Self-Association of Dodecyl Moieties Covalently Linked to a Polyelectrolyte in a Small Amount

Akihito HASHIDZUME, Hiroshi YAMAMOTO, Masanobu MIZUSAKI,
and Yotaro MORISHIMA[†]

*Department of Macromolecular Science, Graduate School of Science,
Osaka University, Toyonaka, Osaka 560-0043, Japan*

(Received February 13, 1999)

ABSTRACT: Self-association behavior of random copolymers of sodium 2-(acrylamido)-2-methylpropane sulfonate (AMPS) and *N*-dodecylmethacrylamide (DodMAM) with low DodMAM contents (f_{Dod}) of 2.5–10 mol% was investigated mainly by QELS. In the case of the copolymer with $f_{\text{Dod}} = 10$ mol%, the relaxation time distribution is unimodal independent of the polymer concentration. On the other hand, in the case of the copolymers with $f_{\text{Dod}} = 2.5$ –7.5 mol%, the relaxation time distributions became bimodal at polymer concentrations > 5 g/L, indicating interpolymer associations occurring at higher concentrations of the polymers. From QELS results, apparent values of hydrodynamic radii (R_h) for unimers and the interpolymer associates were estimated to be ca. 6–7 and ca. 120 nm, respectively. The interpolymer associates were found to be disrupted by the addition of a nonionic surfactant, *n*-dodecyl hexaethylene glycol monoether.

KEY WORDS Random Copolymer / Sodium 2-(Acrylamido)-2-methylpropanesulfonate / *N*-Dodecylmethacrylamide / Intrapolymer Association / Interpolymer Association /

Nano-organized self-assemblies of macromolecules, driven by non-covalent interactions, have been a target of considerable interest over the past decades. Some of the important non-covalent interactions include Coulombic, hydrogen bonding, van der Waals, exchange repulsive, and hydrophobic interactions. Among others, hydrophobic interactions are a major driving force for the self-organization of amphiphilic polymers in water.

The self-association behavior of hydrophobically-modified water-soluble polymers in aqueous solution is of particular importance not only because of their relevance to biological systems but also because of their utility in such applications as water-borne paints and coating fluids, cosmetics, foodstuff, drug delivery systems, oil recovery, and water treatment.^{1–5}

The association of polymer-bound hydrophobes may occur either between different polymer chains or within a single polymer chain or both at a time. Interpolymer hydrophobe association may lead to macroscopic phase separation or gelation whereas intrapolymer association may lead to the formation of single-molecular micelles (unimer micelles). Experimental results reported so far on hydrophobically-modified polyelectrolytes indicate that architecture of the macromolecule, including the type of hydrophobes, their content in a polymer, the sequence distribution of electrolyte and hydrophobic monomer units in a polymer chain, and the type of spacer bonding between hydrophobes and the polymer chain, determines whether intra- or interpolymer hydrophobic association occurs preferentially.^{6–15} Thus, nano-organized structures formed from hydrophobically-modified polyelectrolytes may be controlled via macromolecular designing. For example, random copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (AMPS) and *N*-dodecyl-, *N*-cyclododecyl-, or *N*-adamantylmethacrylamide are soluble

in water up to about 60 mol% of the hydrophobic methacrylamide content and form unimer micelles in aqueous solutions even at very high concentrations of the polymers.^{16–18} On the other hand, random copolymers of AMPS and a cholesterol-bearing methacrylate, cholesteryl 6-methacryloyloxyhexanoate, in aqueous solution showed a strong tendency for interpolymer association,¹⁹ and an intermolecularly bridged “flower-like” micelle has been proposed based on the model proposed by Halperin²⁰ and Semenov et al.²¹ These contrasting behavior of the two AMPS copolymers, with structural variations in the side chains of hydrophobic monomer units, is a clear example of the large effect of macromolecular architecture on the self-organization of hydrophobically-modified polyelectrolytes.

During the course of these earlier studies, we came across a rather counter-intuitive observation of the association behavior of the copolymers of AMPS and *N*-dodecylmethacrylamide (DodMAM). When the DodMAM contents (f_{Dod}) in the copolymers are as high as 20 mol% or more, the self-association of the polymer-bound dodecyl groups occurs completely within a single polymer chain regardless of the polymer concentration, resulting in the unimer micelles. However, if f_{Dod} is lower than about 10 mol%, the dodecyl groups tend to associate not only within a single polymer chain but also between different polymer chains, the tendency for the interpolymer association depending on the polymer concentration.

In this study, we focus on the association behavior of polymer-bound dodecyl groups in the AMPS-DodMAM copolymers of $f_{\text{Dod}} \leq 10$ mol% with an emphasis placed on the interpolymer self-association of the dodecyl groups and competitive associations of the polymer-bound hydrophobes with nonionic surfactant molecules. The association behavior of the copolymers was characterized by gel-permeation chromatography (GPC) and quasielastic light scattering (QELS) techniques. Based on experimental results, we proposed conceptual models for the self-

[†] To whom correspondence should be addressed.

association and competitive association with the surfactant in the AMPS-DodMAm copolymers with $f_{\text{Dod}} \leq 10$ mol%.

EXPERIMENTAL

Materials

Copolymers used in this study were prepared by free-radical polymerization of mixtures of 2-(acrylamido)-2-methylpropanesulfonate (AMPS) and *N*-dodecylmethacrylamide (DodMAm) (2.5–10 mol%) in DMF in the presence of 2,2'-azobis(isobutyronitrile) (AIBN) at 60 °C. The details of the procedures for the polymer synthesis were reported elsewhere.^{14,15} The compositions of the copolymers were determined by elemental analysis (N/C ratio). *n*-Dodecyl hexaethylene glycol monoether (C_{12}E_6) was used as supplied by Nikko Chemical Co. without further purification. A high purity of C_{12}E_6 was confirmed by a sharp single peak in a high performance liquid chromatograph (HPLC) with use of a silica gel column. NaCl (Wako Pure Chemicals) was used without further purification. Milli-Q water was used for all measurements.

poly(A/DodMAm(*x*))

C_{12}E_6

Measurements

GPC measurements were performed on a Jasco GPC-900 chromatograph equipped with Shodex Asahipak GF-7M HQ columns using a 0.2 M solution of LiClO_4 in methanol as an eluent. Molecular weights were calibrated with poly(ethylene glycol) standards (Scientific Polymer Products, Inc.).

QELS data were obtained using an Otsuka Electronics Photol DLS-7000 light scattering spectrometer equipped with a 75-mW Ar laser lamp and detector optics. An ALV-5000E digital multiple- τ correlator (Langen GmbH) was employed for data collection. The autocorrelation function was measured at different angles at 25 °C. Sample solutions in 0.2 M NaCl were filtered with a 0.2- μm membrane filter prior to measurement. After filtration, the polymer concentrations did not change. The concentration ranges for the polymers and C_{12}E_6 employed for QELS measurements were 1.0–10.0 g/L and 0–10.0 mM, respectively.

Figure 1. GPC elution diagrams for poly(A/DodMAm(*x*))s with $f_{\text{Dod}} = 2.5\text{--}10$ mol% using methanol containing 0.2 M LiClO_4 as an eluent at 40 °C.

Table I. M_w and M_w/M_n values for poly(A/DodMAm(*x*))^a

f_{Dod}	$M_w \times 10^{-4}$	M_w/M_n
2.5	4.0	5.0
5.0	6.0	6.3
7.5	6.2	5.8
10.0	3.7	6.2

^a Determined by GPC calibrated by poly(ethylene glycol) standards by using 0.2 M solution of LiClO_4 in methanol as an eluent.

RESULTS AND DISCUSSION

GPC for poly(A/DodMAm(*x*))

Figure 1 shows GPC elution diagrams for poly(A/DodMAm(*x*)) with $f_{\text{Dod}} = 2.5, 5, 7.5$, and 10 mol%. From these diagrams, the values of M_w and M_w/M_n for the polymers were determined with a calibration curve obtained with poly(ethylene glycol) standards. These results are listed in Table I.

QELS for poly(A/DodMAm(*x*))

Figure 2 shows the relaxation time distributions obtained from the autocorrelation functions of QELS for poly(A/DodMAm(*x*))s of $f_{\text{Dod}} = 2.5, 5, 7.5$, and 10 mol% at varying polymer concentrations in 0.2 M NaCl aqueous solutions. In the case of the copolymer with $f_{\text{Dod}} = 10$ mol%, the relaxation time distribution is practically unimodal and independent of the polymer concentration. On the other hand, in the case of poly(A/DodMAm(*x*)) of $f_{\text{Dod}} = 2.5, 5.0$, or 7.5 mol%, the relaxation time distribution becomes bimodal with a slower relaxation mode (i.e., a longer relaxation time) appearing at a certain polymer concentration ([polymer] = 2.0 g/L for $f_{\text{Dod}} = 2.5$ mol% and [polymer] = 5.0 g/L for $f_{\text{Dod}} = 5$ and 7.5 mol%) upon an

Figure 2. Relaxation time distributions for poly(A/DodMAM(x))s ($x = 2.5, 5, 7.5$, and 10 mol%) at varying polymer concentrations in 0.2 M NaCl measured at $\theta = 90^\circ$ at 25°C .

Figure 3. Angular dependence of Γ in QELS for poly(A/DodMAM(2.5)).

Table II. Apparent values of R_h for the slow and fast modes of poly(A/DodMAM(x)) in 0.2 M NaCl

f_{Dod} , mol%	R_h , nm	
	fast mode	slow mode
2.5	5.9 ± 0.3	114 ± 8
5.0	6.2 ± 0.2	127 ± 10
7.5	6.8 ± 0.3	122 ± 7
10.0	6.9 ± 0.4	—

increase in the polymer concentration. The intensity of the slow mode peak increases as the polymer concentration is increased. These observations indicate that some polymer chains undergo interpolymer association when the concentration is higher than a certain level while some polymer chains remain as a single-molecular state (i.e., unimers).

Based on QELS data obtained at different measuring angles, the average relaxation rates (Γ) were plotted as a function of the square of the scattering vector (q^2). Figure 3 illustrates examples of the Γ versus q^2 plots for the fast and slow modes for poly(A/DodMAM(x)) of $f_{\text{Dod}} = 2.5$ mol% at 10.0 g/L in 0.2 M NaCl. The linear relationship passing through the origin, as depicted in Figure 3, indicates that these two relaxation modes are virtually due to diffusive processes. Apparent hydrodynamic radii (R_h) for the fast and slow modes were calculated to be 5.9 ± 0.3

Figure 4. Hydrodynamic radius, R_h , as a function of the polymer concentration for poly(A/DodMAM(x))s with $f_{\text{Dod}} = 2.5$ (○), 5 (□), 7.5 (△), and 10 mol% (◇).

and 114 ± 8 nm, respectively, from the Stokes-Einstein relation along with the viscosity of water with use of approximate values of the diffusion coefficients (D) estimated from the slopes of the Γ - q^2 plots. Apparent values of R_h for the fast and slow modes for the other polymers were determined in the same way, as listed in Table II. The values of R_h from the fast mode are reasonable values for unimers. The values of R_h for the interpolymer aggregates estimated from the slow mode relaxation times are approximately twenty times larger than those for the unimers.

It is to be noted that the peaks due to the slow relaxation mode for poly(A/DodMAM(x)) with $f_{\text{Dod}} = 2.5$, 5, and 7.5 mol%, presented in Figure 2, shift towards shorter relaxation times as the polymer concentration is increased. A similar tendency is observed also for the fast mode peaks, although it is not as clear as that for the slow mode peaks. In the case of the polymer with $f_{\text{Dod}} = 10$ mol%, the relaxation peak shifts only slightly towards longer relaxation times in a low polymer concentration region but remains at a nearly constant relaxation time when $[\text{polymer}] \geq 5$ g/L. The apparent values of R_h for the fast and slow modes are plotted as a function of the polymer concentration in Figure 4. The copolymers with $f_{\text{Dod}} = 2.5$, 5, and 7.5 mol% show essentially the same R_h values for the fast relaxation mode, decreasing from about 11 to 6.5 nm with increasing the polymer concentration from 1.0 to 10.0 g/L. The values of R_h for the slow relaxation mode are largely different for the polymers with different f_{Dod} when $[\text{polymer}] \leq 5$ g/L; the R_h value is markedly larger for the polymer with higher f_{Dod} .

However, as can be seen in Figure 4, the R_h value decreases with increasing the polymer concentration, reaching a constant value of about 120 nm regardless of f_{Dod} at $[\text{polymer}] \geq 7.5$ g/L.

These rather peculiar observations may be explained as follows. As can be seen from the GPC data in Figure 1 and Table I, the polymers have a quite broad distribution in the molecular weight (i.e., the chain length). At a lower polymer concentration, only longer chains can associate to form larger interpolymer aggregates. As the polymer concentration is increased, a little shorter chains may become possible to participate in the interpolymer association event, producing interpolymer aggregates with a little smaller size. If that is the case, average R_h values for the interpolymer aggregates would become smaller at higher polymer concentration. Furthermore, such preferential interpolymer association for longer chains would leave shorter chains as unimers, which leads to a decrease in the average size of the unimers with an increase in the polymer concentration. The fact that the average R_h values for the interpolymer aggregate becomes essentially constant at $[\text{polymer}] \geq 7.5$ g/L suggests the presence of a critical chain length for the interpolymer association to be allowed. If the chain length is shorter than the critical value, no such interpolymer association may occur regardless of the polymer concentration.

We are about to undertake a systematic study of the effect of the polymer chain length on the association behavior with a focus on the critical chain length for interpolymer association.

QELS for the mixture of poly(A/DodMAM(x)) and $C_{12}E_6$

The interpolymer association of poly(A/DodMAM(x))s of $f_{\text{Dod}} = 2.5$, 5, and 7.5 mol% is further manifested by an effect of a nonionic surfactant added to polymer solutions. Figure 5 compares relaxation time distributions for the copolymers with $f_{\text{Dod}} = 2.5$, 5, 7.5, and 10 mol% at a 10.0 g/L polymer concentration in the presence of varying concentrations of *n*-dodecyl hexaethylene glycol monoether ($C_{12}E_6$). In the case of the polymer with $f_{\text{Dod}} = 10$ mol%, there is practically no effect of $C_{12}E_6$ added up to 5 mM. In the cases of the copolymers with $f_{\text{Dod}} = 2.5$, 5, and 7.5 mol%, however, the slow mode component decreases significantly with an increase in the $C_{12}E_6$ concentration and completely disappears at a high concentration of $C_{12}E_6$. These observations indicate that the interpolymer self-association of the polymer-bound dodecyl groups is prevented via preferential association of the polymer-bound hydrophobes with $C_{12}E_6$. Given the fact that the association of polyelectrolyte-bound hydrophobes occurs in competition with electrostatic repulsions under steric constraints exerted by the polymer chain, it is reasonable that the association of the polymer-bound dodecyl groups with $C_{12}E_6$ is more favorable than their self-association.

For $f_{\text{Dod}} = 2.5$ and 5.0 mol%, the relaxation time distributions become completely unimodal at $C_{12}E_6$ concentrations ≥ 0.5 mM. For $f_{\text{Dod}} = 7.5$ mol%, however, there is a broad distribution tail on the slower side at $[C_{12}E_6] = 0.5$ mM; it requires a higher concentration of $C_{12}E_6$ for the

Figure 5. Relaxation time distributions for poly(A/DodMAM(x))s ($x = 2.5, 5, 7.5$, and 10 mol%) at a 10.0 g/L polymer concentration in 0.2 M NaCl measured at $\theta = 90^\circ$ at 25°C in the presence of varying concentrations of C_{12}E_6 .

Figure 6. Conceptual illustration of hydrophobic association of the poly(A/DodMAM(x))s ($x = 2.5, 5$, and 7.5 mol%) and the disruption of the interpolymer associates with C_{12}E_6 .

distribution to become completely unimodal. There is a tendency that the remaining fast mode peaks shift towards longer relaxation times as the concentration of the surfactant is increased. These findings indicate that the surfactant molecules disrupt the interpolymer self-associates of the polymer-bound dodecyl groups, leading to unimer-surfactant complexes, as conceptually illustrated in Figure 6.

CONCLUSION

QELS studies on the self-association behavior of random copolymers of AMPS and DodMAM with f_{Dod} ranging from 2.5 to 10 mol% led us to the following conclusions. The copolymers with $f_{\text{Dod}} = 2.5$ – 7.5 mol% show a tendency for interpolymer association at polymer concentrations higher than about 5 g/L, giving a bimodal distribution in the relaxation time in QELS whereas the copolymer with $f_{\text{Dod}} = 10$ mol% shows a unimodal distribution regardless of the polymer concentration. The apparent values of R_h for unimers and the interpolymer associates were estimated to be 6 – 7 and ca. 120 nm, respectively. The interpolymer association was suggested to depend on the chain length of the copolymers, longer chains undergoing interpolymer association at lower polymer concentrations leaving shorter chains as unimers. Furthermore, the presence of a critical chain length was suggested for the interpolymer association to occur. The presence of the interpolymer associates was manifested by a finding that they were completely

disrupted by the addition of a small amount of $C_{12}E_6$.

Acknowledgments. This work was supported in part by a Grant-in-Aid on Priority-Area-Research, "New Polymers and Their Nano-Organized Systems" (No. 277/08246236), from the Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES

1. "Principles of Polymer Science and Technology in Cosmetics and Personal Care," E. D. Goddard and J. V. Gruber, Eds., Marcel Dekker, New York, 1999.
2. C. L. McCormick, J. Bock, and D. N. Schultz, "Encyclopedia of Polymer Science and Engineering," John Wiley, New York, 1989; Vol. 17, p. 730.
3. J. Bock, R. Varadaraj, D. N. Schulz, and J. J. Maurer, In "Macromolecular Complexes in Chemistry and Biology," P. L. Dubin, J. Bock, R. M. Davies, D. N. Schulz, and C. Thies, Eds, Springer-Verlag, Berlin, 1994, p. 33.
4. "Polymers as Rheology Modifiers," D. N. Schulz and J. E. Glass, Eds, Advances in Chemistry Series 462, American Chemical Society, Washington, DC, 1991.
5. "Hydrophilic Polymer, Performance with Environmental Acceptability," J. E. Glass, Ed., Advances in Chemistry Series 248, American Chemical Society, Washington DC, 1996.
6. Y. Chang and C. L. McCormick, *Macromolecules*, **26**, 6121 (1993).
7. C. L. McCormick and Y. Chang, *Macromolecules*, **27**, 2151 (1994).
8. M. C. Kramer, C. G. Welch, J. R. Steger, and C. L. McCormick, *Macromolecules*, **28**, 5248 (1995).
9. Y. Hu, M. C. Kramer, C. J. Boudreaux, and C. L. McCormick, *Macromolecules*, **28**, 7100 (1995).
10. K. D. Branham, H. S. Snowden, and C. L. McCormick, *Macromolecules*, **29**, 254 (1996).
11. M. C. Kramer, J. R. Steger, Y. Hu, and C. L. McCormick, *Macromolecules*, **29**, 1992 (1996).
12. Y. Hu, G. L. Smith, M. F. Richardson, and C. L. McCormick, *Macromolecules*, **30**, 3526 (1997).
13. Y. Hu, R. S. Armentrout, and C. L. McCormick, *Macromolecules*, **30**, 3538 (1997).
14. Y. Morishima, S. Nomura, T. Ikeda, M. Seki, and M. Kamachi, *Macromolecules*, **28**, 2874 (1995).
15. H. Yamamoto, M. Mizusaki, K. Yoda, and Y. Morishima, *Macromolecules*, **31**, 3588 (1998).
16. Y. Morishima, S. Nomura, T. Ikeda, M. Seki, and M. Kamachi, *Macromolecules*, **28**, 2874 (1995).
17. Y. Morishima, *Trends Polym. Sci.*, **2**, 31 (1994).
18. Y. Morishima, In "Solvents and SelfOrganization of Polymers," S. E. Webber, D. Tuzar, P. Munk, Eds., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1996, P. 331.
19. S. Yusa, M. Kamachi, and Y. Morishima, *Langmuir*, **14**, 6059 (1998).
20. A. Halperin, *Macromolecules*, **24**, 1418 (1991).
21. A. N. Semenov, J.-F. Joanny, and A. R. Khokhlov, *Macromolecules*, **28**, 1066 (1995).