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Control of Intermolecular Cross-Linking Reaction in Free-Radical Cross-Linking Monovinyl/Divinyl Copolymerizations by the Aid of Amphiphilic Nature of Primary Polymer Chains and Cross-Link Units with Opposite Polarities

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ABSTRACT: The control of the intermolecular cross-linking reaction in free-radical cross-linking monovinyl/divinyl copolymerizations resulting in amphiphilic network polymers was attempted by the aid of amphiphilic nature of primary polymer chains and cross-link units with opposite polarities. First, benzyl methacrylate (BzMA)/tricosaethylene glycol dimethacrylate (PEGDMA-23) (95/5) copolymerizations in 1,4-dioxane (DO) and DO/H_2O (85/15) mixed solvent were investigated. The assembly of short primary polymer chains induced the restricted motion of propagating polymer radical, leading to a suppressed increment of molecular weight with conversion. Second, 2-hydroxyethyl methacrylate (HEMA)/henicosapropylene glycol dimethacrylate (PPGDMA-21) (95/5) copolymerizations in DO, DO/H_2O (80/20) mixture, and DO/H_2O (70/30) mixture were explored. The assembly of nonpolar cross-link units led to an enhanced occurrence of intermolecular cross-linking reaction. Moreover, the assembly of polar primary polymer chains consisting of poly(HEMA) in DO suppressed the cross-linking reaction as is the case with BzMA/PEGDMA-23 (95/5) copolymerizations. Then, the solvent effect on gelation was generalized by using various solvents. Especially, our attention was focused on acetonitrile (ACN) and *N*,*N*-dimethylformamide (DMF) as solvents because the resulting gel in HEMA/PPGDMA-21 (95/5) copolymerization swelled in DMF but shrank in ACN despite almost the same solubility parameters for both solvents. Thus, both primary polymer chains and cross-link units of amphiphilic prepolymers would not assemble in DMF, whereas primary polymer chains having hydroxyl groups would assemble in ACN. The assembly of short primary polymer chains in ACN led to a suppressed increment of molecular weight with conversion as a reflection of the restricted motion of propagating polymer radical. Conclusively, the assembly of short primary polymer chains suppressed the occurrence of intermolecular cross-linking reaction, whereas the assembly of long cross-link units promoted it.

Introduction

Network polymers are insoluble because of their three-dimensional or space network structure of one gigantic molecule. They are commonly referred to as cross-linked polymers or thermosetting polymers as infusible, cured materials. The insoluble, infusible properties result in the difficulty of a full understanding of network polymers as the lack of suitable analytical methods for their characterization. In general, the polymerization of divinyl monomer as a typical example of multivinyl monomers leads to the formation of a gel polymer, except for special cases in which only cyclic, linear polymers are obtained.[1,2] Early in polymerization, the prepolymer consisting of cyclized and uncyclized units, the latter of which have pendant double bonds, is formed. The cross-linking reaction between the pendant double bond of the prepolymer and the growing polymer radical gradually becomes more important with the progress of polymerization. Eventually, gelation occurs and the viscosity of the system suddenly increases. Bubbles no longer rise in the reaction mixture, and stirring becomes impossible. This was attributed to the formation of a three-dimensional network or gel of indefinitely large size.[3] Gelation during polymer synthesis should normally be avoided because it can have disastrous consequences if it occurs in a large-scale reactor. Thus, it is important to understand the relationship between gelation and the extent of reaction and, furthermore, to control the network formation, although gelation occurs at the critical conversion or gel point.

The network formation mechanism and the fine structure of cured resins have been a controversial problem for a long time because of the complexity of the reactions involved and the insolubility of the products. In particular, the free-radical cross-linking polymerization and copolymerization of multivinyl monomers are the cases. Since the pioneering theoretical and experimental works,[4−6] many papers have published, especially including ethylene dimethacrylate (EDMA),[6−21] divinylbenzene (DVB),[22−31] and diallyl dicarboxylates[21,32−37] as typical divinyl monomers; the studies have been complicated by different workers and gelling systems and frequently provide scattered data.

The importance of cyclization leading to the formation of microgel-like particles has been emphasized.[38] The predictions of classical Flory−Stockmayer (FS) gelation theory[5] have been tested for the establishment of a network by free-radical cross-linking polymerization.[20] The discussion on the cross-linking mechanism and the characterization of network microstructure have been

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extended to the development of kinetic gelation models.[39] The latter two research groups have dealt with the copolymerization of methyl methacrylate with EDMA, the historical copolymerization system which was first investigated in 1945 by Walling.[6] Similarly, styrene/DVB copolymers have been under investigation for more than 50 years because of their commercial importance as the resins for size-exclusion chromatography and ion exchangers.

We have been concerned with the network formation in the free-radical cross-linking polymerization and copolymerization of multivinyl monomers, especially those including diallyl esters and dimethacrylates, by focusing our attention on the mechanistic discussion of the deviation from FS theory.[40] 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.[41] This was completely opposed to the cases where numerous reports on microgel formation were published in the homopolymerizations of multivinyl monomers and their copolymerizations with monovinyl monomers.[9−11,14,27,31,42,43] 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 of an occurrence of monomer chain transfer, i.e., a well-known degradative chain transfer.[44] Therefore, the oligomerization of neopentyl glycol dimethacrylate, a sparingly cyclopolymerizable divinyl monomer, was conducted in bulk 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.[45] The gelation behavior was compared with diallyl terephthalate polymerization as a typical example of multiallyl polymerizations. 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, the network formation through multiallyl polymerization or multivinyl oligomerization in the presence of a chain transfer agent apparently seems to be quite different from the ordinary multivinyl polymerizations[9−11,14,27,31,42,43] in the absence of a chain transfer agent. Thereafter, we have pursued the generalization through both multiallyl and multivinyl polymerizations.[21,46−57] As our discussion has been based on a classical FS theory,[5] the validity of FS theory was confirmed by conducting the free-radical cross-linking monovinyl/divinyl copolymerizations[53,55−57] 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. Then, we extended the above mechanistic discussion based on multiallyl polymerization to the preparation of novel amphiphilic polymers[58] as the precursors of the homogeneous cross-linked monovinyl/divinyl copolymers biased toward the ideal network polymer governed by FS theory. Thus, an oligomeric, long cross-linker was introduced, and concurrently, oligomeric, short primary polymer chains were formed by the copolymerization in the presence of a chain transfer agent. Both lengths of primary polymer chain and cross-link unit were adjusted in a comparable order. Although a wide variety of amphiphilic polymers were prepared because of their potential importance in applications such as paints, inks, coatings, adhesives, oil recovery, flocculants, drugs, and personal care goods, as well as because of their biological relevance, they are different from our cross-linked polymer precursors.

As a further extension of the preparation of novel amphiphilic polymers,[58] our preceding articles[59,60] reported two types of novel amphiphilic vinyl-type network polymers. The first one[59] consists of nonpolar, short primary polymer chains and polar, long cross-link units, and the second one[60] consists of polar, short primary chains and nonpolar, long cross-link units. 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. Thus, the amphiphilic network polymers with abundant dangling chains of our present interest are quite different from the ordinary vinyl-type network polymers with long primary polymer chains obtained by the free-radical cross-linking monovinyl/divinyl copolymerizations in the absence of a chain transfer agent. These dangling chains could influence as an increase in their swelling ratios and, moreover, result in the characteristic swelling behavior of the resulting gels. In the former article,[59] the swelling behavior of resulting amphiphilic gels was discussed by focusing on the influence of characteristic dangling chains. The enhanced incorporation of dangling chains into the network polymer was brought by shortening the primary polymer chain length. Furthermore, the copolymerization with methoxytricosaethylene glycol methacrylate enforced the incorporation of flexible dangling poly(oxyethylene) chains into the network polymer. The dangling chains with freely mobile end segments influenced the swelling response of gels. The amphiphilic gels with less entangled, collapsed cross-link units exhibited faster swelling response than the ones with more entangled, collapsed primary chains. On the other hand, the latter article[60] referred to the amphiphilic network polymer consisting of primary poly(2-hydroxyethyl methacrylate) chains and poly(oxypropylene) cross-link units, rather biased toward a hydrogel. 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.

Thus, our novel network polymers having short primary polymer chains and long cross-link units with opposite polarities changed drastically their conformations in solvent mixtures such as *tert*-butylbenzene (*t*-BB)/MeOH, MeOH/H_2O, and acetone/H_2O, i.e., the assembly of primary polymer chains, the random conformation, or the assembly of cross-link units according to the feed ratio of solvent mixtures. This finding prompted us to explore in more detail the free-radical cross-linking monovinyl/divinyl copolymerization leading to the formation of amphiphilic network polymers in terms of the control of intermolecular cross-linking reaction by the aid of amphiphilic nature of primary polymer chains and cross-link units with opposite polarities.

Recently, Elliott and Bowman[61] reported the effects of solvent quality during polymerization on network structure of cross-linked methacrylate copolymers, although their attention was focused on how the solvent quality affects the extent of primary cyclization and the resulting mechanical properties, especially the molecular weight between cross-links, which is a measure of the mesh size of the polymer.

Experimental Section

Benzyl methacrylate (BzMA) and 2-hydroxyethyl methacrylate (HEMA) (Kyoeisha Chemical Co., Ltd.) as monomers, 2,2′-azobis(isobutyronitrile) (AIBN; Wako Pure Chemical Industries, Ltd.) as an initiator, and 1,4-dioxane (DO), *N*,*N*-dimethylformamide (DMF), acetonitrile (ACN) (Wako Pure Chemical Industries, Ltd.), and H_2O as solvents were purified by conventional methods. Tricosaethylene glycol dimethacrylate [$CH_2{=}C(CH_3)CO(OCH_2CH_2)_{23}OCOC(CH_3){=}CH_2$, PEGDMA-23], henicosapropylene glycol dimethacrylate [$CH_2{=}C(CH_3)CO(OCH(CH_3)CH_2)_{21}OCOC(CH_3){=}CH_2$, PPGDMA-21] (monomers, Kyoeisha Chemical Co., Ltd.), and LM (Wako Pure Chemical Industries, Ltd.; extra pure reagent commercially available) were used without further purification.

Polymerization was carried out in a glass ampule containing the required amounts of monomers, AIBN, solvent, and LM. The ampule was degassed three times by the usual freezing and thawing technique under a vacuum 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 (M_w's) of the resulting polymers were measured by light scattering (LS). The LS measurements were carried out in THF or 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 of 632.8 nm.

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

Characteristic Swelling Behavior of Amphiphilic Gels. As discussed in the preceding articles,[59,60] the profiles of the solvent component dependencies of the swelling ratios were characteristic of novel amphiphilic network polymers having short primary polymer chains and long cross-link units with opposite polarities. That is, Figure 1 typically exemplifies the correlations of the normalized swelling ratios of the amphiphilic gels obtained by BzMA/PEGDMA-23 (95/5)[59] and HEMA/PPGDMA-21 (95/5)[60] copolymerizations with the content of MeOH in the mixed solvents consisting of nonpolar *t*-BB and polar MeOH. The normalization was done by dividing each swelling ratio by the maximum swelling ratio. BzMA/PEGDMA-23 (95/5) copolymerization afforded the amphiphilic gel which swelled maximally at 20 vol % MeOH, and HEMA/PPGDMA-21 (95/5) copolymerization gave the one with a maximum swelling ratio at 70 vol %. The reasons for the different swelling behavior of both amphiphilic gels are explained as follows. That is, in the case of the gel obtained by BzMA/PEGDMA-23 (95/5) copolymerization, nonpolar primary polymer chains consisting of poly(BzMA) would expand in *t*-BB, whereas polar cross-link units with poly(oxyethylene) moiety would shrink. Therefore, the total gel volume became small at 0 vol % MeOH (i.e., in pure *t*-BB). On the other hand, in pure MeOH the shrinkage of nonpolar primary polymer chains would induce the collapse of total gel volume. The solvent interactions with nonpolar primary polymer chains and polar cross-link units are completely opposite. Thus, the maximum swelling ratio appeared at the appropriate volume percent MeOH. Moreover, each content of nonpolar and polar units in the network polymer would influence greatly on the swelling behavior of amphiphilic gels. The peak of the curve was biased toward a nonpolar side for the amphiphilic BzMA/PEGDMA-23 (95/5) gel because the major part of gel consists of nonpolar poly(BzMA) primary polymer chains. In the case of HEMA/PPGDMA-21 (95/5) gel with polar poly(HEMA) primary polymer chains and nonpolar poly(oxypropylene) cross-link units, the situation would be vice versa.

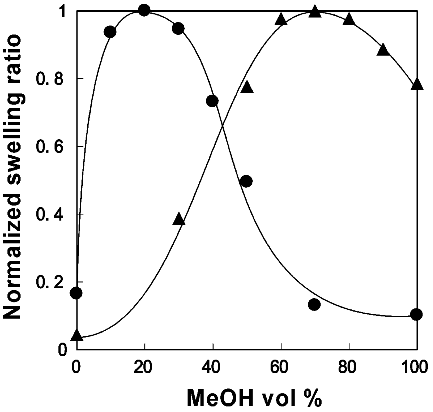


Figure 1. Correlations of the normalized swelling ratios of resulting gels with the content of MeOH in the mixed solvents consisting of nonpolar *t*-BB and polar MeOH for (circles) BzMA/PEGDMA-23 (95/5)[59] and (triangles) HEMA/PPGDMA-21 (95/5)[60] copolymerizations.

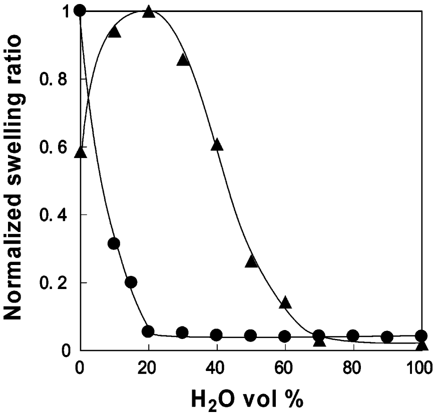
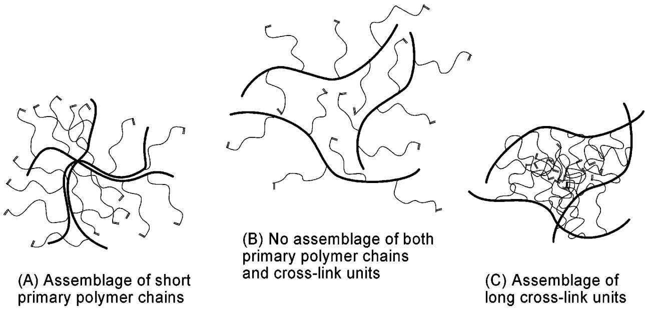


Figure 2. Correlations of the normalized swelling ratios of resulting gels with the content of H_2O in the mixed solvents consisting of DO and H_2O (see Figure 1).

Figure 2 shows the correlations of the normalized swelling ratios of the amphiphilic gels obtained by BzMA/PEGDMA-23 (95/5) and HEMA/PPGDMA-21 (95/5) copolymerizations with the content of H_2O in the mixed solvents consisting of DO and H_2O. In the case


(A) Assemblage of short primary polymer chains

(B) No assemblage of both primary polymer chains and cross-link units

(C) Assemblage of long cross-link units

Figure 3. Three typical conformations of amphiphilic prepolymers consisting of (bold lines) short primary polymer chains and (regular lines) long cross-link units with opposite polarities at an early stage of polymerization where the intermolecular cross-linking would be negligible.

of BzMA/PEGDMA-23 (95/5) copolymerization, the resulting gel swelled maximally in pure DO, and it shrank rapidly by adding H_2O until it collapsed completely at more than 20 vol %. This is due to the assembly of nonpolar poly(BzMA) primary polymer chains caused by a strong nonsolvency of H_2O. On the contrary, the swelling ratio of HEMA/PPGDMA-21 (95/5) gel increased with an increase in volume percent H_2O, reached the maximum value at 20%, and then it decreased up to 70%. The difference in the profiles of the solvent component dependencies of the swelling ratios would be caused by the following fact that HEMA/PPGDMA-21 (95/5) gel consisting of polar poly(HEMA) primary polymer chains, a major part of amphiphilic gel, is able to form hydrogen bond with H_2O. At more than 70 vol % H_2O, the gel collapsed completely due to the shrinkage of cross-link units consisting of the poly(oxypropylene) moiety by a strong nonsolvency of H_2O.

By considering these results, Figure 3 depicts three typical conformations of amphiphilic prepolymers consisting of short primary polymer chains and long cross-link units with opposite polarities at an early stage of polymerization where the occurrence of intermolecular cross-linking reaction to make a cross-link would be negligible: (A) assemblage of short primary polymer chains, (B) no assemblage of both primary polymer chains and cross-link units, and (C) assemblage of long cross-link units. Thus, we tried to explore the gelation behavior of these copolymerizations with the intention of the control of intermolecular cross-linking reaction by the aid of the difference in the conformations of amphiphilic prepolymers. That is, the assembly of short primary polymer chains would lead to a suppressed occurrence of intermolecular cross-linking reaction by a steric excluded-volume effect because the active site is located at the end of growing polymer radical assembled with preformed primary polymer chains, and thus, the radical cited close to the primary polymer chain is far from the vinyl groups sited at the end of long cross-link units. On the contrary, the intermolecular cross-linking would be enhanced by the assembly of long cross-link units because the radical site is close to the vinyl groups. This opposite situation would become more remarkable with the progress of polymerization for the intermolecular cross-linking reaction between the growing polymer radical and prepolymer with higher molecular weights (see Figure 4) as a key reaction for the increment of weight-average molecular weight of resulting prepolymer with conversion. As a result, the former would lead to a delayed gelation and the latter to an enhanced gelation, as compared with no assembly of both primary polymer chains and cross-link units.

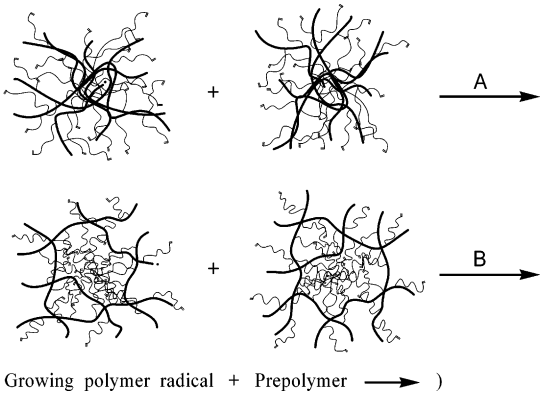


Figure 4. Schematic pictures of intermolecular cross-linking reaction between growing polymer radical and prepolymer consisting of (bold lines) short primary polymer chains and (regular lines) long cross-link units with opposite polarities: (A) assembly of short primary polymer chains; (B) assembly of long cross-link units.

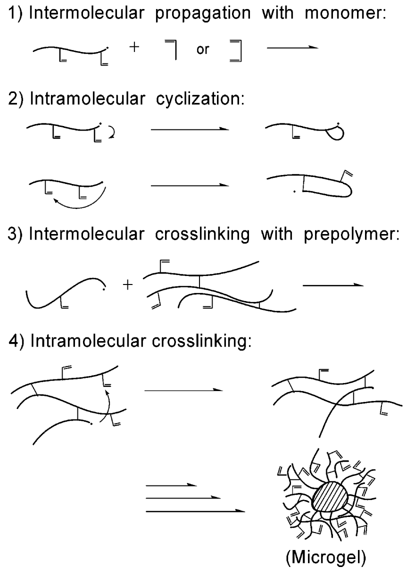


Figure 5. A reaction scheme for the network formation processes in the free-radical cross-linking monovinyl/divinyl copolymerization.

Cross-Linking Polymerization Mechanism To Form Novel Amphiphilic Network Polymer Biased toward Ideal Network Polymer Governed by FS Theory. As is mentioned in the Introduction, the amphiphilic network polymers with abundant dangling chains of our present interest are quite different from the ordinary vinyl-type network polymers with long primary polymer chains obtained by the free-radical cross-linking monovinyl/divinyl copolymerizations in the absence of a chain transfer agent. Thus, Figure 5 shows the reaction scheme for the network formation processes in a free-radical cross-linking monovinyl/divinyl copolymerization, which essentially involves four reactions of a growing polymer radical: intermolecular propagation with two types of monomer; intramolecular cyclization leading to the formation of ring or loop structures; intermolecular cross-linking with the prepolymer to form an effective cross-link, eventually leading to the gel; and intramolecular cross-linking leading to the formation of multiple cross-links, the locally extensive occurrence of which would induce microgelation. The network structure of the resulting cross-linked polymer could be designed by controlling the elementary reactions shown in Figure 5. The intermolecular cross-linking is the key reaction for the control of gelation as the formation of a three-dimensional network of indefinitely large size, whereas the key reaction for the control of the network structure is the intramolecular cross-linking that leads to the formation of multiple cross-links generating the network structure of the cross-linked polymer. As a result, there are two extreme cross-linked polymers as an ideal network polymer governed by FS theory[5] 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 rather homogeneous network structure biased toward the ideal network polymer to an inhomogeneous one biased toward the microgel, depending on the polymerization conditions. Here it should be noted that, for the ordinary cross-linked polymer biased toward the microgel obtained by the free-radical cross-linking monovinyl/divinyl copolymerization in the absence of a chain transfer agent, the bimolecular termination reaction between growing polymer radicals would be a crucial factor for an inhomogeneous network structure formation. That is, a suppressed occurrence of bimolecular termination caused by the complication of prepolymer structure leads to the living-type radical formation that induces the enlargement of the primary polymer chain length and, furthermore, would play an important role for microgelation.[40] On the other hand, the presence of a rather large amount of chain transfer agent would change drastically the termination reaction from a bimolecular one between growing polymer radicals to a chain transfer reaction of growing polymer radical to the chain transfer agent, the latter which is accompanied by shortening the primary polymer chain and keeping the chain length constant. Thus, the homogeneous network polymer biased toward the ideal network polymer governed by FS theory would be produced by the free-radical cross-linking monovinyl/divinyl copolymerization in the presence of a chain transfer agent 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.[53,55−57]

Effect of Assembly of Short Primary Polymer Chains or Long Cross-Link Units on Gelation. As is mentioned above, three typical conformations of amphiphilic prepolymers consisting of short primary polymer chains and long cross-link units with opposite polarities are depicted in Figure 3, based on the results of the solvent component dependencies of the swelling ratios of corresponding amphiphilic network polymers. The assembly of short primary polymer chains or of long cross-link units would depend on the solvent component, and thus, the solvent effect on the gelation is expected.

First, we tried to explore the gelation behavior of BzMA/PEGDMA-23 (95/5) solution copolymerizations in different solvents with the intention of the control of intermolecular cross-linking reaction by the aid of the difference in the conformations of amphiphilic prepolymers. Figure 6 shows the conversion vs time curves for BzMA/PEGDMA-23 (95/5) copolymerizations in DO and DO/H_2O (85/15) mixture because both primary polymer chains and cross-link units of amphiphilic prepolymers would not assemble in DO, whereas nonpolar primary polymer chains consisting of poly(BzMA) would assemble in DO/H_2O (85/15) mixture (see Figure 2). A little increment of polymerization rate and the delayed gelation toward a higher gel-point conversion were observed in DO/H_2O (85/15) mixture. The assembly of short primary polymer chains could lead to a suppressed occurrence of termination reaction and, moreover, of intermolecular cross-linking reaction as is in accordance with our expectation. The latter was directly supported by the dependence of weight-average molecular weights of resulting prepolymers on conversion (see Figure 7). Obviously, the delayed increment of molecular weight with conversion was observed in DO/H_2O (85/15) mixture, as compared to that in DO. Thus, the assembly of short primary polymer chains induced the restricted motion of propagating polymer radical, leading to a suppressed occurrence of intermolecular cross-linking reaction.

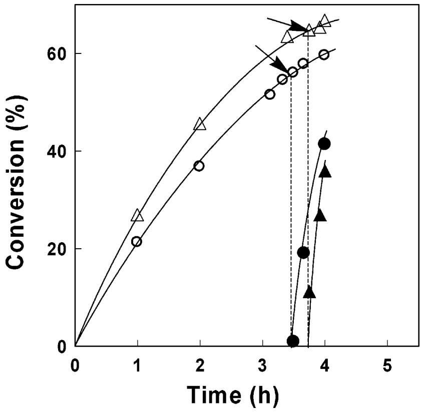


Figure 6. Conversion vs time curves for BzMA/PEGDMA-23 (95/5) solution copolymerizations in (circles) DO and (triangles) DO/ H_2O (85/15) at a dilution of 1/5 using 0.04 mol/L AIBN at 50 °C in the presence of LM ([LM]/[total monomer] = 1/50). Open and filled symbols correspond to total and gel polymers, respectively. The arrows denote the gel points.

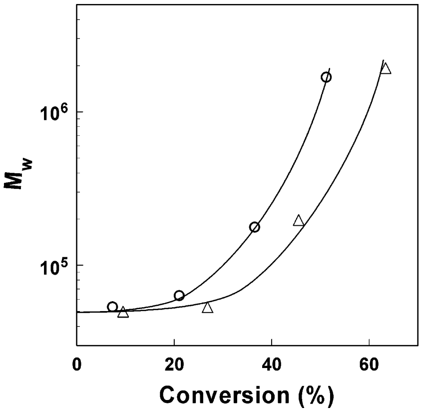


Figure 7. Dependence of M_w on conversion (see Figure 6).

Second, we tried to explore the gelation behavior of HEMA/PPGDMA-21 (95/5) solution copolymerizations in different solvents with the intention of the control of intermolecular cross-linking reaction. Figure 8 shows the conversion vs time curves for HEMA/PPGDMA-21 (95/5) copolymerizations in DO, DO/H_2O (80/20) mixture, and DO/H_2O (70/30) mixture because short primary polymer chains would assemble in DO, both primary polymer chains and cross-link units would be in random-conformations in DO/H_2O (80/20) mixture, and long cross-link units would assemble in DO/H_2O

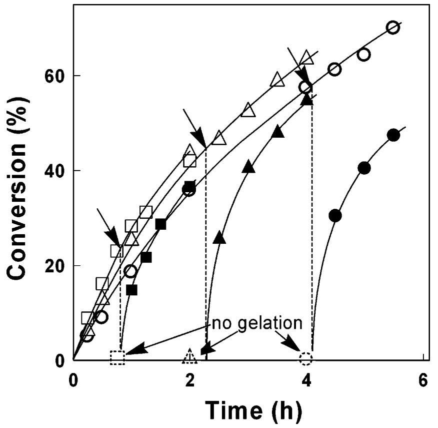


Figure 8. Conversion vs time curves for HEMA/PPGDMA-21 (95/5) solution copolymerizations in (circles) DO, (triangles) DO/ H_2O (80/20), and (squares) DO/ H_2O (70/30) at a dilution of 1/3 using 0.04 mol/L AIBN at 50 °C in the presence of LM ([LM]/[total monomer] = 1/50). Open and filled symbols correspond to total and gel polymers, respectively. The arrows denote the gel points.

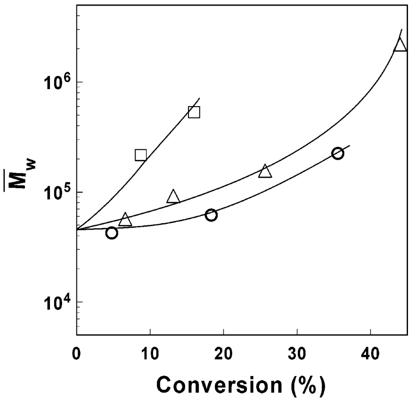


Figure 9. Dependence of M_w on conversion (see Figure 8).

(70/30) mixture (see Figure 2). The polymerization rate was obviously accelerated with an increase in the volume percent H_2O in mixed solvents and the gel point shifted toward a lower conversion. The assembly of nonpolar cross-link units caused by a strong nonsolvency of H_2O led to an enhanced occurrence of intermolecular cross-linking reaction, as is in conformity with our expectation. On the contrary, the assembly of polar primary polymer chains consisting of poly(HEMA) suppressed the cross-linking reaction in DO, as was the case with BzMA/PEGDMA-23 (95/5) copolymerization in DO/ H_2O (85/15) mixture mentioned above. The enhanced intermolecular cross-linking caused by the assembly of long cross-link units was reflected directly on the dependence of weight-average molecular weight of resulting prepolymer on conversion, as shown in Figure 9. That is, the largest increment of molecular weight with conversion was observed in DO/H_2O (70/30) mixture where the nonpolar poly(oxypropylene) cross-link units of prepolymers would assemble, whereas the smallest one was observed in DO where the polar poly(HEMA) primary polymer chains would assemble. Conclusively, the assembly of short primary polymer chains suppressed the occurrence of intermolecular cross-linking reaction, whereas the assembly of long cross-link units promoted it. Table 1 summarizes the results as a comparison of actual gel points with theoretical ones for the BzMA/PEGDMA-23 (95/5) and HEMA/PPGDMA-21 (95/5) copolymerizations in different solvents. Suppressed or enhanced occurrence of intermolecular cross-linking caused by the assembly of short primary polymer chains or long cross-link units was reflected as increased or decreased deviation from FS theory, respectively, i.e., a larger or smaller ratio of the actual gel point to the theoretical one.

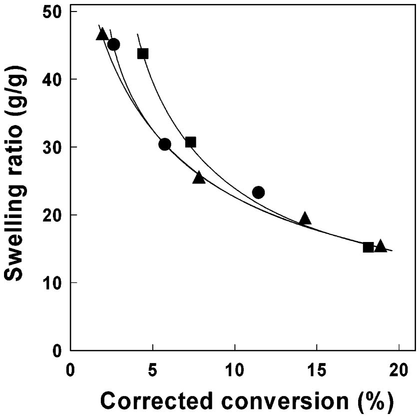


Figure 10. Decrease in the swelling ratios of resulting gels in THF with the progress of polymerization beyond the gel point (see Figure 8). The conversion in the abscissa is corrected such that the corresponding gel point is 0% of conversion.

Then, we examined the variation of the swelling ratios of resulting gels with the progress of polymerization beyond the gel point, as exemplified in Figure 10. 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. The controlled intermolecular cross-linking reaction by the aid of the difference in the conformations of amphiphilic prepolymers was not reflected significantly on the swelling ratios of resulting gel, although the gel biased strongly toward the ideal network polymer obtained in DO/H_2O (70/30) mixture exhibited a bit higher swelling ratio just beyond the gel-point conversion. In this connection, Figure 11 shows the increment of gel fraction with the progress of gelation; beyond the

Table 1. Comparison of Actual and Theoretical Gel Points in the BzMA/PEGDMA-23 (95/5)[a] and HEMA/PPGDMA-21 (95/5)[b] Copolymerizations in the Presence of LM

copolymerization	solvent DO/H_2O	$\bar{P}_{w,0}$[c]	gel point (%)		actual gel point[f]/ theoret gel point[d]
			theoret[d]	actual[e]	
BzMA/PEGDMA-23(95/5)[a]	100/0	220	4.8	55.9 (44.7)[f]	9.3
	85/15	220	4.8	64.7 (51.8)[f]	10.8
HEMA/PPGDMA-21(95/5)[b]	100/0	260	4.1	58.4 (43.0)[f]	10.6
	80/20	260	4.1	45.0 (33.2)[f]	8.2
	70/30	260	4.1	23.8 (17.5)[f]	4.3

[a] Dilution 1/5, [AIBN] = 0.04 mol/L, [LM]/[total monomer] = 1/50, 50 °C. [b] Dilution 1/3, [AIBN] = 0.04 mol/L, [LM]/[total monomer] = 1/50, 50 °C. [c] Estimated by LS measurement. [d] Theoretical gel point: $\alpha_c = (1/\rho)(\bar{P}_{w,0} - 1)^{-1}$. [e] Obtained on monomer basis. [f] Obtained as the vinyl group conversion calculated by assuming equal reactivity of all vinyl groups.

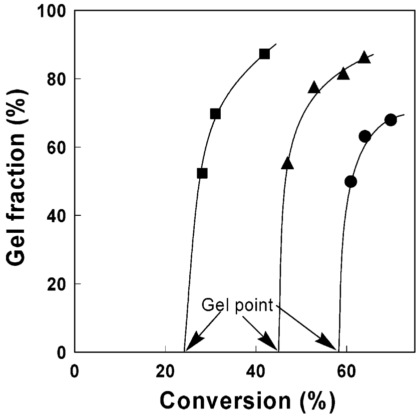


Figure 11. Increment of gel fraction with the progress of polymerization beyond the gel point (see Figure 10).

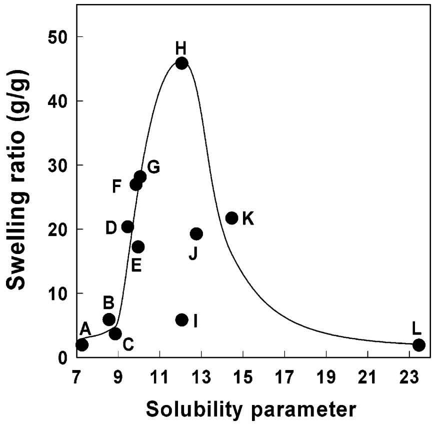


Figure 12. Swelling ratios of poly(HEMA-*co*-PPGDMA-21) (95/5) gel in various solvents: A, hexane; B, toluene; C, carbon tetrachloride; D, acetone; E, chloroform; F, DO; G, THF; H, DMF; I, ACN; J, ethanol; K, MeOH; L, H_2O.

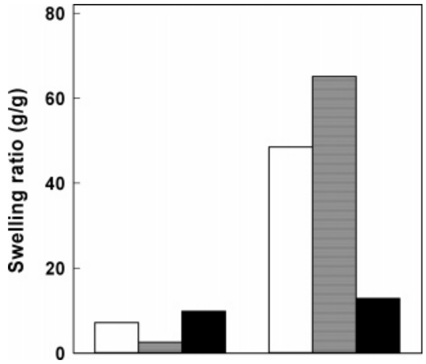


Figure 13. Swelling ratios of (A) poly(HEMA-*co*-PPGDMA-21), (B) poly(HEMA), and (C) poly(PPGDMA-21) gels in ACN and DMF. The respective gels were obtained by HEMA/PPGDMA-21 (95/5) copolymerization, HEMA/ethylene dimethacrylate (99.9/0.1) copolymerization, and PPGDMA-21 homopolymerization.

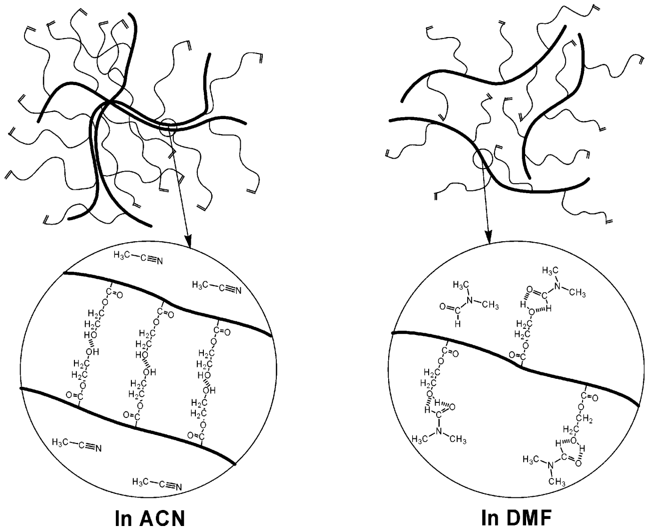


Figure 14. Schematic pictures of amphiphilic poly(HEMA-PPGDMA-21) prepolymers consisting of (bold lines) short primary polymer chains and (regular lines) long cross-link units with opposite polarities in ACN and DMF.

gel point, the sol was rapidly incorporated into the gel and the increasing tendency of the gel fraction became steeper for the gel obtained in DO/H_2O (70/30) mixture as a reflection of a homogeneous network structure formation.

Generalization of Solvent Effect on Gelation. The intermolecular cross-linking reaction was obviously controlled by the aid of the difference in the conformations of amphiphilic prepolymers. As the mixed solvents consisting of DO and H_2O were used, however, we tried to generalize the solvent effect on gelation by using various solvents. Figure 12 shows the swelling ratios of the amphiphilic gels obtained by HEMA/PPGDMA-21 (95/5) copolymerization in various solvents. Especially, our attention was focused on ACN and DMF as solvents because the resulting gel swelled maximally in DMF but shrank in ACN despite of the fact that the solubility parameters of both solvents are almost same. To clarify the striking difference of swelling behavior in both solvents, we prepared two kinds of gels consisting predominantly of poly(HEMA) chains or only of PPGDMA-21 units and then examined the swelling ratios of poly(HEMA-*co*-PPGDMA-21), poly(HEMA), and poly(PPGDMA-21) gels in ACN and DMF, as shown in Figure 13. Thus, the relative swelling ratios for corresponding gels were calculated to be 0.15, 0.04, and 0.76, respectively, by dividing the swelling ratio in ACN by that in DMF. The poly(HEMA) gel remarkably shrank in ACN, in contrast to its high swellability in DMF. These results were due to the difference of hydrogen-bonding powers between hydroxyl groups of poly(HEMA) chain and each solvent. In ACN, the hydrogen bonds between hydroxyl groups of poly(HEMA) chains are stronger than the ones between hydroxyl groups of poly(HEMA) chain and solvent molecules. The situation in DMF is vice versa. By considering these situations, the conformations of poly(HEMA-*co*-PPGDMA-21) prepolymers in both ACN and DMF can be depicted in Figure 14.

Then, we explored the gelation in HEMA/PPGDMA-21 (95/5) solution copolymerizations in both solvents. Figure 15 shows the conversion vs time curves, and moreover, the dependence of weight-average molecular weight of resulting prepolymer on conversion was demonstrated in Figure 16. Both primary polymer chains and cross-link units of amphiphilic prepolymers would not assemble in DMF, whereas primary polymer chains having hydroxyl groups would assemble in ACN (see Figure 14). The gel point shifted toward a higher conversion, and the increment of molecular weight with conversion became gradual in ACN. Again, the assembly of short primary polymer chains led to a suppressed increment of molecular weight on conversion as a reflection of the restricted motion of propagating polymer radical, which is in line with our expectation. Table

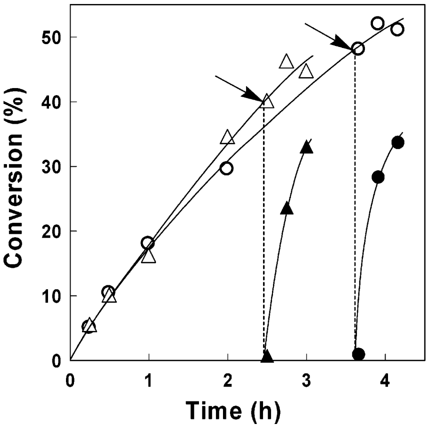


Figure 15. Conversion vs time curves for the solution copolymerization of HEMA with 5 mol % of PPGDMA-21 in (circles) ACN and (triangles) DMF at a dilution of 1/3 using 0.04 mol/L AIBN at 50 °C in the presence of LM ([LM]/[total monomer] = 1/50). Open and filled symbols correspond to total and gel polymers, respectively. The arrows denote the gel points.

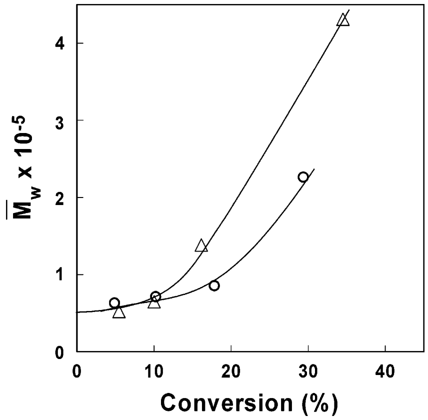


Figure 16. Dependence of M_w on conversion (see Figure 15).

Table 2. Comparison of Actual and Theoretical Gel Points in the HEMA/PPGDMA-21 (95/5) Copolymerizations in the Presence of LM[a]

solvent	$\bar{P}_{w,0}$[b]	gel point (%) theoret[c]	gel point (%) actual[d]	actual gel point[e]/ theoret gel point[c]
ACN	260	4.1	47.7 (35.1)[e]	8.7
DMF	260	4.1	40.0 (29.5)[e]	7.3

[a] Dilution 1/3, [AIBN] = 0.04 mol/L, [LM]/[total monomer] = 1/50, 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.

2 summarizes the results as a comparison of actual gel points with theoretical ones for the HEMA/PPGDMA-21 (95/5) copolymerizations in ACN and DMF. The suppressed occurrence of intermolecular cross-linking caused by the assembly of short primary polymer chains in ACN was reflected as the increased deviation from FS theory, i.e., a larger ratio of the actual gel point to the theoretical one.

Conclusion

We tried to explore the gelation behavior of free-radical cross-linking monovinyl/divinyl copolymerizations resulting in novel amphiphilic network polymers having short primary polymer chains and long cross-link units with opposite polarities with the intention of the control of intermolecular cross-linking reaction by the aid of the difference in the conformations of amphiphilic prepolymers.

First, the gelation behavior of BzMA/PEGDMA-23 (95/5) solution copolymerizations was explored in DO and DO/H_2O (85/15) mixture. A little increment of polymerization rate and the delayed gelation toward a higher gel point conversion were observed in DO/H_2O (85/15) mixture. The suppressed occurrence of intermolecular cross-linking reaction was supported by the dependence of weight-average molecular weights of resulting prepolymers on conversion. Thus, the assembly of short primary polymer chains induced the restricted motion of propagating polymer radical, leading to a suppressed intermolecular cross-linking.

Then, the gelation behavior of HEMA/PPGDMA-21 (95/5) solution copolymerizations was explored in DO, DO/H_2O (80/20) mixture, and DO/H_2O (70/30) mixture. The polymerization rate was obviously accelerated with an increase in the volume percent H_2O in mixed solvents, and the gel point shifted toward a lower conversion. The assembly of nonpolar cross-link units caused by a strong nonsolvency of H_2O led to an enhanced occurrence of intermolecular cross-linking reaction as reflected directly on the dependence of weight-average molecular weight of resulting prepolymer on conversion. The assembly of polar primary polymer chains consisting of poly(HEMA) suppressed the cross-linking reaction in DO. Suppressed or enhanced occurrence of intermolecular cross-linking caused by the assembly of short primary polymer chains or long cross-link units was reflected as increased or decreased deviation from FS theory, respectively, i.e., a larger or smaller ratio of the actual gel point to the theoretical one.

Finally, we tried to generalize the solvent effect on gelation by using various solvents. Especially, our attention was focused on ACN and DMF as solvents because the resulting gel swelled maximally in DMF but shrank in ACN despite the fact that the solubility parameters of both solvents are almost same. In ACN, the hydrogen bonds between hydroxyl groups of poly(HEMA) chains are stronger than the ones between hydroxyl groups of poly(HEMA) chain and solvent molecules. The situation in DMF is vice versa. The gelation in HEMA/PPGDMA-21 (95/5) solution copolymerizations was explored in both solvents. Again, the assembly of short primary polymer chains led to a suppressed increment of molecular weight on conversion as a reflection of the restricted motion of the propagating polymer radical. The suppressed occurrence of intermolecular cross-linking caused by the assembly of short primary polymer chains in ACN was reflected as the increased deviation from FS theory.

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