Micelle Formation of “Nonamphiphilic” Poly(vinylphenol-*co*-styrene) Random Copolymers by Hydrogen Bond Cross-linking by α,ω -Diamine

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ABSTRACT: Well-defined poly(vinylphenol-*co*-styrene) random copolymers (P(VPh-*r*-St)) were prepared by living radical polymerization mediated by 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl. The copolymers showed no micellization in 1,4-dioxane, the nonselective solvent. Dynamic light scattering demonstrated that the copolymers formed micelles in the presence of α,ω -diamine. The copolymer with the molecular weight of $M_n = 8690$ and the VPh/St unit ratio of 0.50/0.50 produced the micelles with *ca.* 90 nm as a hydrodynamic radius at 0.2 of the molar ratio of 1,4-butanediamine (BDA) to the VPh unit. It was found that the micellization occurred by intermolecular aggregation through hydrogen bond cross-linking between the VPh units by BDA, because the hydrodynamic radius and the aggregation number of the micelles increased with an increase in the copolymer concentration. The hydrodynamic radius of the micelles decreased with increasing the molecular weight of the copolymer, supporting the micellization by the intermolecular aggregation. And further, the micellar size also decreased with a decreasing the VPh ratio in the copolymer at the molecular weight constant.

KEY WORDS Nonamphiphilic Poly(vinylphenol-*co*-styrene) Random Copolymers (P(VPh-*r*-St)) / Micelles / Unimers / Micellization / Hydrodynamic Radius / VPh/St Unit Ratio /

Micelles have a great variety of applications in many fields of drug delivery,^{1,2} separation technologies,^{3,4} detergency,^{5,6} coloring,^{7,8} and coating.^{9–11} Many useful micelles consist of macromolecules.^{12–14} Recently, the importance of the macromolecular micelles has been increasing because of the structural stability and the environmental safety. There are a number of publications on micelles prepared from amphiphilic block^{15–22} and graft copolymers.^{23,24} An increase in the number of publications on them has been accelerated since well-defined block and graft copolymers came to be prepared more easily by living radical polymerization techniques than by living ionic polymerization.^{25–27} Micelles for amphiphilic random copolymers have also been well-studied on the basis of the advantage of convenient procedure for preparing the random copolymers over block and graft copolymers.^{28–32}

While many amphiphilic copolymers are utilized for preparing micelles, “nonamphiphilic” copolymers attract considerable attention in recent years because of the advantages in the molecular design. We have already released publications on the micelle formation of a nonamphiphilic block copolymer consisting of poly(vinylphenol) and polystyrene (PVPh-*b*-PSt).^{33,34} The copolymer forms the micelles in the presence of α,ω -diamine through hydrogen bond cross-linking in a nonselective solvent. We found that poly(vinylphenol-*co*-styrene) random copolymers (P(VPh-*r*-St))

showed a great difference from the PVPh-*b*-PSt diblock copolymer in the micellization by α,ω -diamine. This paper describes the micelle formation of the nonamphiphilic P(VPh-*r*-St) random copolymers by α,ω -diamine.

EXPERIMENTAL

Measurements

Gel permeation chromatography (GPC) was performed with a HLC-802A instrument by Tosoh Corp. equipped with RI and UV detectors. Two polystyrene gel columns, Tosoh TSK gel G4000H₈ and G2000H₈, were used with THF as the eluent at 42 °C. ¹H NMR spectra were obtained with a Bruker ARX-500 NMR spectrometer by Bruker Co. Light scattering experiments were performed at 20 °C at an angle of 90°, with a Photol Otsuka Electronics DLS-7000 super dynamic light scattering spectrometer equipped with LS-71 control unit, an LS-72 pump controller, and an argon ion laser operating at $\lambda = 488$ nm.

Materials

4-*tert*-Butoxystyrene (¹BSt) was supplied from Hokko Chemical Industry Co., Ltd. ¹BSt and commercial-grade styrene (St) were washed with aqueous alkaline solution and water, and were distilled over calcium hydride. 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-Methoxy-TEMPO) was prepared as

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reported previously.³⁵ Benzoyl peroxide (BPO) was precipitated from chloroform, and crystallized in methanol at 0 °C. 1,4-Butanediamine (BDA), ethylenediamine (EDA), and *n*-butylamine were distilled over calcium hydride. THF and 1,4-dioxane were purified by refluxing on sodium for several hours, and were distilled over sodium.

Synthesis of P(VPh-*r*-St) Random Copolymers: General Procedure

^tBSt (3.20 g, 18.2 mmol), St (1.89 g, 18.2 mmol), BPO (80 mg, 0.330 mmol), and 4-methoxy-TEMPO (80 mg, 0.430 mmol) were placed in an ampule. After the contents were degassed, the ampule was sealed *in vacuo*. The polymerization was carried out at 125 °C for 44 h and was terminated by cooling with liquid nitrogen. The reaction mixture was dissolved into dichloromethane and poured into methanol to precipitate the polymer. The precipitate was then dried *in vacuo* for several hours to obtain the P(^tBSt-*r*-St) random copolymer (4.16 g).

P(^tBSt-*r*-St) (1.0 g) was dissolved in THF (30 mL), and conc. HCl (2 mL) was added to the solution at room temperature. The mixture was kept at 90 °C for 9 h. The resulting mixture was then poured into water (1 L) to precipitate the polymer. The precipitate was collected by filtration and then dried *in vacuo* for several hours. P(VPh-*r*-St) (0.69 g) was obtained.

Light Scattering Measurements

The P(VPh-*r*-St) copolymer (VPh/St = 0.50/0.50, $M_n = 8690$ by ¹H NMR) (10 mg) dissolved in 1,4-dioxane (3.1 mL) and using a syringe, the resulting solution was injected through a microporous filter into a cell. The solution was subjected to light scattering

measurement at 20 °C. After the measurement, 2 μL of BDA solution in 1,4-dioxane ([BDA] = 4.48 M) was added to the copolymer solution in the cell, and the mixture was shaken vigorously. The solution was allowed to stand at 20 °C for 10 min, and then subjected to light scattering measurement again. This procedure was repeated until no changes in the hydrodynamic radius were observed in cumulant analysis.

RESULTS AND DISCUSSION

The P(VPh-*r*-St) random copolymers were obtained by hydrolysis of a poly(4-*tert*-butoxystyrene-*co*-styrene) random copolymers (P(^tBSt-*r*-St)) prepared through the living radical polymerization. The radical polymerization of ^tBSt with St proceeds in accordance with ideal copolymerization because of their similar reactivity.³⁶ The living radical copolymerization of ^tBSt and St was performed at 125 °C by BPO as an initiator and 4-methoxy-TEMPO as a mediator (Scheme 1). The hydrolysis of the resulting P(^tBSt-*r*-St) random copolymers were carried out in THF in the presence of hydrochloric acid under reflux. Figure 1 shows ¹H NMR spectra of the P(^tBSt-*r*-St) copolymer before (a) and after the hydrolysis (b). A signal originating from the *tert*-butyl group was observed at 1.30 ppm in the spectrum of the copolymer before the hydrolysis. The unit ratio of ^tBSt to St was estimated as 0.50/0.50 by using the intensities of the signals at 1.1–1.4 ppm attributed to the main chains and the *tert*-butyl groups and of the signals at 6.2–7.6 ppm to the aromatic rings. The methoxy and tetramethyl protons of 4-methoxy-TEMPO attached to the polymer chain end were discerned at 3.25 and 0.95 ppm, respectively. The molecular weight of the

Scheme 1. Synthesis of P(VPh-*r*-St) random copolymers.

Figure 1. ^1H NMR spectra for the P('BSt-*r*-St) copolymer ('BSt/St = 0.50/0.50, M_n = 10400, and M_w/M_n = 1.20) before (a, solvent: CDCl_3) and after the hydrolysis (b, solvent: 1,4-dioxane- d_8 , a copolymer concentration = 3.23 g/L) and a spectrum for the micelles of the P(VPh-*r*-St) copolymer (c, VPh/St = 0.50/0.50, M_n = 8690, solvent: 1,4-dioxane- d_8 , a copolymer concentration = 3.23 g/L).

P('BSt-*r*-St) copolymer was estimated on the basis of the signal intensities of this methoxy protons and the aromatic protons. The molecular weights estimated by ^1H NMR showed a good agreement with those by GPC. After the hydrolysis, signals originating from the phenolic hydroxyl groups were observed at 7.3–7.7 ppm. The complete disappearance of the signals for the *tert*-butyl groups indicates that the hydrolysis of the 'BSt units proceeded quantitatively to produce a P(VPh-*r*-St) copolymer. The signal of the tetramethyl protons was still discerned after the hydrolysis, suggesting that 4-methoxy-TEMPO was attached to the chain end of P(VPh-*r*-St). The P('BSt-*r*-St) and P(VPh-*r*-St) random copolymers are listed in Table I.

The P(VPh-*r*-St) copolymers formed no micelles in 1,4-dioxane, the nonselective solvent. Dynamic light scattering demonstrated that the copolymers showed

Figure 2. Variation in the hydrodynamic radius of the P(VPh-*r*-St) copolymer (VPh/St = 0.50/0.50, M_n = 8690) in the presence of BDA (●), EDA (▲), and *n*-butylamine (■) at a copolymer concentration = 3.23 g/L.

micellization in the presence of α,ω -diamine in the solvent, as were the PVPh-*b*-PSt diblock copolymers.³³ Figure 2 shows the variation in the hydrodynamic radius of the P(VPh-*r*-St) copolymer versus the ratio of α,ω -diamines to the VPh unit through the micellization. P(VPh-*r*-St) formed no micelles by *n*-butylamine, while the copolymer showed the micellization by BDA and EDA. The copolymer needed more EDA to complete the micellization as compared with the case of BDA. These results were in a good agreement with the results on the micellization for the PVPh-*b*-PSt diblock copolymer by α,ω -diamine.³³

The micellization of the P(VPh-*r*-St) random copolymer should be caused by formation of hydrogen bond cross-linking between the VPh units *via* BDA, as is the micellization of the PVPh-*b*-PSt block copolymer. The ^1H NMR analysis confirmed that the formation of the micelles occurred through the hydrogen bond cross-linking by the α,ω -diamine. Figure 1c shows the spectrum of the random copolymer micelles prepared at BDA/VPh = 0.2. The signals of the phe-

Table I. Synthesis of the P('BSt-*r*-St) and P(VPh-*r*-St) random copolymers

Feed ratio		Yield %	M_w/M_n^a	P('BSt- <i>r</i> -St)		Unit ratio ^b		P(VPh- <i>r</i> -St)
				GPC	NMR	'BSt	St	M_n^b
0.50	0.50	92	1.30	6620	6280	0.53	0.47	4970
0.50	0.50	82	1.20	10400	10900	0.50	0.50	8690
0.50	0.50	92	1.28	19100	20600	0.49	0.51	16600
0.50	0.50	92	1.44	26200	27300	0.52	0.48	21700
0.30	0.70	85	1.16	12300	10300	0.33	0.67	8830
0.10	0.90	100	1.22	9440	10100	0.12	0.88	9540
0.70	0.30	76	1.16	11300	12700	0.73	0.27	9380
0.85	0.15	64	1.14	13200	10600	0.89	0.11	9220

^aEstimated by GPC based on PSt standards. ^bEstimated by ^1H NMR.

Scheme 2. Micelle formation of P(VPh-*r*-St) by α,ω -diamine through hydrogen bond cross-linking.

nolic OH disappeared by the addition of BDA to the copolymer solution, indicating that the micelles were formed through the hydrogen bond cross-linking between the VPh units via BDA (Scheme 2). The signals at 1.40 and 2.60 ppm attributed to the two different methylene protons of BDA showed no shifts by the micellization. There were no changes in the location of these signals even by more addition of BDA to the micellar solution. The no shifts of the BDA signals through the micellization imply that the cores of the micelles are not covered with the coronas, because the micellar cores are composed of the solvophilic units.

Figure 3 shows the variability in the hydrodynamic radius and the aggregation number of the P(VPh-*r*-St) copolymer over time, after BDA was added to the copolymer solution. The solution contained the BDA/VPh ratio of 0.2. The aggregation numbers (N_{agg}) of the micelles were estimated as relative aggregation numbers using the scattering intensities of the micelles and the unimers. This is based on the fact that the copolymer concentration was immutable through the micellization and that the formation of the hydrogen bonding between the VPh units and BDA made no changes in the scattering intensity. The hydrodynamic radius increased rapidly and reached 80 nm at 10 min. After that, it got the size gradually until 60 min. The non-negatively constrained least squares (NNLS) analysis³⁷ suggests that the micellization occurred by the intermolecular aggregation. Figure 4

Figure 3. Variability in the hydrodynamic radius and the aggregation number of the P(VPh-*r*-St) copolymer (VPh/St = 0.50/0.50, M_n = 8690) over time at BDA/VPh = 0.2 for a copolymer concentration = 3.23 g/L.

Figure 4. Intensity distribution of the hydrodynamic radius of the P(VPh-*r*-St) copolymer (VPh/St = 0.50/0.50, M_n = 8690) at 0 (a), 5 (b), 10 (c), and 60 min (d) at BDA/VPh = 0.2 for a copolymer concentration = 3.23 g/L.

shows the variation in the intensity distribution of the hydrodynamic radius over time. The distribution originating from the unimers was still discerned at 5 min after the addition of BDA to the copolymer solution. The distribution of the unimers was absent after 10 min. All the unimers were converted to the micelles. The distribution of the micelles was shifted to a higher side of the hydrodynamic radius over time. We deduced that the first rapid increase in the hydrodynamic radius was based on the growth of the micelles by gaining the unimers, and that the micellization was almost completed within 10 min. The second gradual increase should be caused by adsorption of a trace amount of the unimers on the micelles, because the aggregation number also showed a slight increase after 10 min.

The investigation on the dependence of the copolymer concentration on the hydrodynamic radius of the micelles confirmed that the micellization occurred by the intermolecular aggregation. Figure 5 shows the plots of the hydrodynamic radius of the micelles versus the copolymer concentration. The micellar size increased with an increase in the copolymer concentra-

Figure 5. Plots of the hydrodynamic radius of the micelles prepared from the P(VPh-*r*-St) copolymer (VPh/St = 0.50/0.50, M_n = 8690) versus the copolymer concentration.

Figure 6. Plots of the aggregation number of the micelles prepared from the P(VPh-*r*-St) copolymer (VPh/St = 0.50/0.50, M_n = 8690) versus the copolymer concentration.

tion, suggesting that the micelles consist of more unimers at higher copolymer concentration. In fact, the aggregation number of the micelles increased as a result of increasing the copolymer concentration (Figure 6). The degree of the increase in the aggregation number of the micelles disagreed with that in the hydrodynamic radius. This can be accounted for by the fact that the aggregation numbers were estimated only from the scattering intensities. The size in hydrodynamic radii determined by the cumulant analysis is not surely correlative to the scattering intensity. The P(VPh-*r*-St) random copolymer micelles have a great difference from the PVPh-*b*-PSt block copolymer micelles in the dependence of the copolymer concentration on the micellar size. This is because the size of the block copolymer micelles was independent of the copolymer concentration, although the aggregation number of the micelles was dependent on it.³⁴

Figure 7. Plots of the hydrodynamic radius of the micelles versus the molecular weight of the copolymers at VPh/St = 0.5/0.5 for a copolymer concentration = 3.23 g/L.

The relationship between the size of the micelles and the molecular weight of the random copolymers also supports the intermolecular aggregation. Figure 7 shows the plots of the hydrodynamic radius of the micelles and the molecular weight of the copolymers at the VPh/St unit ratio constant. The hydrodynamic radius of the micelles decreased with increasing the molecular weight of the copolymer in this region. The aggregation numbers of the micelles also decreased as the molecular weight increased. The relative aggregation numbers were 17, 7, and 6 for the molecular weights of 8690, 16600, and 21700, respectively. The aggregation number of the micelles for the copolymer with $M_n = 4970$ could not be estimated because the scattering intensity of the unimers was too low to detect. The copolymers with lower molecular weights produced larger micelles with higher aggregation numbers. The copolymers with lower molecular weights aggregate easily, resulting in formation of the large size of micelles by large quantity of the unimers aggregating. In the micelle formation of the PVPh-*b*-PSt block copolymers by BDA, the hydrodynamic radius of the micelles was proportional to the molecular weight of the block copolymers, but was independent of the aggregation number. Consequently, the size of the micelles of the block copolymers is determined by the molecular weight of the copolymer,³⁶ while the micellar size of the random copolymers is dependent not only on the molecular weight but also on the aggregation number. This is the second point in difference between the random and the block copolymer micelles.

The unit ratio in the random copolymer also had effect on the size of the micelles. Figure 8 shows the variation in the hydrodynamic radii of the copolymers with the different unit ratios. The size of the micelles decreased with decreasing the VPh ratio at the molec-

Figure 8. Variation in the hydrodynamic radius of the copolymers with the VPh/St unit ratios of 0.12/0.88 (■), 0.33/0.67 (▲), and 0.50/0.50 (●) at a copolymer concentration = 3.23 g/L.

ular weight constant. The copolymer with lower VPh ratio should be more difficult to aggregate into the micelles. This consequence reflects the result that the copolymer at a lower copolymer concentration formed smaller micelles.

The P(VPh-*r*-St) random copolymers with higher ratios of VPh than St are expected to form crew-cut micelles. We explored the formation of the crew-cut micelles using two different random copolymers: one has 0.73/0.27 of the VPh/St ratio and $M_n = 9380$, and the other 0.89/0.11 of VPh/St and $M_n = 9220$. The copolymers produced the micelles without any gelation and precipitation. The hydrodynamic radii of the micelles were 96.5 nm for the copolymer with VPh/St = 0.73/0.27, and 94.2 nm for VPh/St = 0.89/0.11, respectively. These copolymers provided the micelles with similar size to the micelles of the copolymer with 0.50/0.50 of VPh/St. For the copolymer containing the VPh units over a certain VPh/St ratio, the micellar size is independent of the VPh ratio, because not all the VPh units engage in the formation of the hydrogen bond cross-linking with BDA.

CONCLUSIONS

The P(VPh-*r*-St) random copolymers with the molecular weights well-controlled were prepared by the living radical polymerization mediated by 4-methoxy-TEMPO. The random copolymers formed the micelles in the nonselective solvent in the presence of the α,ω -diamines, as were the PVPh-*b*-PSt diblock copolymers. The micellization of the random copolymers were completed within 10 min, and were stable until 1 h at 20 °C. It was found that the micellization occurred by the intermolecular aggregation through the hydrogen bond cross-linking between the VPh units by BDA, because the hydrodynamic radius and

the aggregation number of the micelles increased with an increase in the copolymer concentration. There was a great difference between the P(VPh-*r*-St) random copolymer and the PVPh-*b*-PSt block copolymer not only in the dependence of the copolymer concentration on the micellar size but also in the dependence of the molecular weight of the copolymer on it. The micellar size of the random copolymers decreased with an increase in the molecular weight of the copolymer, while that of the block copolymers increased with an increase in it. The random copolymers with lower molecular weights aggregate easily, producing the large size of micelles by large quantity of the unimers aggregating. And further, the size of the micelles also decreased as a result of decreasing the VPh ratio in the copolymer. This is the first light scattering study demonstrating that the size of micelles for the nonamphiphilic random copolymer is controlled by the copolymer concentration, the molecular weight of the copolymer, and the unit ratio in the copolymer.

REFERENCES

1. K. A. Yoon and D. J. Burgess, *J. Pharm. Pharmacol.*, **49**, 478 (1997).
2. M. J. Lawrence, S. M. Lawrence, and D. J. Barlow, *J. Pharm. Pharmacol.*, **49**, 594 (1997).
3. M. Ismael and C. Tondre, *Langmuir*, **8**, 1039 (1992).
4. Q.-L. Chang and J.-Y. Chen, *Chem. Eng. J.*, **59**, 303 (1995).
5. A. R. L. Piero and G. Petrone, *Biochem. Mol. Biol. Int.*, **32**, 181 (1994).
6. B. V.-L. Normand and J. L. Eisele, *Anal. Biochem.*, **208**, 241 (1993).
7. D. Cohen, E. Hitchcock and S. Pohl, Eur. Patent Appl. EP 640335 A2 (Mar. 1, 1995).
8. H. Rajaraman, U.S. Patent US 6500896 B1 (Dec. 31, 2002).
9. A. J. M. Knoef and H. Slingerland, *Surf. Coat. Int.*, **75**, 335 (1992).
10. T. Saji, K. Ebata, K. Sugawara, S. Liu, and K. Kobayashi, *J. Am. Chem. Soc.*, **116**, 6053 (1994).
11. A. R. Pitt, S. D. Morley, N. J. Burbidge, and E. L. Qiuckenden, *Colloids Surf. A*, **114**, 321 (1996).
12. I. Hama, M. Sakaki, and H. Sakamoto, *J. Am. Oil Chem. Soc.*, **74**, 823 (1997).
13. Y. Sakurai, T. Okano, K. Kataoka, M. Yokoyama, S. Katayose, S. Suwa, and A. Harada, Eur. Patent Appl. EP 721776 A1 (Jul. 17, 1996).
14. J. M. Kim, Y. Sakamoto, Y. K. Hwang, Y.-U. Kwon, O. Terasaki, S.-E. Park, and G. D. Strucky, *J. Phys. Chem. B*, **106**, 2552 (2002).
15. C. S. Patrickios, C. Forder, S. Armes, P. Steven, and N. C. Billingham, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 1529 (1996).
16. V. S. Trubetskoy, G. S. Gazelle, G. L. Wolf, and V. P. Torchilin, *J. Drug Targeting*, **4**, 381 (1997).
17. J. Allgaier, A. Poppe, L. Willner, and D. Richter, *Macromolecules*, **30**, 1582 (1997).
18. D. Chillura-Martino, R. Triolo, J. B. McClain, J. R. Combes, D. E. Betts, D. A. Canelas, J. M. DeSimone, E. T. Samulski, H. D. Cochran, J. D. Londono, and G. D. Wignall, *J. Mol. Struct.*, **383**, 3 (1996).
19. K. Aoi, A. Motoda, M. Ohno, K. Tsutsumiuchi, M. Okada, and T. Imae, *Polym. J.*, **31**, 1071 (1999).
20. C. Kim, S. C. Lee, H. Jung, J.-S. Yoon, I. C. Kwon, and S. Y. Jeong, *Macromolecules*, **33**, 7448 (2000).
21. R. Resendes, J. Massey, H. Dorn, M. A. Winnik, and I. Manners, *Macromolecules*, **33**, 8 (2000).
22. E. Yoshida, S. Wells, and J. M. DeSimone, *Kobunshi Ronbunshu*, **58**, 507 (2001).
23. C. K. Nisha, P. Basak, S. V. Monorama, S. Maiti, and K. Jayachandran, *Langmuir*, **19**, 2947 (2003).
24. V. Vangani, J. Duhamel, S. Nemeth, and T.-C. Jao, *Macromolecules*, **32**, 2845 (1999).
25. L. Bes, S. Angot, A. Limer, and D. M. Haddleton, *Macromolecules*, **36**, 2493 (2003).
26. S. Liu, V. M. Weaver, Y. Tang, N. C. Billingham, and S. P. Armes, *Macromolecules*, **35**, 6121 (2002).
27. M. Maniruzzaman, S. Kawaguchi, and K. Ito, *Macromolecules*, **33**, 1583 (2000).
28. A. Narumi, T. Matsuda, H. Kaga, T. Satoh, and T. Kakuchi, *Polym. J.*, **33**, 939 (2001).
29. T. Noda, A. Hashizume, and Y. Morishima, *Polymer*, **42**, 9243 (2001).
30. S. Yusa, A. Sakakibara, T. Yamamoto, and Y. Morishima, *Macromolecules*, **35**, 5243 (2002).
31. J. Persson, L. Nystrom, H. Ageland, and F. Tjerneld, *Biotechnol. Bioeng.*, **65**, 371 (1999).
32. M. L. Fielden, P. M. Claesson, and K. Schillen, *Langmuir*, **14**, 5366 (1998).
33. E. Yoshida and S. Kunugi, *J. Polym. Sci., Polym. Chem. Ed.*, **40**, 3063 (2002).
34. E. Yoshida and S. Kunugi, *Macromolecules*, **35**, 6665 (2002).
35. T. Miyazawa, T. Endo, S. Shiihashi, and M. Okawara, *J. Org. Chem.*, **50**, 1332 (1985).
36. E. Yoshida and Y. Takiguchi, *Polym. J.*, **31**, 429 (1999).
37. D. Morrison, E. F. Grabowski, and C. A. Herb, *Langmuir*, **1**, 496 (1985).