate the temperature in °C when the solutions were mixed and measured, respectively

conclusions because of the irregular and complicated shapes. The peak at $R_{\mathrm{H,app}}$ of ~50 for D65-65 was higher than that for D25-25, which suggests the enhancement of aggregation at higher temperature. This is consistent with the results of static light scattering shown in Fig. 4.

Instead of estimating the $R_{\mathrm{H,app}}$ for each peak, we calculated the average apparent hydrodynamic radius to estimate the dimensions of the aggregates. Because the peak with $R_{\mathrm{H,app}}$ of ~50 nm had the largest peak area, this averaged $R_{\mathrm{H,app}}$ mainly reflects the dimensions of the aggregates with dimensions of ~50 nm.

Figure 6 summarizes the results of dynamic light scattering for the aggregates formed by mixing aqueous solution of the diblock copolymer of PEOX and PEO and that of PMAA mixed and measured at 25 and 65 °C to estimate the averaged $R_{\mathrm{H,app}}$. The data points were shifted vertically by the values indicated in the parentheses to avoid overlap in the figure. The solvent viscosity, Boltzmann constant, measuring temperature, and first cumulant were designated as η, k_{B}, T, and Γ, respectively. The slope of this plot is proportional to the diffusion constant, that is, inversely proportional to $R_{\mathrm{H,app}}$. The solution mixed at 65 °C and measured at 25 °C had a slightly gentler slope than the others, which indicates that the aggregates in this solution had slightly larger hydrodynamic dimensions.

Figure 7 shows the results of static light scattering by the aggregates formed by aqueous solution of the triblock copolymer of PEOX and PEO and that of PMAA mixed and measured at 25 and 65 °C. While the values of Kc/R_θ for the solution mixed at 65 °C and measured at 25 °C were comparable with those from the solution mixed and measured at 65 °C, the values of Kc/R_θ for the solution mixed and measured at 25 °C was larger than the others. These results suggested that the molar mass of the aggregates formed by the triblock copolymer and PMAA was mainly determined by the mixing temperature and was only partially altered by changing the temperature after mixing.

Because the relaxation spectra of the aggregates formed by the triblock copolymer and PMAA were not constant, as shown in Fig. 5 for the aggregates formed by the diblock copolymer and PMAA, we calculated the averaged $R_{\mathrm{H,app}}$ as shown in Fig. 8. The slope for the solution mixed at 65 °C and measured at 25 °C was gentler than the others, which indicates the larger hydrodynamic dimension of the aggregates in this solution.

The results of static and dynamic light scattering experiments are summarized in Table 1.

Discussion

Based on the experimental results described in the previous section, a schematic model of the aggregates was proposed as

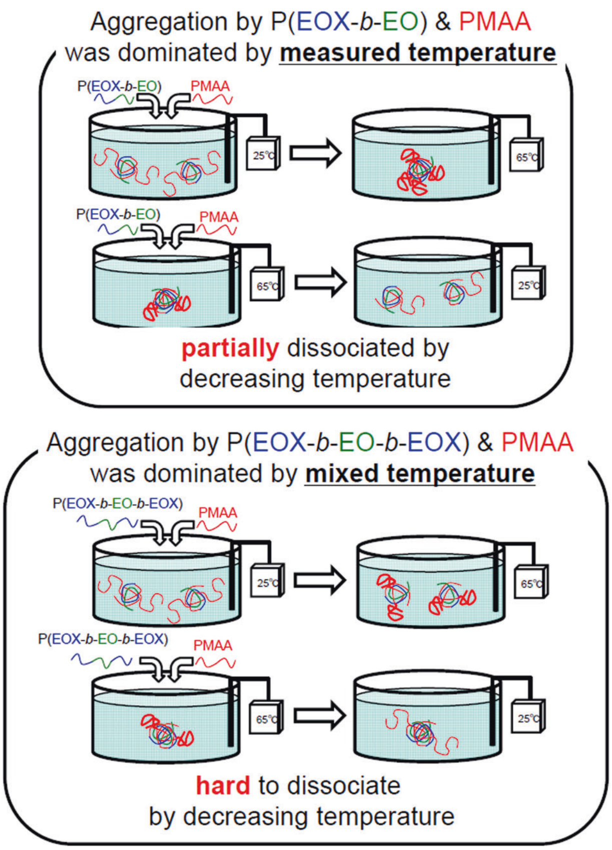


Fig. 9 Schematic images of the block copolymers and PMAA at different temperatures. The blue, green, and red lines illustrate PEOX, PEO, and PMAA chains, respectively

shown in Fig. 9. The aggregation number of the aggregates formed in water at 65 °C which is a nonsolvent for PEOX was larger than that the aggregation number of the aggregates formed at 25 °C. While the aggregation behavior of the aggregates formed by the diblock copolymer and PMAA was dominated by the measuring temperature, that of the aggregates formed by the triblock copolymer and PMAA was dominated by the mixing temperature. The values of R_0/Kc which reflect the averaged aggregation number, for the aggregates in the D25-25 and D65-25 solutions were significantly smaller than those of the D25-65 and D65-65 solutions. This suggests that the aggregates formed by the diblock copolymers and PMAA were dissociated by decreasing the temperature and associated by increasing the temperature. Infrared spectroscopy and elemental analyses indicated that aggregates with molar ratios deviating from the equimolar compositions can be formed with the diblock copolymers and PMAA. These results indicate that the aggregates formed by the diblock copolymers and PMAA had dangling PMAA chains forming no aggregates with the diblock copolymers and flexible structures that were changeable with temperature.

The ratios of the radius of gyration and hydrodynamic radius are known to reflect the shape of polymer chains or polymer aggregates [32]. This ratio for spheres with uniform density is 0.775 and that for random coils is 1.3–1.5. Spherical micelles with a high-density core and corona chains have a ratio smaller than 0.775. The ratios of the apparent radius of gyration and apparent hydrodynamic radius shown in Table 1 support the formation of spherical micelles with corona chains by the aggregates in the D25-25, D65-25, T25-25, and T65-25 solutions.

The values of $R_{\mathrm{H,app}}$ which reflect hydrodynamic dimensions, for the aggregates in D25-25 and D65-25 solutions were larger than those for D25-65 and D65-65. The decrease in $R_{\mathrm{H,app}}$ caused by elevating temperature might be caused by shrinkage of dangling corona chains.

On the other hand, the values of R_0/Kc for the aggregates in the T25-65 solution were slightly larger than those for the T25-25 solution, but those for the T65-65 solution were significantly larger than those in T25-25 solution. This indicates that the triblock copolymer and PMAA formed aggregates, for which the aggregation number was determined by the temperature when the solutions were mixed and was unchanged by temperature change occurring after mixing. These results indicated that the aggregates formed by the triblock copolymer and PMAA had a stronger thermal hysteresis than those formed by the diblock copolymer and PMAA. This behavior can be useful for designing polymer aggregates with different thermal properties. Diblock copolymers are more suitable for the preparation of polymer aggregates whose structures can be switched by changing the temperature, while triblock copolymers are convenient for forming polymer aggregates whose structures are stable to temperature fluctuations.

The reason why the diblock copolymer and PMAA formed aggregates that can be changed flexibly with temperature, and the triblock copolymer and PMAA formed inflexible aggregates, should be discussed in our future study. One of the possible causes is that the PEOX blocks in a triblock copolymer can form multiple linkages with PMAA in an aggregate. Because the PEOX blocks in the triblock copolymer form strong aggregative interactions with multiple aggregation points in a polymer chain, the triblock copolymer is expected to form aggregates with equimolar compositions and with less flexibility.

Conclusion

Interpolymer aggregates were formed by mixing an aqueous solution of PMAA and that of the diblock or triblock copolymers of PEOX and PEO. The results of infrared spectroscopy and elemental analysis indicated that the triblock copolymer tended to form equimolar aggregates with PMAA when the solutions were mixed at 65 °C. Static and dynamic light scattering measurements indicated that aggregates with larger aggregation numbers were formed when solutions were mixed at 65 °C rather than at 25 °C. The aggregation behavior of the aggregates formed by the diblock copolymer and PMAA was dominated by the measurement temperature, and that of the aggregates formed by the triblock copolymer and PMAA was dominated by the mixing temperature. This difference of the aggregation behaviors can be explained by the formation of inflexible aggregates with multiple aggregation points in a polymer chain for the aggregates formed by the triblock copolymer and PMAA.

The results in this study indicated that aggregates exhibiting different thermal hysteresis can be formed by using diblock and triblock copolymers which can be aggregated through both by thermoresponsive interactions and formation of hydrogen bonds. These aggregation behaviors have potential for use in forming aggregates that response to complicated surrounding environments.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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