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Novel flexible network polymers consisting of oligomeric primary polymer chains originated in the mechanistic discussion of multiallyl crosslinking polymerization

Akira Matsumoto (✉), Masato Doura, Tadahiro Kiguchi, Hideo Ito, Hiroyuki Aota

Department of Applied Chemistry, Faculty of Engineering and High Technology Research Center, Kansai University, Suita, Osaka 564-8680, Japan
E-Mail: amatsu@ipcku.kansai-u.ac.jp; Fax: 0081-6-6339-4026

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Summary

It is well known that allyl monomers polymerize only with difficulty and yield polymers having low molecular weights, i.e., oligomers. Inevitably, free-radical multiallyl crosslinking polymerization provides network polymers consisting of oligomeric primary polymer chains, i.e., having abundant dangling chains. This led to the development of novel flexible network polymers such as amphiphilic network polymers (**I**) consisting of short primary polymer chains and long crosslink units with opposite polarities, simultaneous interpenetrating networks (**II**) consisting of both polyurethane (PU) and polymethacrylate (PM) networks with oligomeric primary polymer chains, and network polymers (**III**) consisting of centipede-type primary polymer chains. Thus, the solution copolymerizations of benzyl methacrylate with tricosaethylene glycol dimethacrylate in the presence of lauryl mercaptan yielded **I** consisting of nonpolar, short primary polymer chains and polar, long crosslink units. The opposite type of **I** was prepared by the copolymerization of 2-hydroxyethyl methacrylate, a polar monomer having a hydroxyl group, with heneicosapropylene glycol dimethacrylate, a nonpolar monomer having a poly(oxypropylene) unit. The equimolar polyaddition crosslinking reaction of poly(methyl methacrylate-*co*-2-methacryloyloxyethyl isocyanate) with tri(oxytetramethylene) glycol, leading to PU networks, and the free-radical crosslinking copolymerization of methyl methacrylate with tri(oxytetramethylene) dimethacrylate in the presence of CBr_4, leading to PM networks, were progressed simultaneously, providing **II** formed via the topological crosslink between PU and PM network structures. The post-copolymerizations of oligomeric allyl methacrylate/alkyl methacrylate precopolymers, having different amounts of pendant allyl groups and different molecular weights, with allyl benzoate/vinyl benzoate monomer mixtures were conducted to give **III**.

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Introduction

The free-radical polymerization of allyl monomers, generally referred to as "allyl polymerization", has received much less attention than the corresponding vinyl polymerization of common vinyl monomers. Compared with other monomers, allyl monomers polymerize only with difficulty and yield polymers having low molecular weights, i.e., oligomers [1-4]. This is ascribed to "degradative monomer chain transfer" [5], characteristic of allyl polymerization; thus, the hydrogen atoms attached to the carbon atom alpha to the double bond, i.e., allylic hydrogens are responsible for this monomer chain transfer that would be essentially a termination reaction.

Although the facile monomer chain transfer prevents the production of useful high-molecular-weight homopolymers from monoallyl monomers, multiallyl monomers can be readily polymerized to produce a range of commercially important thermoset products, which include diallyl phthalate (DAP) resins as representative allyl resins [6,7]. The free-radical crosslinking polymerization of diallyl dicarboxylates has been investigated by Simpson [8, 9], Gordon [10], and Oiwa [11]. However, the results obtained have not always been consistent and the approximate kinetics assumed appear perhaps to warrant reappraisal. Thereafter, we have carried out detailed mechanistic studies of the polymerization of a variety of multiallyl monomers, especially in terms of cyclopolymerization, cyclocopolymerization, and gelation; the mechanistic discussion of the polymerization of multiallyl monomers and its extension to common multivinyl monomers, based on the experimental results obtained mainly in our laboratory, were reviewed [12, 13].

Here, our mechanistic discussion was extended to the development of novel flexible network polymers that should be originated in the above mentioned multiallyl crosslinking polymerization. That is, the characteristic feature of the free-radical multiallyl crosslinking polymerization that provides the network polymers consisting of oligomeric primary polymer chains led to the development of novel flexible network polymers such as amphiphilic network polymers consisting of short primary polymer chains and long crosslink units with opposite polarities [14, 15], simultaneous interpenetrating networks consisting of both polyurethane and polymethacrylate networks with oligomeric primary polymer chains [16, 17], and network polymers consisting of centipede-type primary polymer chains [18].

Mechanistic discussion of the free-radical crosslinking polymerization of multiallyl and/or multivinyl monomers

We have been concerned with network formation in the free-radical 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 Flory-Stockmayer (FS) gelation theory [19]. 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 polymerization. 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 DAP [20]. This was completely opposed to the cases where numerous reports on microgel formation were published in the homopolymerization of multivinyl monomers and their copolymerization with monovinyl monomers [21-28]. 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 [5]. 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 [29]. The gelation behavior was compared with diallyl terephthalate polymerization as a typical example of multiallyl polymerization. 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 mechanism through multiallyl polymerization or multivinyl oligomerization in the presence of a chain transfer agent apparently seems to be quite different from the ordinary multivinyl polymerization [21-28] in the absence of a chain transfer agent. Figure 1 illustrates a rough sketch of network formation processes in the free-radical crosslinking monoallyl/diallyl copolymerization.

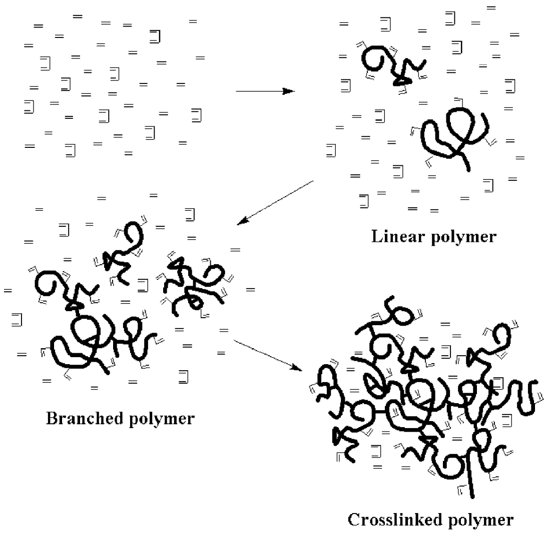

Figure 1. A rough sketch of network formation processes in the free-radical crosslinking monoallyl/diallyl copolymerization.

At an early stage of polymerization, only oligomeric linear or looped-structured prepolymer is formed to generate the core of network polymer, as completely opposed to the case of common multivinyl polymerization where high-molecular-weight swollen polymer particle is presumed to be formed [30,31]. With the progress of polymerization, an enhanced occurrence of intermolecular crosslinking enlarges the core from linear to branched polymer. This branched prepolymer grows further to give highly branched polymer with conversion, and eventually gelation occurs as a result of indefinitely large sized network polymer formation. This network formation process may fall into the category of FS gelation model. Thereafter, we have pursued

Figure 2. Two extreme structures of crosslinked polymers as (A) an ideal network polymer and (B) a microgel.

the generalization through both multiallyl and multivinyl polymerizations [32-44]. As our discussion has been based on a classical FS theory [19], the validity of FS theory was confirmed by conducting the free-radical crosslinking monovinyl/divinyl copolymerizations [40, 42-44] under the polymerization conditions in which the significance of the thermodynamic excluded-volume effect and intramolecular crosslinking, the respective primary and secondary factors for the greatly delayed gelation, was removed.

Now, we can have two extreme crosslinked polymers as an ideal network polymer governed by FS theory and a microgel greatly deviated from the theory [45] (see Figure 2), although the structures of the actual crosslinked polymers would be between the two extreme cases.

Flexible amphiphilic network polymers consisting of short primary polymer chains and long crosslink units with opposite polarities

We extended the above mechanistic discussion based on free-radical multiallyl crosslinking polymerization to the preparation of novel amphiphilic network polymers as the homogeneous crosslinked polymers biased toward the ideal network polymer [14, 15]. In the free-radical crosslinking monovinyl/divinyl copolymerization an oligomeric, long crosslinker was introduced and concurrently, oligomeric, short primary polymer chains were formed in the presence of a chain transfer agent, in which both lengths of primary polymer chain and crosslink unit are in a comparable order.

First, benzyl methacrylate (BzMA), a nonpolar monomer, was copolymerized radically with 5 mol % (corresponding to 27.5 wt %) tricosaethylene glycol dimethacrylate [$CH_2=C(CH_3)CO(OCH_2CH_2)_{23}OCOC(CH_3)=CH_2$] (PEGDMA-23), a polar monomer having a poly(oxyethylene) unit, in the presence of LM to provide flexible amphiphilic vinyl-type network polymers consisting of nonpolar, short primary polymer chains and polar, long crosslink units [14]. The enhanced incorporation of dangling chains into the network polymer was brought by shortening the primary polymer chain length, and the copolymerization with methoxytricosaethylene glycol methacrylate, a mono-ene counterpart of PEGDMA-23, enforced the incorporation of flexible dangling poly(oxyethylene) chains into the network polymer, although the former dangling chains as terminal parts of primary poly(BzMA) chains were rather rigid.

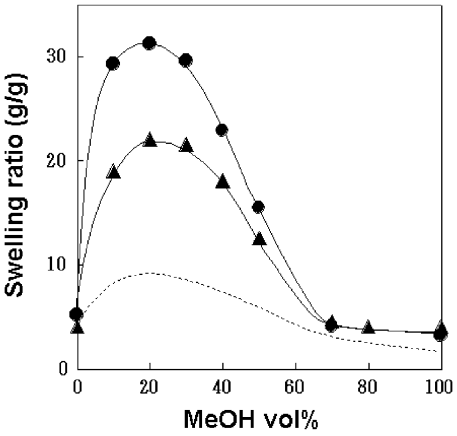

Figure 3. Correlations of the swelling ratios of resulting gels with MeOH content in mixed solvents consisting of *t*-BB and MeOH for BzMA/PEGDMA-23 (95/5) copolymerizations in the presence of LM ([LM]/[total monomer] = (circle) 1/20 and (triangle) 1/200). Dotted line corresponds to the gel obtained by BzMA/PEGDMA-23 (95/5) copolymerizations in the absence of LM.

Then, the influence of characteristic dangling chains on the swelling behavior of amphiphilic gels was examined in the mixed solvents consisting of nonpolar *t*-butylbenzene (*t*-BB) and polar MeOH. *t*-BB has an affinity to short primary polymer chains consisting of nonpolar poly(BzMA)s, although it acts as a nonsolvent for polar, long poly(oxyethylene) crosslink units. The situation of MeOH was the opposite. The profiles of the solvent component dependencies of the swelling ratios (SRs) were characteristic of amphiphilic gels (see Figure 3). The characteristic swelling behavior of resulting amphiphilic gels was sharper with reduced primary polymer chain length or an increased number of dangling chains. The introduction of dangling poly(oxyethylene) chains led not only to an increased SR but also to sharpened swelling behavior of amphiphilic gels. Swelling-deswelling change responsible for external stimulation is one of the significant properties of gels. A preliminary attempt was done to check the swelling response of amphiphilic gels by changing the external solvent polarity. The dangling chains with freely mobile end segments influenced the swelling response of gels. The amphiphilic gels with less entangled, collapsed crosslink units exhibited a faster swelling response than the ones with more entangled, collapsed primary polymer chains.

Second, the opposite type of amphiphilic network polymers consisting of polar, short primary polymer chains and nonpolar, long crosslink units were prepared by the 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 [CH_2=C(CH_3)CO($OCHCH_3CH_2$)$_{21}$OCOC(CH_3)=CH_2] (PPGDMA-21), a nonpolar monomer having a poly(oxypropylene) unit, in MeOH at a dilution of 2/3 in the presence of different amounts of LM [15]. The homogeneity of the resulting network polymers was discussed by the comparison of actual gel points with theoretical ones calculated according to FS theory. In addition, the SRs 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 features, especially when the primary polymer chain length is short. The amphiphilicity of the resulting gels was checked by measuring their SRs in the *t*-BB/MeOH mixed solvents. Thus, with an increase in the MeOH volume percent, the gels shrank to the smallest SR 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 %,

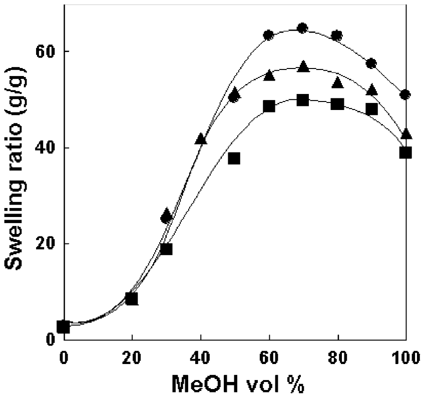

Figure 4. Correlations of the swelling ratios of resulting gels with MeOH content in mixed solvents consisting of *t*-BB and MeOH for HEMA/PPGDMA-21 (95/5) copolymerizations in the presence of LM ([LM]/[total monomer] = (circle) 1/20, (triangle) 1/50, and (square) 1/100).

and then shrank gradually up to a rather high SR at the terminal (i.e., in pure MeOH) (see Figure 4).

The solvent component dependencies of the SRs 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) crosslink units than MeOH, the influence of H_2O on the characteristic swelling behavior of resulting amphiphilic gels was examined by measuring their SRs in the mixed solvents consisting of MeOH/H_2O or acetone/H_2O. Conclusively, the role of crosslink 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 crosslink units on the characteristic swelling behavior of novel amphiphilic gel would depend on the different combinations of primary polymer chains and crosslink 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 crosslink units with opposite polarities are typically depicted in Figure 5.

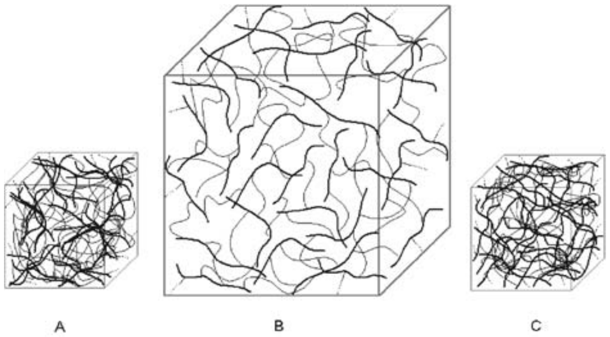

Figure 5. Three typical conformations of network segments of amphiphilic gel consisting of short primary polymer chains and long crosslink units with opposite polarities: (A) shrinkage of short primary polymer chains, (B) random conformation, and (C) shrinkage of long crosslink units.

Simultaneous interpenetrating networks consisting of both polyurethane and polymethacrylate networks with oligomeric primary polymer chains

Most of reports treated, so far, of the interpenetrating polymer networks (IPNs) with the intention of the improvement of the mechanical properties of network polymers or thermosetting resins. However, a detailed crosslinking polymerization mechanism leading to IPN formation at a molecular level has not been established yet. Especially, the formation of a true simultaneous interpenetrating network (SIN) may appear doubtful considering the usual occurrence of phase separation in IPN. Thus, we felt strongly the necessity of clarifying the IPN formation processes in terms of the reaction mechanism, especially in connection with our continuing studies aimed at the elucidation of the crosslinking polymerization mechanism and the control of network formation to molecularly design a variety of network polymers with high performance and high functionality. Our research target was focused on the IPNs consisting of both polyurethane (PU) and polymethacrylate (PM) networks, i.e., representatives of two typical types of network polymers formed through step growth and chain growth mechanisms, respectively. Thus, the research program for clarifying the IPN formation mechanism is a successive understanding of (1) the polyaddition crosslinking reaction leading to PU network formation, (2) the reaction mechanism forming semi-IPNs consisting of PU networks and linear PMs, and (3) the reaction mechanism forming SINs consisting of both PU and PM networks.

First, we have discussed in detail the polyaddition crosslinking reactions leading to PU network formation [46, 47]. The equimolar polyaddition crosslinking reactions of poly(methyl methacrylate-*co*-2-methcryloyloxyethyl isocyanate)s (poly(MMA-*co*-MOI)s), having pendant isocyanate (NCO) groups, with ethylene glycol, 1,6-hexane diol, and 1,10-decane diol (DD) were explored in detail. The reason that we chose poly(MMA-*co*-MOI)s as novel multifunctional polyisocyanates is that poly(MMA-*co*-MOI)s are desirable for easier miscibility with our target PM networks, typical vinyl-type network polymers, as another component of SINs. Furthermore, the chain length of poly(MMA-*co*-MOI) is easily adjustable through changes in the amount of a chain transfer agent. The miscibility significantly depends on the chain length, especially for polymers of intermediate molecular weights between the low molecular weight (or oligomeric) and high molecular weight (or polymeric) molecules.

Second, we have discussed the reaction mechanisms forming semi-IPNs consisting of both PU networks and linear PMs [16]. Notably, a direct evidence of semi-IPN formation was obtained by pursuing the incorporation of the linear PM into the resulting PU networks by ^{1}H NMR and ultraviolet-visible (UV-vis) spectroscopy. The copolymers containing a small amount of pyrenyl methacrylate (PyMA) were used as the probe for UV-vis spectroscopic determination.

Finally, we pursued the ideal SIN formation via topological crosslinks based on both polyaddition crosslinking polyisocyanate/diol reaction and free-radical crosslinking monomethacrylate/dimethacrylate copolymerization. The origin of ideal SIN is in the topological crosslink formation between PU and PM network structures introduced by the respective intramolecular crosslinking reactions. In general, the phase separation occurs during IPN formation processes because of the immiscibility of two types of network polymer chains and the decreased entropy of mixing. This difficulty for ideal SIN formation would be surmounted by choosing two types of network polymers having oligomeric primary polymer chains and similar structures. The direct evidence for the occurrence of such a topological crosslinking could be obtainable by pursuing the interaction between PU and PM network polymer precursors. Here a lower concentration would be preferred as an appropriate polymerization condition, in order to omit the possibility of a topological network formation due to the reinforced entanglement of both network polymer chains in a highly viscous solution at a higher concentration.

Thus, the equimolar polyaddition crosslinking reaction of poly(MMA-*co*-MOI) with tri(oxytetramethylene) glycol leading to PU networks was carried out in methyl benzoate. Simultaneously, the free-radical crosslinking copolymerization of MMA with tri(oxytetramethylene) dimethacrylate (TOTMDMA) leading to PM networks was progressed at a dilution of 1/10 in the presence of CBr_4 as a chain transfer agent. Under these polymerization conditions, no gelation was observed for respective crosslinking homopolymerizations leading to PU and PM homo-networks because respective intramolecular crosslinking reactions would be enhanced at a diluted solution. On the contrary, the simultaneous crosslinking polymerizations resulting in PU/PM SIN led to the gel formation via the topological crosslinks between PU and PM network structures introduced by the respective intramolecular crosslinking reactions. Then, the topological crosslink formation between PU and PM network polymer precursors was pursued by SEC monitored with a multichannel UV-vis spectrometer device. The pyrenyl groups of PyMA units in poly(MMA-*co*-PyMA-*co*-MOI) and MMA/PyMA/TOTMDMA (89/1/10) network polymer precursor were employed as the probe. The enhanced occurrence of intermolecular crosslinking via the topological crosslink formation led to gelation. This was clearly reflected on the variations of both the UV-vis monitored SEC curves and the molecular weights of the resulting PU and PM network polymer precursors with NCO and methacrylate monomer conversion, respectively (see Figures 6 and 7).

The swelling ratio of the resulting gel was much higher than that of poly(MMA-*co*-MOI)/DD networks or PM homo-networks. This suggests a rather low crosslink density of PU/PM (MMA/TOTMDMA = 90/10) SIN produced through the topological crosslink formation between PU and PM network polymer precursors.

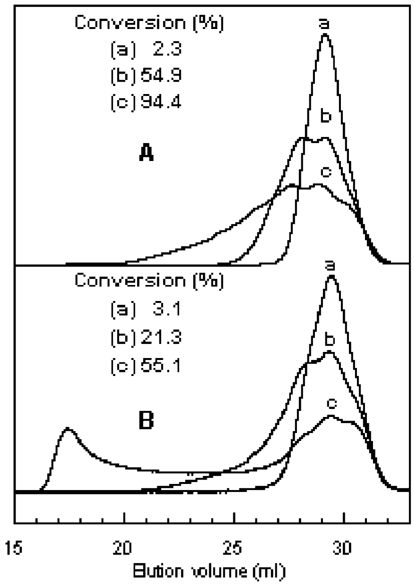

Figure 6. Comparison of UV-vis monitored (345 nm) SEC curves with conversion for the free-radical crosslinking copolymerizations of MMA with 10 mol % of TOTMDMA in (A) PM networks and (B) PU/PM (MMA/TOTMDMA = 90/10) SIN formation.

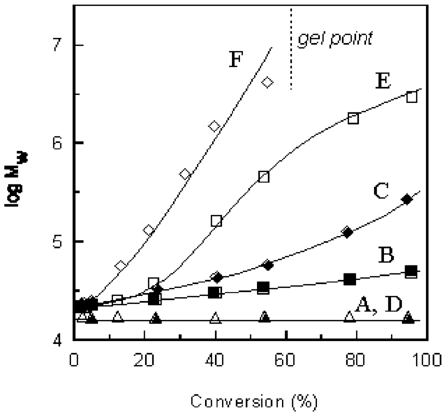

Figure 7. Dependence of Mw of (A) PM linear polymer, PM (MMA/TOTMDMA = (B) 95/5 and (C) 90/10), (D) PU/PM semi-IPN, and PU/PM (MMA/TOTMDMA = (E) 95/5 and (F) 90/10) SIN precursors on conversion.

Flexible network polymers consisting of centipede-type primary polymer chains

In order to interpret the greatly delayed gelation from FS theory reasonably, the mechanistic discussion has been done in terms of the intramolecular cyclization, the reduced reactivity of the prepolymer, the intramolecular crosslinking, the microgelation, the thermodynamic excluded volume effect on the intermolecular crosslinking, and the steric excluded volume effect [12]. In the connection with the reactivity of pendant double bonds in the prepolymer, the polymerization of allyl methacrylate (AMA) and its copolymerizations with alkyl methacrylates (RMA) were examined in detail in terms of the gelation [48,49]. Because AMA has two different types of double bonds, i.e., conjugated methacryloyl and unconjugated allyl groups, and the reactivity of the methacryloyl group relative to the allyl group is quite high, the preferential polymerization of methacryloyl group leading to the formation of prepolymer having abundant pendant allyl groups occurs at an early stage of polymerization. Thus, AMA prepolymers and AMA/RMA precopolymers which have different amounts of pendant allyl groups and different molecular weights were prepared by AMA homopolymerization and AMA/RMA copolymerizations, respectively, in the presence of LM. Then, they were subjected to the solution copolymerizations with allyl benzoate (ABz) in order to clarify the reactivity of pendant double bonds in the prepolymer for a deepened mechanistic discussion of the greatly delayed gelation from FS theory.

Subsequently, the synthesis and properties of novel network polymers having abundant dangling chains have been explored. Notably, this type of network polymer contains primary polymer chains having abundant oligomeric side-chains as a reflection of characteristic allyl polymerization (see Figure 8). That is, the polymerization of allyl monomers proceeds with the unimportant occurrence of a bimolecular termination between growing polymer radicals because the allylic hydrogen abstraction of growing polymer radical from monomer will be an essential termination reaction [5]. The bimolecular termination leads to the formation of crosslinkage between primary polymer chains to produce the complicated network structure, while allyl polymerization forms only oligomeric side-chains through the copolymerization with pendant allyl groups. This finding was extended to the preparation of novel centipede polymers [18]. Thus, AMA was copolymerized with various RMAs to give allylic prepolymers with abundant pendant allyl groups. Then,

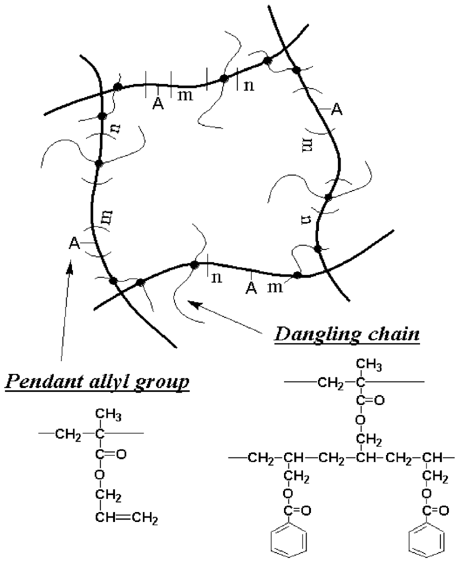

Figure 8. A rough sketch of network polymer consisting of primary polymer chains having abundant oligomeric side-chains.

the allylic prepolymers were copolymerized with ABz to provide novel centipede polymers by the suppression of intermolecular crosslinking reaction (see Figure 9). Moreover, the preparation of novel inhomogeneous network polymers with abundant dangling chains was done by employing densely netted AMA/RMA/ethylene dimethacrylate precopolymers. The swelling-deswelling response of resulting lipogels was much faster compared to that of the lipogels derived from corresponding homogeneous network polymers.

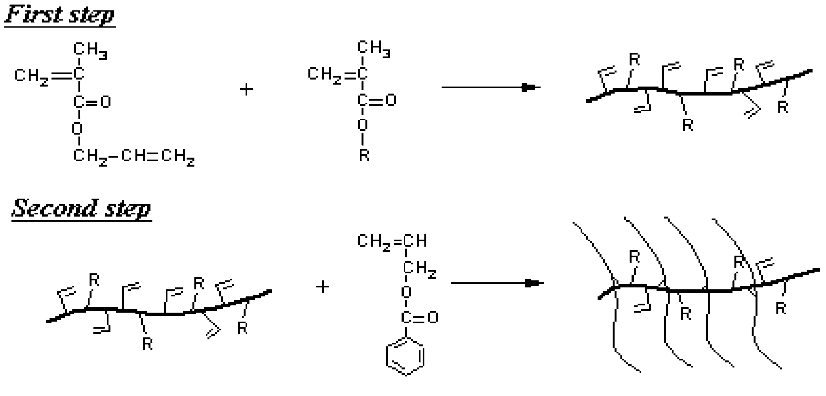

Figure 9. Preparation of centipede polymer.

Abbreviations

ABz	allyl benzoate
AMA	allyl methacrylate
t-BB	*t*-butylbenzene
BzMA	benzyl methacrylate

DAP	diallyl phthalate
DD	1,10-decane diol
FS	Flory-Stockmayer
HEMA	2-hydroxyethyl methacrylate
IPN	interpenetrating polymer network
LM	lauryl mercaptan
MMA	methyl methacrylate
MOI	2-methacryloyloxyethyl isocyanate
NCO	isocyanate
PEGDMA-23	tricosaethylene glycol dimethacrylate
PM	polymethacrylate
PPGDMA-21	heneicosapropylene glycol dimethacrylate
PU	polyurethane;
PyMA	pyrenyl methacrylate
RMA	alkyl methacrylate
SIN	simultaneous interpenetrating network
SR	swelling ratio
TOTMDMA	tri(oxytetramethylene) dimethacrylate
UV-vis	ultraviolet-visible

References

1. G. Odian, *Principles of Polymerization,* 4th ed. Wiley, New York (2004) p. 263
2. C. E. Schildknecht, *Allyl Compounds and Their Polymers*, Wiley, New York (1973)
3. R. C. Laible, *Chem. Rev.*, **58**, 807 (1958)
4. V. I. Volodina, A. I. Tarasov, S. S. Spasskii, *Russ. Chem. Rev.*, **39**, 140 (1970)
5. P. D. Bartlett, R. Altschul, *J. Am. Chem. Soc.*, **67**, 812, 816 (1945)
6. R. C. Laible, *Encyclopedia of Polymer Science and Technology*, Vol. 1, Wiley, New York (1964) p.750
7. C. E. Schidknecht, *Encyclopedia of Polymer Science and Engineering*, Vol. 4, Wiley, New York (1986) p. 779
8. W. Simpson, T. Holt, R. J. Zetie, *J. Polym. Sci.*, **10**, 489 (1953)
9. W. Simpson, T. Holt, *J. Polym. Sci.*, **18**, 335 (1955)
10. M. Gordon, *J. Chem. Phys.*, **22**, 610 (1954)
11. M. Oiwa, Y. Ogata, *Nippon Kagaku Zasshi*, **79**, 1506 (1958)
12. A. Matsumoto, *Adv. Polym. Sci.*, **123**, 41 (1995)
13. A. Matsumoto, *Prog. Polym. Sci.*, **26**, 189 (2001)
14. M. Doura, H. Aota, A. Matsumoto, *J. Polym. Sci.: Part A: Polym. Chem.*, **42**, 2192 (2004)
15. M. Doura, Y. Naka, H. Aota, A. Matsumoto, *Macromolecules*, **36**, 8477 (2003)
16. T. Kiguchi, H. Aota, A. Matsumoto, *J. Appl. Polym. Sci.*, **94**, 1198 (2004)
17. T. Kiguchi, H. Aota, A. Matsumoto, *Macromolecules*, **37**, 8249 (2004)
18. A. Matsumoto, H. Ito, N. Okamoto, H. Aota, *Polym. Prep. Jpn.*, **53(1)**, 394 (2004)
19. W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944)
20. A. Matsumoto, H. Nakajima, M. Oiwa, *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.),* **9**, 141 (1988)
21. H. Staudinger, E. Huseman, *Chem. Ber.*, **68**, 1618 (1935)
22. K. Horie, A. Otagawa, M. Muraoka, I. Mita, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 445 (1975)
23. H. Galina, K. Dusek, Z. Tuzar, M. Bohdanecky, J. Stokr, *Eur. Polym. J.*, **16**, 1043 (1980)
24. J. Spevacek, K. Dusek, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 2027 (1980)
25. A. C. Shah, I. W. Parsons, R. N. Haward, *Polymer*, **21**, 825 (1980)
26. R. Leicht, J. Fuhrmann, *Polym. Bull.*, **4**, 141 (1981)
27. M. Antonietti, C. Rosenauer, *Macromolecules*, **24**, 3434 (1991)

28. W. Funke, O. Okay, and B. Joos-Muller, *Adv. Polym. Sci.*, **136**, 139 (1998)
29. A. Matsumoto, D. Mitomi, H. Aota, J. Ikeda, *Polymer*, **41**, 1321 (2000)
30. C. Walling, *J. Am. Chem. Soc.*, **67**, 441 (1945)
31. K. Dusek, M. Duskova-Smrckova, *Prog. Polym. Sci.*, **25**, 1215 (2000)
32. A. Matsumoto, S. Yonezawa, M. Oiwa, *Eur. Polym. J.*, **24**, 703 (1988)
33. A. Matsumoto, H. Ando, M. Oiwa, *Eur. Polym. J.*, **25**, 385 (1989)
34. A. Matsumoto, H. Ando, M. Oiwa, *Kobunshi Ronbunshu*, **46**, 583 (1989)
35. A. Matsumoto, Y. Yamashita, M. Oiwa, *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.),* **12**, 135 (1991)
36. A. Matsumoto, E. Nishi, M. Oiwa, J. Ikeda, *Eur. Polym. J.*, **27**, 1417 (1991)
37. A.Matsumoto, *Makromol. Chem., Macromol. Symp.*, **76**, 33 (1993)
38. A. Matsumoto, Y. Yamashita, M. Oiwa, *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.),* **14**, 139 (1993)
39. A. Matsumoto, Y. Hasei, H. Aota, *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.),* **15**, 117 (1994)
40. A. Matsumoto, S. Okuno, H. Aota, *Macromol. Symp.*, **93**, 1 (1995)
41. A. Matsumoto, S. Takahashi, T. Morita, *Nettowaku Porima (J. Net. Polym. Jpn.),* **17**, 139 (1996)
42. A. Matsumoto, A. Okamoto, S. Okuno, H. Aota, *Angew. Makromol. Chem.*, **240**, 275 (1996)
43. A. Matsumoto, A. Taniguchi, *Polym. J.*, **31**, 711 (1999)
44. A. Matsumoto, Y. Kitaguchi, O. Sonoda, *Macromolecules*, **32**, 8336 (1999)
45. A. Matsumoto, T. Ohashi, H. Oe, H. Aota, J. Ikeda, *J. Polym. Sci.: Part A: Polym. Chem.*, **38**, 4396 (2000)
46. T. Kiguchi, H. Aota, A. Matsumoto, *J. Polym. Sci.: Part A: Polym. Chem.*, **41**, 606 (2003)
47. T. Kiguchi, H. Aota, A. Matsumoto, *J. Polym. Sci.: Part A: Polym. Chem.*, **41**, 3243 (2003)
48. A. Matsumoto, S. Asai, H. Aota, *Macromol. Chem. Phys.*, **201**, 2735 (2000)
49. A. Matsumoto, S. Asai, S. Shimizu, H. Aota, *Eur. Polym. J.*, **38**, 863 (2002)