Molecular Design of Patchwork-Type Network Polymers Utilizing Network Polymer Precursors Consisting of Oligomeric Primary Polymer Chains Originated in Multiallyl Crosslinking Polymerization

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SYNOPSIS

The molecular design of novel patchwork-type network polymers originated in multiallyl crosslinking polymerization is based on the pursuit of the inhomogeneous crosslinked polymers biased toward the microgel greatly deviated from Flory-Stockmayer gelation theory. Thus, the patchwork-type network polymers were prepared by patching two kinds of core-shell type dendritic network polymer precursors (NPPs) consisting of oligomeric primary polymer chains with opposite polarities. 2-Hydroxyethyl methacrylate/nonaethylene glycol dimethacrylate and benzyl methacrylate/heptapropylene glycol dimethacrylate copolymerizations were carried out radically in MeOH and t-butylbenzene, respectively, at a dilution of 1/5 in the presence of lauryl mercaptan to provide polar and nonpolar NPPs. Both types of NPPs were post-copolymerized using amphiphilic NPPs as compatibilizers. A detailed characterization of the patches of patchwork-type network polymer was done using SEC-MALLS-viscometry, providing the correlation of intrinsic viscosity versus molecular weight of fractionated samples. The profiles of the solvent-component dependencies of the swelling ratios of patchwork-type network polymer gels were characteristic of amphiphilic gels.

1. 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\(^1\text{-}^4\). 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 linear high-molecular-weight polymers from monoallyl monomers, multiallyl monomers can be readily polymerized to produce a range of commercially important crosslinked polymers, i.e., thermoset products, which include diallyl phthalate (DAP) resins as representative allyl resins. The free-radical crosslinking polymerization of diallyl dicarboxylates has been investigated by Simpson, Gordon, and Oiwa. However, the results obtained have not always been consistent and the approximate kinetics assumed appears 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. Here, our mechanistic discussion was focused on the deviation from Flory-Stockmayer gelation theory (FS theory) and the reasons for the greatly delayed gelation were discussed mechanistically in detail. The validity of FS theory was confirmed by conducting the free-radical crosslinking monovinyl/divinyl copolymerization under the 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. Then, we extended the above mechanistic discussion to the preparation of novel amphiphilic network polymers as the homogeneous crosslinked polymers biased toward the ideal network polymer governed by FS theory. In the 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. Thus, benzyl methacrylate (BzMA), a nonpolar monomer, was copolymerized radically with tricosaethylene glycol dimethacrylate (PEGDMA-23), a polar monomer having a poly(oxyethylene) unit, in the presence of lauryl mercaptan (LM) to provide flexible amphiphilic vinyl-type network polymers. 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. The influence of characteristic dangling chains on the swelling behavior of amphiphilic gels was examined in the mixed solvent consisting of nonpolar t-butylbenzene (t-BB) and polar MeOH. The profiles of the solvent component dependencies of the swelling ratios were characteristic of amphiphilic gels.

In the present article, we proceeded to the molecular design of novel patchwork-type network polymers as the inhomogeneous crosslinked polymers biased toward the microgel greatly deviated from FS theory. The patchwork-type network polymers were prepared preliminarily by patching two types of branched network polymer precursors (NPPs) consisting of oligomeric primary polymer chains with opposite polarities. Here it should be noted that the branched NPP is molecularly designed as a result of pursuit of an extreme precursor of microgel and thus, its structure seems to be core-shell type dendritic as the tree model is proposed for network formation. Thus, 2-hydroxyethyl methacrylate (HEMA)/nonaethylene glycol dimethacrylate (PEGDMA-9) and BzMA/heptapropylene glycol dimethacrylate (PPGDMA-7) copolymerizations were carried out in MeOH and t-BB, respectively, at a dilution of 1/5 in the presence of LM to provide polar and nonpolar NPPs. Both types of NPPs were post-copolymerized in the presence of amphiphilic NPPs as compatibilizers to give novel patchwork-type network polymers. A detailed characterization of the patches of patchwork-type network polymer was done considering that the structure of NPP consisting of oligomeric primary polymer chains is dendritic; mainly, the correlation of intrinsic viscosities versus molecular weights was estimated using size-exclusion chromatography (SEC) with both multiangle laser light scattering (MALLS) and viscosity detectors, providing the correlation of intrinsic viscosity ([η]) versus molecular weight (Mw) of fractionated samples.
Here it should be noted that different types of polymer chains are generally incompatible as it is well known. Especially, in the case of our core-shell type dendritic NPPs, the situation would become worse. So, we need to overcome this incompatibility of different types of dendritic NPP patches. One procedure is to use amphiphilic NPP as compatibilizer. Another one is to reduce the primary polymer chain length as our idea is originated in multiallyl crosslinking polymerization.

2. Experimental part

Materials. BzMA, HEMA, and EGDMA (Kyoeisha Chemical Co., Ltd.) as monomers, 2,2'-azobisisobutyronitrile (AIBN) (Wako Pure Chemical Industries, Ltd.) as an initiator, and t-BB and MeOH as solvents were purified by conventional methods. Polyethylene glycol dimethacrylate \([\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}(\text{OCH}_2\text{CH}_2)_n\text{OOC}(\text{CH}_3)\text{=CH}_2, \text{PEGDMA-9 (n=9) and PEGDMA-23 (n=23)}]\) and polypropylene glycol dimethacrylate \([\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}(\text{OCH}(\text{CH}_3)\text{CH}_2)_n\text{OOC}(\text{CH}_3)\text{=CH}_2, \text{PPGDMA-7 (n=7) and PPGDMA-21 (n=21)}]\) (monomers, Kyoeisha Chemical Co., Ltd.) and LM (Wako Pure Chemical Industries, Ltd.; extra pure reagent commercially available) were used without further purification.

Polymerization. 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 60±0.1 °C. After a predetermined reaction time, the resulting NPP patch 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 NPP patch was done by reprecipitation from a tetrahydrofuran (THF)-precipitant system.

Preparation of patchwork-type network polymers. Both polar and nonpolar NPP patches were prepared by HEMA/PEGDMA-9 and BzMA/PPGDMA-7 copolymerizations. Here polymerizations were carried out in MeOH and in t-BB, respectively, at a dilution of 1/5 at 60 °C in the presence of LM as a chain transfer agent. Amphiphilic NPPs as compatibilizers were prepared according to our previous paper [22]. Then, polar and nonpolar NPP patch solutions were mixed along with amphiphilic NPPs and subsequently, the post-copolymerization of the mixed solution was performed at 60 °C to give the patchwork-type network polymer.

Measurements. The resulting polymers were subjected to SEC-MALLS-viscosity measurement in order to estimate the correlation of \([\eta]\) versus \(M_n\) by SEC using a triple detector system set in the direction of flow. This system consisted of viscometer, MALLS device and a differential refractometer in sequence. The measurements were carried out at 40 °C in THF using a three-column Shodex GPC KF-806L at polymer concentrations of 0.1-0.5% (w/v) and at a flow rate of 1 mL/min. The MALLS device was a DAWN model F (Wyatt Technology Corp.); the laser beam had a wavelength of 632.8 nm and was focused on a 67-µL flow cell. A Wyatt ViscoStar (Wyatt Technology Corp.) was employed as the viscometer.

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.

3. Results and discussion

3.1 Mechanistic discussion of the free-radical crosslinking polymerization of multiallyl and 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 FS theory [14]. 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
deep 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 23). 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 24-31). 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 14). 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 monomer chain transfer 5). Therefore, the oligomerization of neopentyl glycol dimethacrylate, a sparingly cyclopolymerizable divinyl monomer, was conducted in bulk in the presence of LM as a chain transfer agent in order to reduce the primary polymer chain length to a comparable order in diallyl polymerization 32). 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 24-31) in the absence of a chain transfer agent. Fig. 1 illustrates 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 NPP is formed to generate the core of network polymer, as completely opposed to the case of common multivinyl polymerization where high-molecular-weight NPP as swollen polymer particle is presumed to be formed 33,34). With the progress of polymerization, an enhanced occurrence of intermolecular crosslinking enlarges the core from linear to branched NPP. The branched NPP grows further to give highly branched NPP with conversion, and eventually gelation occurs as a result of indefinitely large sized network polymer formation. The structure of the highly branched NPP consisting of oligomeric primary polymer chains seems to be core-shell type dendritic as the tree model is proposed for network formation 21). This drew our idea of the preparation of novel patchwork-type network polymers utilizing NPPs of inhomogeneous crosslinked polymers biased toward the microgel greatly deviated from FS theory.

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

1) Intermolecular propagation with monomer:

2) Intramolecular cyclization:

3) Intermolecular crosslinking with prepolymer:

4) Intramolecular crosslinking:

Fig. 2 Reaction scheme for the network formation processes in the free-radical crosslinking monovinyl/divinyl copolymerization.
3.2 Design of patchwork-type network polymer utilizing dendritic NPPs as patches and amphiphilic NPPs as compatibilizers

Under the controlled bimolecular termination without gel effect as is in multiallyl polymerization (12,13) or multivinyl oligomerization in the presence of a chain transfer agent (32), we could simplify the ordinarily complicated reaction scheme for the network formation processes in multivinyl polymerization. Thus, in a free-radical crosslinking monovinyl/divinyl copolymerization, the network formation processes essentially involve four reactions of a growing polymer radical as is depicted in Fig.2. If the intermolecular crosslinking reaction could occur preferentially, the ideal network polymer having only one crosslink between primary polymer chains could be formed. The completely opposite case would be the microgel formation if the intramolecular crosslinking reaction could occur locally and extensively (see Fig.3). This prompted us to design a patchwork-type network polymer as a new type of network polymer which could be formed by combining both ideal network polymer and microgel formation. That is, we used dendritic NPPs as the patches of patchwork-type network polymer and concurrently, amphiphilic NPPs as the compatibilizers, since without compatibilizers, dendritic NPP patches with a similar polarity are easily assembled to induce inhomogeneous gel formation. Notably, both polar and nonpolar dendritic NPP patches could be stabilized by the aid of amphiphilic NPPs as compatibilizers.

Then, NPP patches were prepared as is schematically depicted in Fig.4. The core-shell type, polar dendritic NPP patch was prepared by the crosslinking copolymerization of HEMA, having hydroxyl group, with PEGDMA-9, having polar poly(oxyethylene) unit. The opposite nonpolar dendritic NPP patch was obtained by the crosslinking copolymerization of nonpolar BzMA with PPGDMA-7, having nonpolar poly(oxypropylene) unit.

On the other hand, amphiphilic NPPs as compatibilizers were prepared according to our previous paper (22). Here we chose two types of amphiphilic NPPs obtained by HEMA/PPGDMA-21 and BzMA/PEGDMA-23 copolymerizations, providing the former NPP having polar, short primary polymer chains and nonpolar, long crosslink units and the latter one having nonpolar, short primary polymer chains and polar, long crosslink units, respectively.

Now, we could have core-shell type dendritic NPP patches and amphiphilic NPP compatibilizers. Therefore, the patchwork-type network polymers were experimentally designed as follows. Firstly, HEMA/
PEGDMA-9 and BzMA/PPGDMA-7 copolymerizations were carried out, providing core-shell type, polar and nonpolar NPP patch solutions, respectively. Secondly, these NPP patch solutions were mixed along with amphiphilic NPP and then, the post-copolymerization of the mixed solution was performed to provide the patchwork-type network polymer.

3.3 Influence of primary polymer chain length on the compatibility of different types of NPPs

It should be noted that different type of polymer chains are usually incompatible. Especially, in the case of core-shell type dendritic NPPs mentioned above, the situation would become worse compared with linear polymers. This restriction of incompatibility of different types of polymer chains should be removed for the preparation of patchwork-type network polymer. One of our ideas is to use amphiphilic NPP as compatibilizer. Another one is to reduce the primary polymer chain length since different polymer chains could be compatible each other when the polymer chain length is in the range of oligomer.

In this connection, we examined the influence of primary polymer chain length on the inhomogenization of polymerization system. As can be easily expected, the homogeneous, transparent gel was obtained when the primary polymer chain length was quite short as the degree of polymerization is equal to 60. To the contrary, when the degree of polymerization of primary polymer chain became longer and reached 120, the inhomogeneous gel was obtained as the polymerization solution became turbid.

3.4 Characterization of nonpolar NPP patches by SEC-MALLS-viscometry

We tried to characterize nonpolar core-shell type dendritic NPP patches by SEC-MALLS-viscometry, providing the correlation of $[\eta]$ versus $M_w$ of fractionated samples. Thus, the characterization results of polystyrene measured by SEC-MALLS-viscometry are typically exemplified as follows. Fig. 5 shows RI-monitored SEC curve and both correlation lines of $M_w$ and $[\eta]$ versus elution volume for polystyrene. Then, the correlation of $[\eta]$ versus $M_w$ was plotted in Fig. 6; a reasonable result was obtained as the slope of the correlation line was 0.68. This demonstrates strongly that SEC-MALLS-viscometry is a powerful tool for the characterization of core-shell type dendritic NPP patches. In this connection, it is well known that the most remarkable feature of dendritic polymer is a drastic decrease in its viscosity.

In our previous paper, we concerned with the characterization of ideal NPPs, we have schematically illustrated the effect of intermolecular crosslinking followed by intramolecular crosslinking on the molecular size shrinkage as the correlations of r.m.s. radius of gyration versus $M_w$. This was extended to Fig. 7 that roughly depicts
the correlation of $[\eta]$ versus $M_w$ for different types of polymers, including linear polymer (A), ideal NPP or branched polymer (B), branched polymer with loop structures formed through intramolecular crosslinking (C), and dendritic NPP (D). Thus, the intrinsic viscosity is expected to be quite low when NPP structure is dendritic, eventually being nanogel-like.

**Fig.8** shows the double logarithmic plots of $[\eta]$ versus $M_w$ for nonpolar poly(BzMA-co-PPGDMA-7) (80/20) NPPs obtained at different conversions, along with a dotted line of linear poly(BzMA) as a comparison. Here the solution polymerization was carried out in $t$-BB at a dilution of 1/5 using 0.04 mol/L of AIBN at 60 °C in the presence of LM ([LM]/[total monomer] = 1/10). The $[\eta]$ values of resulting NPPs were lower than that of linear poly(BzMA) and they increased gradually with conversion. Here it should be noted that the intrinsic viscosity ratio, $[\eta]_{NPP}/[\eta]_{Linear}$, is well-known as a measure of branching. In this connection, the $[\eta]$ values of NPPs were divided by those of the corresponding linear poly(BzMA) with a same molecular weight and then, they were plotted against the molecular weight in **Fig.9**. The intrinsic viscosity ratio tended to decrease with an increase in molecular weight, i.e., with conversion. These results are in conformity with our expectation that the structures of poly(BzMA-co-PPGDMA-7) (80/20) NPPs would be dendritic.

Next, we tried to examine the influence of crosslinker on NPP structure formation. EGDMA was chosen as crosslinker in place of PPGDMA-7 having long crosslink segment, probably giving dendritic NPPs with higher crosslink densities or nanogel-like NPPs. **Fig.10** shows the double logarithmic plots of $[\eta]$ versus $M_w$; the $[\eta]$ values of poly(BzMA-co-EGDMA) (80/20) NPPs were quite lower than those of poly(BzMA-co-PPGDMA-7) (80/20) NPPs, especially for high-molecular-weight NPP. This is in accordance with our expectation since the lowest
[\eta_{\text{NPP}}/\eta_{\text{Linear}}] value of poly(BzMA-co-EGDMA) NPP obtained at 78.3% conversion reached 0.027 (M_w = 7.81 x 10^7), demonstrating nanogel-like NPP formation.

3.5 Preparation of patchwork-type network polymer and characteristic swelling behavior of resulting gel

We examined the swelling behavior of the patchwork-type network polymer gels by focusing on the influence of characteristic dangling chains since the patchwork-type network polymers were prepared by patching two kinds of core-shell type dendritic NPPs consisting of oligomeric primary polymer chains with opposite polarities. Here it should be noted that the vinyl-type network polymers are formed via highly branched polymers (see Fig.1). Therefore, the generation of abundant dangling chains would be their characteristic feature when the primary polymer chain is oligomeric because both terminal parts of a primary polymer chain are regarded as dangling chains. These dangling chains inherent in vinyl-type network polymers with oligomeric primary polymer chains could influence the swelling behavior of the resulting gels. Thus, we attempted to check the amphiphilicity of the resulting gels by measuring their swelling ratios in mixed solvents consisting of nonpolar t-BB and polar MeOH. t-BB has an affinity to oligomeric primary polymer chains consisting of nonpolar poly(BzMA)s and nonpolar, long poly(oxypropylene) crosslink units, although it acts as a nonsolvent for polar primary polymer chains, poly(HEMA)s, and polar, long poly(oxyethylene) crosslink units. The situation of MeOH is vice versa.

Fig.11 shows the correlation of the swelling ratio of the resulting patchwork-type network polymer gel having abundant dangling chains with the MeOH volume percentage in the mixed solvents consisting of nonpolar t-BB and polar MeOH. Patchwork-type network polymers consist of HEMA/PEGDMA-9 (90/10), BzMA/PPGDMA-7 (80/20), HEMA/PPGDMA-21 (95/5), and BzMA/PEGDMA-23 (95/5) (feed weight ratio = 1 : 1 : 0.5 : 0.5) post-copolymerization. Here HEMA/PEGDMA-9 (90/10) and BzMA/PPGDMA-7 (80/20) copolymerizations were carried out in MeOH and in t-BB, respectively, at a dilution of 1/5 using 0.04 mol/L of AIBN at 60 °C for 75 and 90 minutes, respectively, in the presence of LM ([LM]/[total monomer] = 1/10). The gel was obtained as the insoluble part consisting of 30-40% gel fraction by extracting the soluble part with THE from the polymer recovered at conversions beyond the gel point. The profile of the solvent-component dependency of the swelling ratio was characteristic of amphiphilic gel. Notably, the gel consisting of only nonpolar NPPs swelled in nonpolar t-BB and shrunk.
in polar MeOH, whereas it was *vice versa* in the case of the gel consisting of only polar NPPs. Considering these results, three typical conformations of NPP patches and NPP compatibilizers in t-BB/MeOH mixed solvents are presumed to be as follows. In nonpolar t-BB, polar NPP patches and polar units of amphiphilic NPP compatibilizers would be shrunken, whereas in polar MeOH, nonpolar NPP patches and nonpolar units of amphiphilic NPP compatibilizers would be shrunken. On the other hand, in t-BB/MeOH (40/60) mixture, no shrinkage of both NPP patches and NPP compatibilizers would be observed, providing the maximum swelling patchwork-type network polymer gel. This maximum swelling ratio shifted toward a lower MeOH vol% as in t-BB/MeOH mixture by increasing the feed ratio of nonpolar NPP patch to polar one (see a dotted line in Fig.11). In addition, when the crosslinker changed from PPGDMA-7 to EGDMA, the swelling ratio decreased relatively with shortening crosslink unit as a reflection of the change of NPP structure from dendritic to nanogel-like.

4. **Conclusion**

The patchwork-type network polymers were preliminarily prepared as an extension of the inhomogeneous crosslinked polymers biased toward the microgel greatly deviated from FS theory, utilizing NPPs consisting of oligomeric primary polymer chains with opposite polarities. Here, the NPP is molecularly designed as a result of pursuit of an extreme precursor of microgel and thus, its structure seems to be core-shell type dendritic. In general, different types of polymer chains are incompatible, especially in the case of our core-shell type dendritic NPPs. This incompatibility was overcome both by using amphiphilic NPP as compatibilizer and by reducing the primary polymer chain length originated in multiallyl crosslinking polymerization. Under the controlled bimolecular termination without gel effect, we could simplify the ordinarily complicated reaction scheme for the network formation processes in multivinyl polymerization. The key reactions for molecular-design of NPPs are the intermolecular and intramolecular crosslinking reactions; an occurrence of the preferential former or the local, extensive latter crosslinking leads to the formation of ideal network or microgel, respectively. Thus, a patchwork-type network polymer as a new type of network polymer was designed by combining both ideal network polymer and microgel formation. Here, dendritic NPPs were used as the patches of patchwork-type network polymer and concurrently amphiphilic NPPs as the compatibilizers. Both polar and nonpolar dendritic NPP patches could be stabilized by the aid of amphiphilic NPPs as compatibilizers. Thus, HEMA/PEGDMA-9 and BzMA/PPGDMA-7 copolymerizations were carried out in MeOH and t-BB, respectively, at a dilution of 1/5 in the presence of LM to provide polar and nonpolar NPPs. Both types of NPPs were post-copolymerized using amphiphilic NPPs as compatibilizers to give novel patchwork-type network polymers. A detailed characterization of the patches of patchwork-type network polymer was done using SEC-MALLS-viscometry, providing the correlation of \([\eta]\) versus \(M_w\) of fractionated samples. The \([\eta]\) values of resulting poly(BzMA-co-PPGDMA-7)-NPP patches were lower than that of linear poly(BzMA) and they decreased gradually with conversion. The intrinsic viscosity ratio, \([\eta]_{NPP}/[\eta]_{Linear}\) as a measure of branching tended to decrease with an increase in molecular weight, i.e., with conversion. These results demonstrate that the structures of NPP patches would be dendritic. The NPP patch structure depended on crosslinker, changing from dendritic to nanogel-like. Finally, the swelling behavior of the patchwork-type network polymer gel was examined by focusing on the influence of characteristic dangling chains inherent in vinyl-type network polymers with oligomeric primary polymer chains. The profiles of the solvent-component dependencies of the swelling ratios of patchwork-type network polymer gels were characteristic of amphiphilic gels.

**Acknowledgment**

This research was financially supported by “High-Tech Research Center” Project for Private Universities: matching fund subsidy from Ministry of Education, Culture, Sports, Science and Technology, 2005-2009.
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