Macromolecules **2003,** *36,* 8477−8482

Novel Amphiphilic Network Polymers Consisting of Polar, Short Primary Polymer Chains and Nonpolar, Long Cross-link Units Obtained by Free-Radical Cross-linking Monomethacrylate/Dimethacrylate Copolymerizations

Masato Doura,[†,‡] Yosuke Naka,[†] Hiroyuki Aota,[†] and Akira Matsumoto*,[†]

Department of Applied Chemistry, Faculty of Engineering and High Technology Research Center,
Kansai University, Suita, Osaka 564-8680, Japan, and Toyo Tire & Rubber Company, Ltd.,
5-7, Nishi-Chujocho, Ibaraki-shi, Osaka 567-0887, Japan

Received May 12, 2003; Revised Manuscript Received August 12, 2003

ABSTRACT: Solution copolymerizations of 2-hydroxyethyl methacrylate (HEMA), a polar monomer having a hydroxyl group, with 5 mol % (corresponding to 35.7 wt %) heneicosapropylene glycol dimethacrylate (PPGDMA-21), a nonpolar monomer having a poly(oxypropylene) unit, were carried out in MeOH at a dilution of 2/3 in the presence of different amounts of lauryl mercaptan as a chain transfer agent, providing novel amphiphilic vinyl-type network polymers consisting of polar, short primary polymer chains and nonpolar, long cross-link units. The vinyl-type network polymers formed via highly branched prepolymers have abundant dangling chains as their characteristic feature, especially when the primary polymer chain length is short, because both terminal parts of primary polymer chain would be dangling chains. The amphiphilicity of the resulting gels was checked by measuring their swelling ratios in the mixed solvents consisting of nonpolar *tert*-butylbenzene (*t*-BB) and polar MeOH; thus, with an increase in the MeOH volume percent, the gels shrank to the smallest swelling ratio at the start point (i.e., in pure *t*-BB), swelled gradually and then rather sharply beyond 20 vol %, reached the maximum swelling at about 70 vol %, and then shrank gradually up to a rather high swelling ratio at the terminal (i.e., in pure MeOH). The profiles of the solvent component dependencies of the swelling ratios are characteristic of novel amphiphilic gels. The conversion dependency of the characteristic swelling behavior suggests that the response of the gel obtained at an earlier stage of gelation was sharper than that of the gel obtained at a late stage of gelation. The influence of H_2O on the characteristic swelling behavior of resulting amphiphilic gels was examined by measuring their swelling ratios in the mixed solvents consisting of MeOH/H_2O or acetone/H_2O in order to collect information about the role of cross-link units on the swelling behavior of amphiphilic gel.

Introduction

We have been concerned with network formation in the free-radical cross-linking polymerization and copolymerization of multivinyl compounds, especially those including diallyl esters and dimethacrylates, by focusing our attention on the mechanistic discussion of the deviation from Flory−Stockmayer (FS) gelation theory.[1] First, the reasons for the greatly delayed gelation in diallyl polymerizations were discussed mechanistically in detail, and then the discussion was satisfactorily extended to a detailed understanding of network formation in common multivinyl polymerizations. Thus, the striking feature of diallyl polymerization was the fact that no microgelation was observed until the gel point conversion in the bulk polymerization of diallyl phthalate,[2] as completely opposed to the cases where numerous reports on microgel formation were published in the homopolymerizations of multivinyl compounds and their copolymerizations with monovinyl monomers.[3−8] In this connection, the most significant difference between allyl and vinyl polymerizations is in the length of the primary polymer chain which has a predominant influence on gelation. In diallyl polymerization only the oligomeric primary polymer chain is formed because an occurrence of monomer chain transfer, i.e., a well-known degradative chain transfer[9] as an allylic hydrogen abstraction reaction of growing polymer radical from monomer to give a resonance-stabilized allyl radical, is quite remarkable. Therefore, the oligomerization of neopentyl glycol dimethacrylate, a sparingly cyclopolymerizable divinyl monomer, was conducted in the presence of lauryl mercaptan (LM) as a chain transfer agent in order to reduce the primary polymer chain length to a comparable order in diallyl polymerization.[10] The gelation behavior was compared with diallyl terephthalate (DAT) polymerization as a typical example of multiallyl polymerizations. No Trommsdorff effect[11] or gel effect was observed, even beyond the gel point conversion, despite the polymerization of divinyl monomer, as were the cases of the bulk polymerizations of multiallyl compounds.[12] The variation of molecular weight distribution curves with conversion was quite similar to DAT polymerization. The deviation of actual gel point from FS theory[13] was also similar. Moreover, the swelling ratio of the gel obtained just beyond the gel point was very high. Thus, no substantial difference was observed between allyl and vinyl polymerizations in the case where the primary polymer chain lengths were adjusted to be comparable. In addition, no microgelation occurred up to the gel point.

As is evident from the above discussion, network formation through multiallyl polymerization or multivinyl oligomerization in the presence of a chain transfer

---

* Corresponding author. Fax: +81-6-6339-4026. E-mail: amatsu@ipcku.kansai-u.ac.jp.
[†] Kansai University.
[‡] Toyo Tire & Rubber Co., Ltd.

10.1021/ma0302715 CCC: $25.00

agent apparently seems to be quite different from the ordinary multivinyl polymerizations[3−8] in the absence of a chain transfer agent, since in the latter case microgelation easily occurred up to the gel point. Thereafter, we have pursued the generalization through both multiallyl and multivinyl polymerizations: many homopolymerizations and copolymerizations of multivinyl compounds were carried out to explore in detail the delay of actual gelation from FS theory.[14−23] Thus, we reached the conclusion that, in the free-radical cross-linking polymerizations of both multiallyl and multivinyl compounds, the deviation of the actual gel point from the theoretical one becomes greater with an increase in the primary polymer chain length, an increase in the content of pendant vinyl groups of the primary polymer chain, and a decrease in the monomer concentration. Its range became quite wide to almost 10^3. The enhancement of the significance of thermodynamic excluded volume effect, the occurrence of intramolecular cross-linking, and the reduced reactivity of prepolymer should lead to greater deviation from theory.[1] As our discussion so far has been based on a classical FS theory,[13] the validity of FS theory was confirmed by conducting the free-radical cross-linking monovinyl/divinyl copolymerizations[24−27] under the polymerization conditions in which the significance of the thermodynamic excluded volume effect and intramolecular cross-linking, the respective primary and secondary factors for the greatly delayed gelation, was removed. Thus, there are two extreme cross-linked polymers as an ideal network polymer governed by FS theory and a microgel greatly deviated from the theory, although the structures of the actual cross-linked polymers would be between the two extreme cases. Certainly, the cross-linked polymer should change from a homogeneous network structure biased toward the ideal network polymer to an inhomogeneous one biased toward the microgel, the formation of which depends on the polymerization conditions.[1]

Thereafter, we extended the above mechanistic discussion based on multiallyl polymerization to the preparation of novel amphiphilic polymers[28] as the precursors of the homogeneous cross-linked polymers biased toward the ideal network polymer in the free-radical cross-linking monovinyl/divinyl copolymerization by introducing an oligomeric, long cross-linker such as tricosaethylene glycol dimethacrylate [$CH_2{=}C(CH_3)CO(OCH_2CH_2)_{23}OCOC(CH_3){=}CH_2$, PEGDMA-23] and concurrently, forming oligomeric, short primary polymer chains in the presence of LM as a chain transfer agent, in which both lengths of primary polymer chain and cross-link unit are in a comparable order. Here benzyl methacrylate (BzMA) was used as a monovinyl monomer because BzMA forms rather rigid, nonpolar primary polymer chains and PEGDMA-23 as a cross-linker contains a flexible, polar poly(oxyethylene) unit leading to novel amphiphilic polymers as vinyl-type network-polymer precursors. Thus, BzMA was copolymerized radically with 5 mol % (corresponding to 27.5 wt %) PEGDMA-23 in the presence of different amounts of LM. The resulting amphiphilic prepolymers were characterized mainly by viscometry using *tert*-butylbenzene (*t*-BB) and a *t*-BB/MeOH (80/20) mixture as solvents. The viscosities in the *t*-BB/MeOH (80/20) mixture were quite high compared with those in *t*-BB, and completely reversed concentration dependencies were observed in the solvents. These have been discussed by considering the difference in conformation and the shrinkage of polar, flexible poly(oxyethylene) units or the entanglement of nonpolar, rigid primary polymer chains.

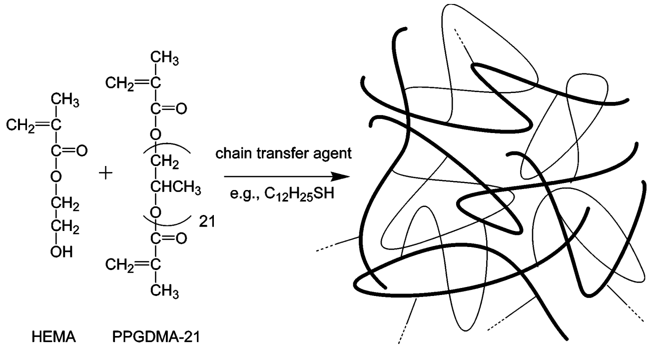

Figure 1. Schematic picture of amphiphilic vinyl-type network polymer consisting of (bold lines) short primary polymer chains and (regular lines) long cross-link units with opposite polarities.

In choosing the above solvents, the amphiphilicity of the resulting gels was checked by measuring their swelling ratios in mixed solvents consisting of nonpolar *t*-BB and polar MeOH. The solvent component dependencies of the swelling ratios were characteristic of novel amphiphilic gels. In this connection, the present article deals with the novel amphiphilic network polymers consisting of polar, short primary polymer chains and nonpolar, long cross-link units as the opposite case of the previous work.[28] Thus, 2-hydroxyethyl methacrylate (HEMA), a polar monomer having a hydroxyl group, was copolymerized radically with 5 mol % heneicosapropylene glycol dimethacrylate [$CH_2{=}C(CH_3)CO(OCH(CH_3)CH_2)_{21}OCOC(CH_3){=}CH_2$, PPGDMA-21], a nonpolar monomer having a poly(oxypropylene) unit, in the presence of LM. The resulting amphiphilic gels, schematically depicted in Figure 1, were characterized by measuring their swelling ratios in various types of mixed solvents.

Experimental Section

HEMA (Kyoeisha Chemical Co., Ltd.) as a monomer, 2,2′-azobisisobutyronitrile (AIBN; Wako Pure Chemical Industries, Ltd.) as an initiator, and MeOH (Wako Pure Chemical Industries, Ltd.) as a solvent were purified by conventional methods. PPGDMA-21 (Kyoeisha Chemical Co., Ltd.) as a monomer and LM (Wako Pure Chemical Industries, Ltd.; extra pure reagent commercially available) as a chain transfer agent were used without further purification.

Polymerization was carried out in a glass ampule containing the required amounts of monomers, AIBN, MeOH, and LM. The ampule was degassed three times by the usual freezing and thawing technique under vacuum, flushed with nitrogen, and then sealed off. It was then placed in a thermostat regulated at 50 ± 0.1 °C. After a predetermined reaction time, the polymer was precipitated by pouring the reaction mixture into a large excess of hexane/2-propanol (6/1 v/v) mixture containing a small amount of 4-*tert*-butylpyrocatechol as an inhibitor. The purification of the polymer was done by reprecipitation from a tetrahydrofuran (THF) precipitant system. The gel fraction of the polymer at conversions beyond the gel point was separated by extracting the sol fraction with THF.

The weight-average molecular weights ($\bar{M}_w$'s) of the resulting polymers were measured by light scattering (LS). The LS measurements were carried out in MeOH at 30 °C with an Otsuka Electronics DLS-7000 dynamic light scattering spectrophotometer over the angular range between 30° and 150°, using unpolarized light of wavelength 632.8 nm.

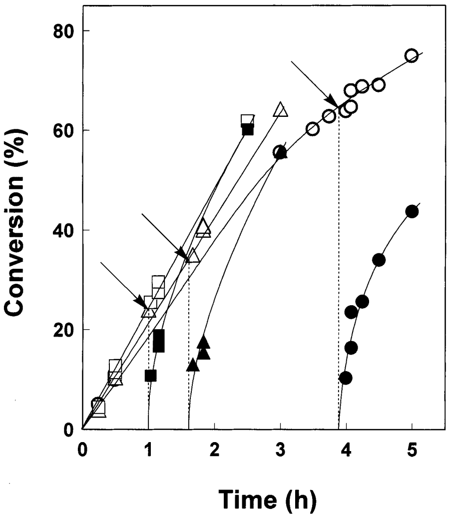

Figure 2. Conversion−time curves for solution copolymerization of HEMA with 5 mol % PPGDMA-21 in MeOH at a dilution of 2/3 using 0.04 mol/L AIBN at 50 °C in the presence of different amounts of LM ([LM]/[total monomer] = (○, ●) 1/20, (△, ▲) 1/50, and (□, ■) 1/100). Open and filled symbols correspond to total and gel polymers, respectively. The arrows denote the gel points.

The swelling ratio was estimated as the ratio of the weight of the swollen gel in the solvent for 48 h to that of the original gel.

Results and Discussion

Preparation of Homogeneous Vinyl-Type Network Polymer. Figure 2 shows the conversion−time curves for the solution copolymerizations of HEMA with 5 mol % (corresponding to 35.7 wt %) PPGDMA-21 in MeOH at a dilution of 2/3 using 0.04 mol/L AIBN at 50 °C in the presence of different amounts of LM ([LM]/[total monomer] = 1/100, 1/50, and 1/20). The percentage of gel polymer obtained by the sol−gel separation is also plotted against time in Figure 2. The actual gel points were determined by extrapolating the gel formation curves to 0%. Thus, the conversions at which the gel started to form (i.e., the gel points) were estimated to be 25.1, 34.3, and 63.2% at [LM]/[total monomer] = 1/100, 1/50, and 1/20, respectively. The gel point became higher with increasing added amount of LM as a reflection of reduced primary polymer chain length.[1] In addition, no gel effect was observed, although the polymerization was accompanied by gelation.

Figure 3 shows the dependence of weight-average molecular weights of resulting precopolymers on conversion; the primary polymer chain length ($\bar{P}_{w,0}$) was calculated from the $\bar{M}_{w,0}$ value determined by the extrapolation of each curve to zero conversion. The $\bar{P}_{w,0}$ value thus obtained was then employed to calculate the theoretical gel point according to Stockmayer's equation:[13]

$$\alpha_c = (1/\rho)(\bar{P}_{w,0} - 1)^{-1}$$

where ρ is the fraction of all double bonds residing on the divinyl units in the initial system.

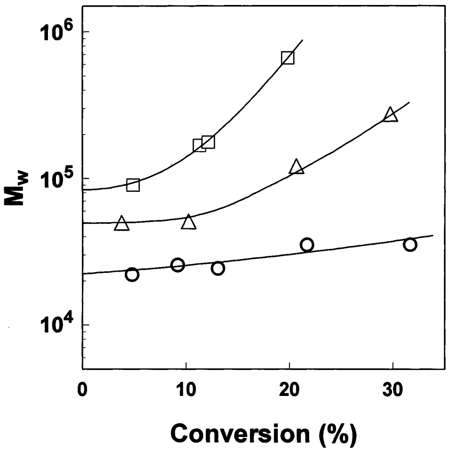

Figure 3. Dependence of $\bar{M}_w$ on conversion (see Figure 2).

Table 1. Comparison of Actual and Theoretical Gel Points in the Polymerizations of HEMA with 5 mol% PPGDMA-21 in the Presence of Different Amounts of LM[a]

[LM]/ [total monomer]	$\bar{P}_{w,0}$[b]	gel point (%) theor[c]	 actual[d]	actual gel point[e]/ theor gel point[c]
1/100	416	2.5	25.1 (18.5)[e]	7.3
1/50	257	4.1	34.3 (25.3)[e]	6.2
1/20	113	9.4	63.2 (46.6)[e]	5.0

[a] In MeOH, dilution 2/3, [AIBN] = 0.04 mol/L, 50 °C. [b] Estimated by LS measurement. [c] Theoretical gel point: $\alpha_c = (1/\rho)(\bar{P}_{w,0} - 1)^{-1}$. [d] Obtained on monomer basis. [e] Obtained as the vinyl group conversion calculated by assuming equal reactivity of HEMA and PPGDMA-21 vinyl groups.

Table 1 summarizes the results obtained as a comparison of actual gel points with theoretical ones for the copolymerizations of HEMA with 5 mol % PPGDMA-21 in the presence of different amounts of LM. The actual gel point was quite delayed from the theoretical one for each polymerization system and the deviation (i.e., the ratio of the actual gel point to the theoretical one) became smaller, from 7.3 to 5.0, with a decrease in the primary polymer chain length. The latter decreased deviation is in line with our previous results.[1,10] Here it should be noted that the formation of a polar growing polymer radical by the incorporation of HEMA unit having a hydroxyl group into the polymer backbone would reduce the occurrence of intermolecular crosslinking reaction with unreacted methacrylic double bonds present at the terminal of a nonpolar poly(oxypropylene) chain as a reflection of reduced interpenetration of growing poly(HEMA) chain and crosslink poly(oxypropylene) chain with opposite polarities. Therefore, despite the delayed gelation from FS theory, the homogeneous network formation was expected. This is also supported by the data of the swelling ratios of the resulting gels: the swelling ratios of the gels obtained just beyond the gel points were extrapolated to be quite high as is shown below (see Figure 4), although the gel should not swell well if it is the agglomerate of microgels leading to an inhomogeneous network polymer opposite the present one.

Conversion Dependency of Swellability of Resulting Gel and Influence of Dangling Chain on Its Swelling Behavior. Figure 4 shows the variation of the swelling ratios of resulting gels with the progress of polymerization beyond the gel point for the solution copolymerizations of HEMA with 5 mol % PPGDMA-21 in MeOH at a dilution of 2/3 in the presence of different amounts of LM ([LM]/[total monomer] = 1/100 and 1/20). Although the swelling ratios were reduced as gelation progressed, the swelling ratios of the gels obtained just beyond the gel points were extrapolated to be quite high as a reflection of the formation of homogeneous network polymers. Also, the swelling ratio

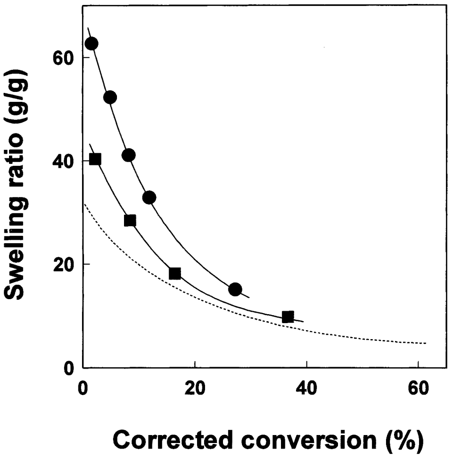

Figure 4. Decrease in swelling ratios of resulting gels in THF with the progress of polymerization beyond the gel point in the presence of LM ([LM]/[total monomer] = (●) 1/20 and (■) 1/100) (see Figure 2). The dotted line denotes the curve of the gels obtained in the absence of LM. The conversion in the abscissa is corrected such that the corresponding gel point is 0% conversion.

became higher with an increase in the amount of LM as a reflection of shorter primary polymer chain length. It is noteworthy here that the vinyl-type network polymers formed via highly branched prepolymers have abundant dangling chains as their characteristic feature, especially when the primary polymer chain length is short, because both terminal parts of primary polymer chain would be dangling chains. These dangling chains inherent in vinyl-type network polymers could influence as an increase in their swelling ratios and, moreover, the characteristic swelling behavior of the resulting gels. In this connection, the solution copolymerizations of HEMA with 5 mol % PPGDMA-21 to produce the network polymer with much longer primary polymer chains was carried out in the absence of LM, although the other polymerization conditions were same as the above cases of the polymerizations in the presence of LM. The swelling ratios of resulting gels were plotted against the corrected conversion in Figure 4; the dotted line was sited below in line with the above discussion.

Then, we attempted to check the amphiphilicity of the resulting gels by measuring their swelling ratios in the mixed solvents consisting of nonpolar *t*-BB and polar MeOH, although in this work we deal with the amphiphilic network polymers consisting of polar primary polymer chains and nonpolar cross-link units as the opposite case of the previous work.[28] MeOH has an affinity to primary polymer chains consisting of polar poly(HEMA) chains, although it acts as a nonsolvent for nonpolar poly(oxypropylene) cross-link units. The situation of *t*-BB is vice versa. Figure 5 shows the correlations of the swelling ratios of the resulting gels with the content of MeOH in the mixed solvents, in which the gels were obtained at conversions just beyond the gel points for the copolymerizations of HEMA with PPGDMA-21 in the presence of different amounts of LM ([LM]/[total monomer] = 1/100, 1/50, and 1/20). Thus, with an increase in volume percent MeOH, the gels shrank to the smallest swelling ratio at the start point (i.e., in pure *t*-BB), swelled gradually and then rather sharply beyond 20 vol %, reached the maximum swelling at about 70 vol %, and then shrank gradually up to a rather high swelling ratio at the terminal (i.e., in pure MeOH). The profiles of the solvent component dependencies of the swelling ratios are characteristic of novel amphiphilic gels. They became somewhat sharp with shorter primary polymer chain length as a reflection of the significance of an increased number of dangling chains.

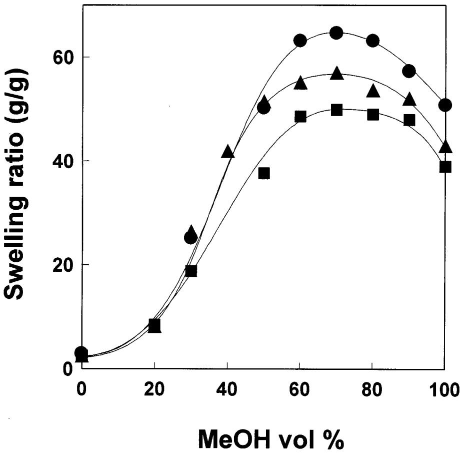

Figure 5. Correlations of swelling ratios of resulting gels with MeOH content in mixed solvents consisting of nonpolar *t*-BB and polar MeOH (see Figure 2; [LM]/[total monomer] = (●) 1/20, (▲) 1/50, and (■) 1/100).

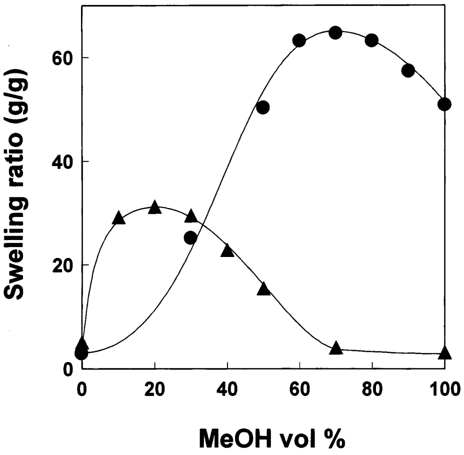

Figure 6. Correlations of the swelling ratios of resulting gels with MeOH content in mixed solvents for (●) poly(HEMA-*co*-PPGDMA-21) and (▲) poly(BzMA-*co*-PEGDMA-23) gels (see Figure 5; [LM]/[total monomer] = 1/20).

For comparison, it should be noteworthy to recall that the highest swelling ratio was observed at 20 vol % MeOH for poly(BzMA-*co*-PEGDMA-23) gel consisting of nonpolar primary poly(BzMA) chains and polar poly(oxyethylene) cross-link units as the opposite case of the present work (see Figure 6).[28] These reversed results suggest that the difference in their primary polymer chains would influence strongly the swelling behavior of resulting gels more than that in their cross-link units, by considering that MeOH has an affinity to primary poly(HEMA) chains and *t*-BB to primary poly(BzMA) chains.

Figure 7 shows the conversion dependencies of the characteristic swelling behavior of the resulting amphiphilic gels with the shortest primary polymer chains for the copolymerization of HEMA with PPGDMA-21 in the presence of the largest amount of LM ([LM]/[total monomer] = 1/20). The profiles of the solvent component dependencies of the swelling ratios changed from a sharp response to a gradual one with the progress of gelation or with an increase in the cross-link density.

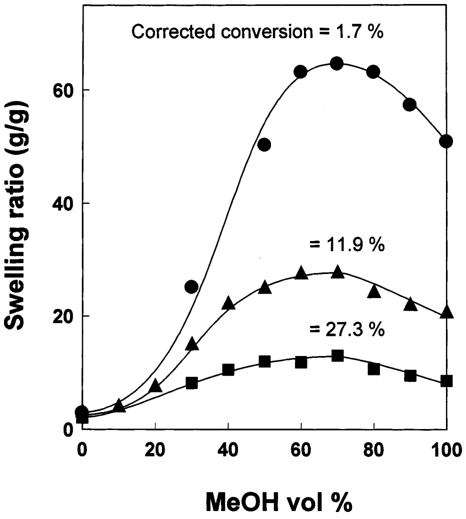

Figure 7. Conversion dependencies of characteristic swelling behavior for poly(HEMA-*co*-PPGDMA-21) gels obtained at corrected conversions = (●) 1.7, (▲) 11.9, and (■) 27.3% (see Figure 2; [LM]/[total monomer] = 1/20).

That is, the response of the gel obtained at an earlier stage of gelation was sharper than that of the gel at a late stage of gelation, although the gel was commonly obtained as the cross-linking polymerization proceeded completely.

Influence of H_2O on Characteristic Swelling Behavior of Amphiphilic Gel. As is shown in Figure 5, the swelling ratios were rather high even at the terminal (i.e., in pure MeOH); this may be ascribed to the fact that the strong affinity of MeOH to primary poly(HEMA) chains leading to a swollen gel played a more significant role than the nonsolvent power of MeOH to poly(oxypropylene) cross-link units leading to a shrunken gel. Therefore, our interest was focused on the influence of H_2O on the characteristic swelling behavior of our novel amphiphilic gels by measuring their swelling ratios in the mixed solvents consisting of MeOH/H_2O or acetone/H_2O because MeOH and acetone have an affinity to primary poly(HEMA) chains and H_2O acts as a stronger nonsolvent to poly(oxypropylene) cross-link units than MeOH. Now, we can collect useful information about the role of cross-link units in the swelling behavior of amphiphilic gel, although the significant role of primary polymer chains or dangling chains was clarified above.

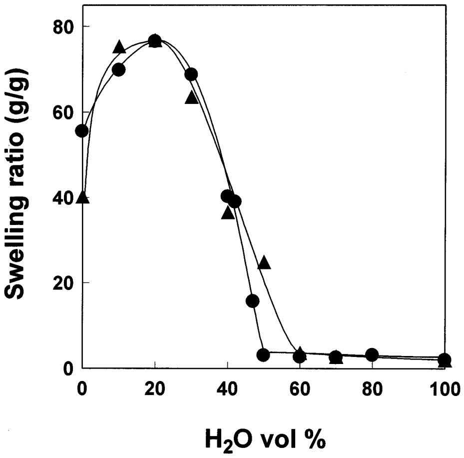

Figure 8. Correlations of swelling ratios of resulting gels with H_2O content in mixed solvents consisting of (●) MeOH/H_2O and (▲) acetone/H_2O for poly(HEMA-*co*-PPGDMA-21) gel (see Figure 2; [LM]/[total monomer] = 1/20).

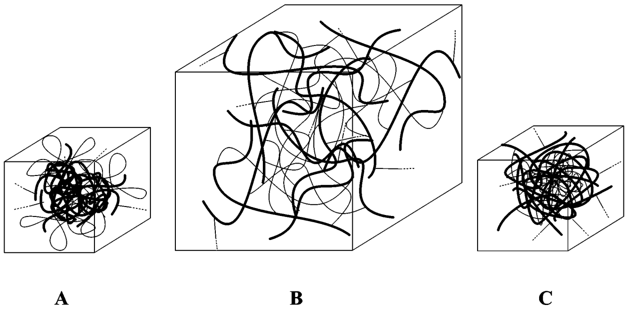

Figure 9. Three typical conformations of network segments of amphiphilic gel consisting of short primary polymer chains and long cross-link units with opposite polarities: (A) shrinkage of short primary polymer chains, (B) random conformation, and (C) shrinkage of long cross-link units.

Figure 8 shows the correlations of the swelling ratios of the resulting gels with volume percent H_2O, in which the gel was obtained at the conversion just beyond the gel point for the copolymerization of HEMA with PPGDMA-21 in the presence of LM ([LM]/[total monomer] = 1/20). Notably, with an increase in volume percent H_2O, the gels obviously swelled to the largest swelling ratio up to 20 vol % and then shrank sharply toward 50−60 vol % H_2O. The former may be ascribed to the collapse of intermolecular hydrogen bond between primary poly(HEMA) chains forming a weak agglomerate by the addition of H_2O. The latter decreasing profile of swelling ratio with an increase in H_2O became sharper in the MeOH/H_2O solvent mixtures as a reflection of cooperative nonsolvency of both MeOH and H_2O to poly(oxypropylene) cross-link units. Thus, the role of cross-link units in the swelling behavior of novel amphiphilic gel was significant as well as that of dangling chains. The significance of both dangling chains and cross-link units on the characteristic swelling behavior of novel amphiphilic gel would depend on the different combinations of primary polymer chains and cross-link units and the different solvent mixtures with different interactive powers. On the whole, three conformations of the network segments of novel amphiphilic gels consisting of short primary polymer chains and long cross-link units with opposite polarities are typically depicted in Figure 9.

Conclusion

Novel amphiphilic vinyl-type network polymers consisting of polar, short primary polymer chains and nonpolar, long cross-link units were prepared by solution copolymerizations of HEMA with 5 mol % PPGDMA-21 in MeOH at a dilution of 2/3 in the presence of different amounts of LM as a chain transfer agent. The homogeneity of the resulting network polymers was discussed by the comparison of actual gel points with theoretical ones calculated according to FS theory. Thus, despite the delayed gelation from FS theory, the homogeneous network formation was expected because the formation of a polar growing polymer radical by the incorporation of HEMA unit having a hydroxyl group into the polymer backbone would reduce the occurrence of intermolecular cross-linking reaction with unreacted methacrylic double bonds present at the terminal of the poly(oxypropylene) chain with an opposite polarity of the growing poly(HEMA) chain. In addition, the swelling ratios of the gels obtained just beyond the gel points were extrapolated to be quite high. Notably, the vinyl-type network polymers formed via highly branched prepolymers have abundant dangling chains as their characteristic feature, especially when the primary polymer chain length is short, because both terminal parts of the primary polymer chain would be dangling chains. These dangling chains inherent in vinyl-type network polymers could influence as an increase in their swelling ratios and, moreover, the characteristic swelling behavior of the resulting gels. The amphiphilicity of the resulting gels was checked by measuring their swelling ratios in mixed solvents consisting of nonpolar *t*-BB and polar MeOH; MeOH has an affinity to primary polymer chains consisting of polar poly(HEMA) chains, although it acts as a nonsolvent for nonpolar poly(oxypropylene) cross-link units. The situation of *t*-BB is vice versa. The profiles of the solvent component dependencies of the swelling ratios are characteristic of novel amphiphilic gels; they became somewhat sharp with shorter primary polymer chain length as a reflection of the significance of an increased number of dangling chains. The conversion dependency of the characteristic swelling behavior suggests that the response of the gel obtained at an earlier stage of gelation was sharper than that of the gel obtained at a late stage of gelation. Because MeOH and acetone have an affinity to primary poly(HEMA) chains and H_2O acts as a stronger nonsolvent to poly(oxypropylene) cross-link units than MeOH, the influence of H_2O on the characteristic swelling behavior of resulting amphiphilic gels was examined by measuring their swelling ratios in the mixed solvents consisting of MeOH/H_2O or acetone/H_2O. Conclusively, the role of cross-link units in the swelling behavior of novel amphiphilic gel was significant as well as that of dangling chains.

References and Notes

(1) Matsumoto, A. *Adv. Polym. Sci.* **1995**, *123*, 41 and references therein.
(2) Matsumoto, A.; Nakajima, H.; Oiwa, M. *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.)* **1988**, *9*, 141.
(3) Staudinger, H.; Husemann, E. *Chem. Ber.* **1935**, *68*, 1618.
(4) Horie, K.; Otagawa, A.; Muraoka, M.; Mita, I. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 445.
(5) Galina, H.; Dusek, K.; Tuzar, Z.; Bohdanecky, M.; Sokr, J. *Eur. Polym. J.* **1980**, *16*, 1043.
(6) Spevacek, J.; Dusek, K. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2027.
(7) Shah, A. C.; Parsons, I. W.; Haward, R. N. *Polymer* **1980**, *21*, 825.
(8) Leicht, R.; Fuhrmann, J. *Polym. Bull.* **1981**, *4*, 141.
(9) Bartlett, P. D.; Altschul, R. *J. Am. Chem. Soc.* **1945**, *67*, 816.
(10) Matsumoto, A.; Mitomi, D.; Aota, H.; Ikeda, J. *Polymer* **2000**, *41*, 1321.
(11) Trommsdorff, E.; Kohle, H.; Lagally, P. *Makromol. Chem.* **1948**, *1*, 169.
(12) Matsumoto, A. *Prog. Polym. Sci.* **2001**, *26*, 189.
(13) Stockmayer, W. H. *J. Chem. Phys.* **1994**, *12*, 125.
(14) Matsumoto, A.; Yonezawa, S.; Oiwa, M. *Eur. Polym. J.* **1988**, *24*, 703.
(15) Matsumoto, A.; Ando, H.; Oiwa, M. *Eur. Polym. J.* **1989**, *25*, 385.
(16) Matsumoto, A.; Ando, H.; Oiwa, M. *Kobunshi Ronbunshu* **1989**, *46*, 583.
(17) Matsumoto, A.; Yamashita, Y.; Oiwa, M. *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.)* **1991**, *12*, 135.
(18) Matsumoto, A.; Nishi, E.; Oiwa, M.; Ikeda, J. *Eur. Polym. J.* **1991**, *27*, 1417.
(19) Matsumoto, A.; Yamashita, Y.; Oiwa, M. *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.)* **1993**, *14*, 139.
(20) Matsumoto, A. *Makromol. Chem., Macromol. Symp.* **1993**, *76*, 33.
(21) Matsumoto, A.; Hasei, Y.; Aota, H. *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.)* **1994**, *15*, 117.
(22) Matsumoto, A.; Okuno, S.; Aota, H. *Makromol. Chem., Macromol. Symp.* **1995**, *93*, 1.
(23) Matsumoto, A.; Takahashi, S.; Morita, T. *Nettowaku Porima (J. Net. Polym. Jpn.)* **1996**, *17*, 139.
(24) Matsumoto, A.; Okuno, S.; Aota, H. *Macromol. Symp.* **1995**, *93*, 1.
(25) Matsumoto, A.; Okamoto, A.; Okuno, S.; Aota, H. *Angew. Makromol. Chem.* **1996**, *240*, 275.
(26) Matsumoto, A.; Taniguchi, A. *Polym. J.* **1999**, *31*, 711.
(27) Matsumoto, A.; Kitaguchi, Y.; Sonoda, O. *Macromolecules* **1999**, *32*, 8336.
(28) Matsumoto, A.; Ohashi, T.; Oe, H.; Aota, H.; Ikeda, J. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4396.

MA0302715