# Further Discussion on Correlation between Brittleness and Inhomogeneous Network Structure of Cross-Linked Resins Originating in Specific Polymerization Behavior of Triallyl Isocyanurate

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*Received April 30, 2008; Revised Manuscript Received August 12, 2008*

ABSTRACT: Nonfilled triallyl isocyanurate (TAIC) cured resin obtained directly by polymerization of TAIC monomer was too brittle for practical use. The brittleness of cross-linked resins has been thought to be due to the inhomogeneity of their network structures, which consist of colloidal particles as evidenced by electron microscopy. However, the complete loss of flexibility of poly(TAIC) chain does not satisfy the prerequisite of locally enhanced occurrence of intramolecular cross-linking reaction inducing microgelation to form a colloidal particle. Therefore, the correlation between brittleness and network structure of TAIC resins was further discussed, especially focusing on the characterization of resulting TAIC network polymer precursors (NPPs) by size-exclusion chromatography (SEC)−multiangle laser light scattering (MALLS)−viscometry since the ordinary explanation for the brittleness of cross-linked resin does not appear to be the true explanation for TAIC resin's extreme brittleness. Thus, an alternative explanation for the brittleness of TAIC resins is provided: insufficient growth of the network structure of TAIC resin because of steric hindrance of the cross-linking reaction between sterically crowded growing polymer radical and pendant allyl groups belonging to the rigid primary polymer chain. This imperfection of cross-linking, providing not only insufficient network structure formation but also incorporation of abundant dangling chains into network polymer, could be one of the principal causes of brittleness, even for common cross-linked resins.

## Introduction

For a long time, it has been thought that cross-linked resins are brittle because of their inhomogeneous network structures consisting of colloidal particles. In 1941, the gelation theory was proposed by Flory.[1] Thereafter, Stockmayer applied Flory's procedure to the special case of chain cross-linking polymerization of symmetrical divinyl monomers, that is, Flory−Stockmayer gelation theory (FS theory).[2] Immediately, Walling[3] attempted to apply FS theory to the gelation in free-radical cross-linking copolymerization of common monovinyl/divinyl systems and gelation greatly delayed from theory was observed; this was explained qualitatively on the basis of the idea that the reaction mixture consists of discrete swollen polymer molecules. Thereafter, numerous reports on microgel formation were published in the homopolymerizations of multivinyl monomers and their copolymerizations with monovinyl monomers.[4−10] In 1963, Erath and Robinson[11] directly observed thermosetting resins as agglomerates of colloidal particles by electron microscopy. Bobalek et al.[12] proposed the model of an alkyd resin gelation process accompanied by microgelation in order to explain the inhomogeneity of cross-linked resin.

We have been concerned with multiallyl cross-linking polymerization[13,14] as opposed to the case of the common multivinyl system; the cross-linking polymerization process should be drastically changed as a reflection of specific allyl polymerization. Thus, in the bulk polymerization of diallyl phthalate (DAP), our detailed investigation[15] to clarify the process of growth of the inhomogeneous cross-linked DAP resin with the progress of polymerization clearly demonstrated that no microgelation occurred up to the gel point. Therefore, the formation of colloidal particles of cross-linked DAP resin observed by electron microscopy[11] should be induced during the polymerization process beyond the gel point. The inhomogenization of the resulting network polymer (that is, quasi-microgelation) proceeds rapidly beyond the gel point, and at a late stage of polymerization, the unreacted monomer mainly polymerizes in microspaces among quasi-microgels. The occurrence of intramolecular cross-linking inside the highly swollen network polymer produced just beyond the gel point would be enhanced with the progress of gelation. The segmental density of the interface among quasi-microgels would be low, and unreacted monomer molecules can move freely without restriction from the swollen network polymer. This kind of microinhomogenization of the network polymer during polymerization beyond the gel point was extended to the microinhomogeneous copolymerization of DAP with comonomers accompanied by the formation of quasi-microgel, with the intention of improving the mechanical properties of DAP resins. Thus, three kinds of glycol bis(allyl phthalate) were copolymerized with DAP to introduce flexible cross-links among quasi-microgels.[16] Moreover, DAP was cocured in bulk with vinyl monomers having long-chain alkyl groups, including lauryl methacrylate (LMA).[17]

Notably, triallyl isocyanurate (TAIC) is commercially important both as a cross-linking agent with comonomers and for the postcuring of preformed polymers, such as olefin copolymers, in electrical insulation.[18,19] However, in the direct preparation of nonfilled TAIC cured resin from TAIC monomer, the resulting material was too brittle for practical use. On the basis of the aforementioned procedures, by which the flexibility of DAP resins was successfully improved, we attempted to improve the mechanical properties of TAIC resins, especially toughness. TAIC was cocured with LMA but the addition effect

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10.1021/ma800974s CCC: $40.75

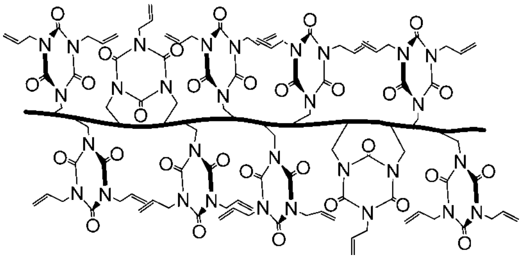

**Figure 1.** Rigid poly(TAIC) chain with bulky side chains.

of LMA was unsatisfactory; only a very brittle resin was obtained. Thus, the modification procedure that had been successful for DAP resins,[20] based on the idea of interpenetrating polymer network formation,[21] was applied with vain efforts.

The above-mentioned unsuccessful results for improvement of toughness of TAIC resins clearly demonstrate the difference in network structure of TAIC and DAP resins. Although DAP resins consisted of microinhomogeneous networks as agglomerates of colloidal particles,[11,15] the polymerization of TAIC may not always provide the formation of colloidal particles. Instead, TAIC polymerization introduces a rather homogeneous network, since the primary polymer chain of TAIC resin would be more rigid than that of DAP. This is due to very bulky side chains (see Figure 1). The complete loss of flexibility of the polymer chain would not satisfy the prerequisites for formation of quasi-microgels as colloidal particles in the cross-linking polymerization of TAIC. This is because the locally enhanced occurrence of intramolecular cross-linking reactions would be required for microgelation.[13]

This paper is concerned with further discussion of the correlation between brittleness and network structure in TAIC resins, especially focusing on the characterization of resultant network polymer precursors (NPPs) or TAIC-NPPs by use of size-exclusion chromatography (SEC) with both multiangle laser light scattering (MALLS) and viscosity detectors. Notably, SEC−MALLS−viscometry is a multidetection system providing correlation of intrinsic viscosity with molecular weight of fractionated samples, and it is useful as a powerful tool for characterization of NPPs with core−shell-type dendritic structures. In addition, the polymerization process beyond the gel-point conversion was pursued, in terms of elucidation of the network formation mechanism.

## Experimental Section

**Materials.** TAIC (Nippon Kasei Chemical Co., Ltd.) and diallyl terephthalate (DAT) (Daiso Co., Ltd.) as monomers, and methyl benzoate (MBz) (Wako Pure Chemical Industries, Ltd.) as a solvent, were purified by vacuum distillation under nitrogen. Dimethyl 2,2′-azobis(isobutyrate) (DMAIB) (Wako Pure Chemical Industries, Ltd.) as an initiator was purified by recrystallization from methanol.

**Polymerization.** Polymerization was carried out in a glass ampule containing suitable amounts of monomer, DMAIB, and MBz. The ampule was degassed three times by the usual freezing and thawing technique under vacuum and then sealed off. It was then placed in a thermostat regulated at 60 °C. After a predetermined reaction time, the reaction mixture was poured into a large amount of chilled methanol to precipitate the polymer. 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 extraction of the sol fraction with THF.

**Measurements.** The weight-average molecular weights ($M_w$) and the root-mean-square radii of gyration ($\langle S^2 \rangle_z^{1/2}$) of the resulting polymers were measured by light scattering (LS). The LS measurements were carried out in THF at 30 °C with an Otsuka Electronics DLS-7000 dynamic light scattering spectrophotometer over the angular range between 30° and 150°; unpolarized light of a wavelength of 632.8 nm was used. The resulting polymers were also subjected to SEC−MALLS−viscosity measurement in order to estimate the correlation of intrinsic viscosities ($[\eta]$) versus $M_w$ by SEC with a triple detector system set in the direction of flow. This system consisted of a viscometer, a MALLS device, and a differential refractometer in sequence. The SEC−MALLS−viscosity measurements were carried out at 40 °C in THF on a three-column Shodex GPC KF-806 L instrument at polymer concentrations of 0.1−0.5% (w/v) with 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-$\mu$L flow cell. A Wyatt ViscoStar (Wyatt Technology Corp.) was employed as the viscometer.

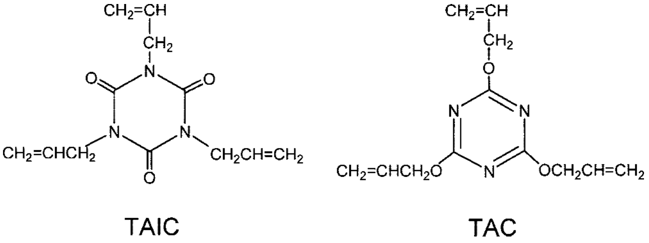

**Figure 2.** Chemical structures of TAIC and TAC.

## Results and Discussion

**Steric Effect on the Polymerization of TAIC.** In our continuing studies of the radical polymerization of multiallyl monomers,[22,23] the polymerization behavior of TAIC and its isomer triallyl cyanurate (TAC) was explored in detail,[24] since only a few basic studies of the polymerization of both monomers have been published.[25,26] Notably, gelation occurred at quite a low conversion in the polymerization of TAIC as compared with that of TAC. The cyclopolymerizability of TAIC was greater than that of TAC; the unreacted pendant double bonds responsible for cross-linking of TAIC-NPP were less abundant than those of TAC-NPP as a reverse result of the promoted gelation. To ascertain the reason for this interesting gelation behavior of TAIC, the primary polymer chain length, closely related to the gelation,[2] was precisely estimated. The primary polymer chain length of TAIC-NPP was quite high, 2.3 times greater than that of TAC-NPP, clearly being the main reason for the promoted gelation.

Considering that TAIC is a typical allyl monomer, the high primary polymer chain length is noteworthy. This has been discussed as follows.[27] In allyl polymerization, the degradative monomer chain transfer is characteristic;[28] the hydrogen atoms attached to the carbon atom alpha to the double bond (that is, allylic hydrogens) are responsible for this monomer chain transfer that would be essentially a termination reaction. Thus, the reciprocal of the monomer chain transfer constant, $C_m$ ($= k_{tr,m}/k_p$, that is, the ratio of the rate constant of monomer chain transfer to that of propagation of the growing polymer radical), would be approximately equal to the degree of polymerization. Notably, the $k_p$ values are not expected to be different for TAIC and TAC polymerizations because the reactivity ratios of both monomers toward styrene (St), methyl methacrylate, and vinyl acetate are essentially equivalent.[26] Therefore, the $k_{tr,m}$ value for TAIC should be smaller than that for TAC. This reduction in monomer chain transfer may result from steric hindrance, considering the structural formulas of TAIC and TAC (see Figure 2). The isourea oxygen atom intervenes between the allyl group and the cyanuric ring in TAC, while in TAIC, the allyl group is directly connected to the isocyanuric ring. The latter situation in TAIC involves more steric crowding for both the growing polymer radical and the allylic hydrogens responsible for monomer chain transfer as compared with TAC. Moreover, this effect may be enhanced by the polar adjacent carbonyl groups. Thus, an interaction between the growing polymer radical and allylic hydrogens in the transition state formation is sterically hindered as a reflection of the following fact: allylic hydrogens are located at the $\beta$-site from the isocyanuric ring, whereas the propagation reaction occurs through attack of the growing polymer radical at the $\gamma$-site vinyl methylene carbon. This results in the reduced transfer to monomer.

The steric effect that is characteristic of TAIC polymerization was discussed further from different viewpoints. First, polymerizations of several diallyl alkyl isocyanurates were investigated by changing alkyl groups from methyl to lauryl.[29] Second, TAIC was copolymerized with allyl benzoate (ABz) in which steric hindrance is reduced with an increase in the proportion of ABz in the feed.[27] Third, telomerization was evaluated in the presence of $CBr_4$. The difference between TAIC and TAC polymerizations was significantly reduced as monomer chain transfer was replaced by chain transfer to $CBr_4$.[27] Fourth, the polymerization and copolymerization of corresponding trimethallyl monomers were carried out.[30] Notably, trimethallyl isocyanurate has additional allylic hydrogens as an $\alpha$-methyl group, in which no steric hindrance may occur in the transition-state formation of monomer chain transfer reaction by the abstraction of allylic hydrogens of the $\alpha$-methyl group, which are located at the $\delta$-site from the isocyanuric ring. On the other hand, the propagation reaction may, inversely, be sterically more hindered as a result of more steric crowding for the growing polymer radical having an $\alpha$-methyl group. Fifth, the high cyclopolymerizability of TAIC could be related to the steric effect on transition-state formation in the reaction at the sterically crowded, terminal reaction site of growing polymer radical caused by the sequential, bulky TAIC units (see Figure 1), that is, the nonterminal units effect on the cyclopolymerization of TAIC.[31]

**Is Microgel Formed through Intramolecular Cross-Linking?** We have been concerned with the elucidation of the cross-linking reaction mechanism and the control of network formation in free-radical cross-linking polymerization and copolymerization of multivinyl monomers, especially including multiallyl monomers, in order to molecularly design three-dimensional vinyl-type network polymers.[13] Thus, in the bulk polymerization of DAP, the actual gel point was found to be 6.9 times higher than the theoretical one. In common multivinyl polymerization systems, the discrepancy was more than 10 times and sometimes more than $10^2$. Moreover, the deviation became greater with increasing primary polymer chain length, content of pendant double bonds in the prepolymer, and dilution. In order to reasonably interpret the greatly delayed gelation, intramolecular cyclization, reduced reactivity of the prepolymer, intramolecular cross-linking, and microgelation have been studied in detail. Finally, we reached the following conclusions: the primary factor is the thermodynamic excluded volume effect on the intermolecular cross-linking reaction between growing polymer radical and NPP, especially at high molecular weight. Beyond the theoretical gel point, a secondary factor is the intramolecular cross-linking, which becomes progressively important with conversion. The latter leads to the restriction of segmental motion of NPP and, moreover, imposes steric hindrance, that is, a shielding effect[32] or steric excluded-volume effect, inducing reduced reactivity of NPP as a tertiary factor.

As a further illustration of this tertiary factor leading to reduced reactivity of pendant double bonds in NPP, intramolecular cross-linking tends to occur locally because formation of the cross-link unit induces a decrease in the interaction between polymer segment and solvent or an increase in the interaction between polymer chains leading to an enhanced occurrence of intramolecular cross-linking. Thus, the locally enhanced occurrence of intramolecular cross-linking accompanied by microsyneresis could lead to formation of a microgel[10,33,34] having a highly cross-linked microdomain, which may induce microphase inversion. Here, the microgel is conceived of as consisting of both core and shell parts of high and low cross-link densities, respectively, although it is soluble due to a strong interaction of the shell part with solvent. This overcomes the presence of the core part, just like a microsolid, having quite a weak interaction with the solvent. That is, different kinds of microgels will be present depending on the combination of various types of core and shell parts; the microgels vary from branched-polymer-like to rigid-sphere-like ones. However, a more detailed understanding of microgels is definitely required, not only for the elucidation of the three-dimensional network formation mechanism but also for molecular design of vinyl-type network polymers with high performance and high functionality.

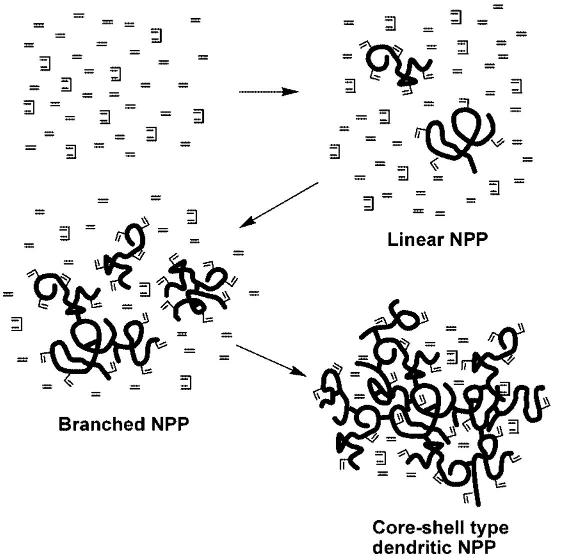

**Figure 3.** Rough sketch of network formation processes in the free-radical cross-linking monoallyl/diallyl copolymerization.

Although the striking feature of diallyl polymerization was the fact that no microgelation was observed until gel-point conversion was reached, as described above, this was completely the opposite of numerous reports about microgel formation that were published on the homopolymerization of common multivinyl monomers and their copolymerization with common monovinyl monomers.[4−8] In this connection, the most significant difference between allyl and common vinyl polymerizations is in the length of the primary polymer chain that has a predominant influence on gelation. In diallyl polymerization, only the oligomeric primary polymer chain is formed, since the occurrence of a monomer chain transfer is quite remarkable.[28] Therefore, the oligomerization of neopentyl glycol dimethacrylate was conducted in the presence of a chain transfer agent in order to reduce the primary polymer chain length to a comparable order in diallyl polymerization.[35] The gelation behavior was compared in detail with the polymerization of DAT as a typical diallyl monomer. No substantial difference was observed between allyl and common vinyl polymerizations in the cases where the primary polymer chain lengths were adjusted to be comparable.

Thus, network formation through multiallyl polymerization or common multivinyl oligomerization appears to be quite different from common multivinyl polymerization in the absence of a chain transfer agent. As is depicted in Figure 3, only oligomeric linear NPP is formed to generate the core of network polymer at an early stage of free-radical cross-linking monoallyl/

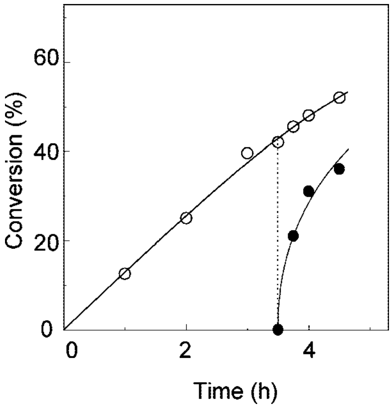

**Figure 4.** Conversion vs time curve for the solution polymerization of TAIC in MBz at a dilution of 1/5 with 0.1 mol/L DMAIB at 60 °C: (○) total and (●) gel polymers.

diallyl copolymerization. This is completely different from the case of common monovinyl/divinyl copolymerization, where high-molecular-weight swollen polymer particle is presumed to be formed.[3,36,37] Here it should be noted that no gel effect[38] was observed in multiallyl polymerization or common multivinyl oligomerization. The key reaction responsible for the gel effect is an intramolecular cross-linking that leads to the complication of NPP structure, generating complicated growing polymer radicals. This kind of complication of NPP structure would influence sterically the intermolecular cross-linkability of pendant vinyl groups, although the steric effect is more remarkable for the vinyl groups located at the inner part of the branched NPP molecule. Such complexity of NPP structure induced by intramolecular cross-linking leads not only to reduced occurrence of intermolecular cross-linking but also to almost no occurrence or inhibition of the bimolecular termination between sterically crowded growing polymer radicals.[39,40] Inevitably, the inhibited termination generates a living-type radical. The specific reaction behavior of this living-type radical must play an important role in microgelation. Thus, the locally extensive occurrence of intramolecular cross-linking is inevitable for the inhomogeneous network or microgel-like structure formation of cross-linked polymer or cured resin.

Although it has been thought until now that the inhomogeneity of network structure is closely related to the brittleness of cured resin, the case of TAIC resins does not fall in this category. As is discussed above in detail, TAIC resin is extremely brittle. However, TAIC is a typical multiallyl monomer, and so its polymerization never generates living-type radical that leads to high-molecular-weight swollen polymer particle formation. Moreover, the complete loss of flexibility of the polymer chain would not satisfy the prerequisite of the locally enhanced occurrence of intramolecular cross-linking reaction leading to microgelation. Thus, we need to find an alternative explanation for the brittleness of TAIC resins. The correlation between brittleness and network structure of TAIC resins will be discussed below, especially focusing on the characterization of resulting TAIC-NPPs by SEC−MALLS−viscometry.

**Solution Polymerization of TAIC.** Our previous paper[24] was concerned with a detailed discussion of the specific gelation behavior of bulk polymerization of TAIC. In order to discuss in more detail the intramolecular cross-linking leading to microgelation, the solution polymerizations of TAIC were conducted in MBz at dilutions of 1/5 and 1/10 [monomer:solvent (v/v) = 1:4 and 1:9, respectively] with 0.1 mol/L DMAIB at 60 °C. Figure 4 shows the conversion versus time curve at a dilution of 1/5, and the percentage of gel polymer is also plotted. The time at which gel starts to form was determined by extrapolating the gel formation curve to 0%. The conversion at which gel starts to form (the gel point) was estimated to be 42.0%. It is noteworthy that no gel effect was observed, even beyond the gel point.

Prior to a detailed discussion about gelation, we should refer to the structure of the primary polymer chain. The TAIC units incorporated into the primary polymer chain show three different types of structures: uncyclized, monocyclic, and bicyclic. However, the formation of a bicyclic ring was not observed experimentally,[31] as it would also be expected from the inspection of a molecular model. Every uncyclized or monocyclic TAIC unit in the primary polymer chain has two or one pendant, unreacted allyl group, respectively, acting as a cross-link unit responsible for intermolecular cross-linking reaction. Thus TAIC would, in practice, behave similarly to a divinyl monomer where cyclization is ruled out.

Thus, the theoretical gel point was tentatively calculated according to Gordon's equation[41] derived for the polymerization of a divinyl monomer:

$$(1 - b_c) = 1 - \{[r(2P_{w,0} - 3) - 1]/[r(2P_{w,0} - 3) + 1]\}^2$$

where $(1 - b_c)$ is the conversion of the monomer at the gel point, $r$ is the fraction of monomer units having pendant double bonds in the polymer, and $P_{w,0}$ is the weight-average number of divinyl monomer units per primary polymer chain.

Now, we need to estimate both $r$ and $P_{w,0}$ values. The $r$ value was assumed to be unity, since every TAIC unit in the primary polymer chain can be useful for producing one cross-link between primary polymer chains as mentioned above. Then the primary polymer chain length $P_{w,0}$ was estimated by extrapolating the conversion dependence of $M_w$ of TAIC-NPP determined by LS to zero conversion. Thus, the results obtained are summarized as follows: for 1/5 dilution, $P_{w,0} = 80$ and gel point = 42.0%; for 1/10 dilution, $P_{w,0} = 48$ and gel point = 62.0%. Then the ratios of the actual gel point to the theoretical one were calculated as 16.7 and 14.7, respectively. Considering the high $P_{w,0}$ value of 280 for the bulk polymerization, the primary chain length clearly became shorter with a decrease in the monomer concentration. This could be ascribed to reduced steric hindrance between the growing polymer radical and allylic hydrogens in the transition-state formation of monomer chain transfer reaction by introducing monocyclic units into primary polymer chain via enhanced intramolecular cyclization at a lower monomer concentration.

Here, the actual gel point was considerably delayed from that predicted by theory as compared with those of the polymerizations of diallyl aromatic dicarboxylates such as DAP, diallyl isophthalate, and DAT.[42] This would be a result of a reduced occurrence of intermolecular cross-linking between sterically crowded growing polymer radical and unreacted pendant double bond of dendritic TAIC-NPP consisting of rigid primary polymer chains, although the dendritic structure formation will be discussed below. Notably, the deviation of the actual gel point from the theoretical one was almost constant regardless of the dilution as it was calculated to be 17.3 in the bulk polymerization.[24] This may also related to the complete loss of flexibility of primary polymer chain of TAIC-NPP, which does not satisfy the prerequisite of locally enhanced occurrence of intramolecular cross-linking reaction leading to microgelation. Almost no occurrence of intramolecular cross-linking in TAIC polymerization will provide a characteristic structure of TAIC-NPP regardless of the monomer concentration.

**Characterization of TAIC-NPPs by SEC−MALLS−Viscometry.** As depicted in Figure 3, the structure of highly branched TAIC-NPP is presumed to be core−shell-type dendritic, with almost no occurrence of intramolecular cross-linking reaction leading to the formation of loop structures. In our

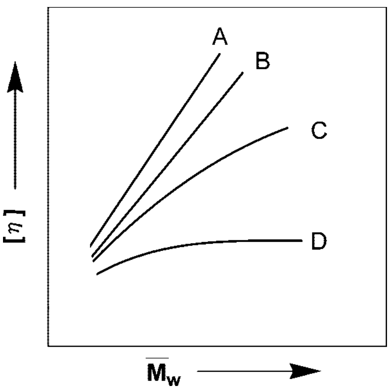

**Figure 5.** Schematically illustrated correlations of $[\eta]$ vs $M_w$ for different types of polymers, including (A) linear polymer, (B) ideal NPP or branched polymer, (C) branched polymer with loop structures formed through intramolecular cross-linking, and (D) dendritic NPP.

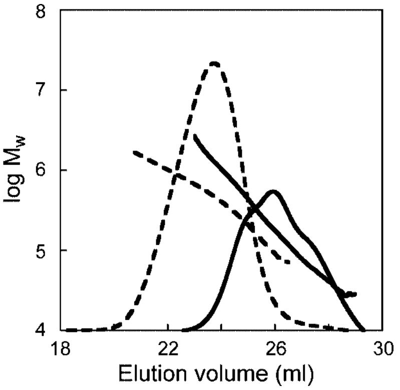

**Figure 6.** RI-monitored SEC curve and correlation of $M_w$ vs elution volume for (—) TAIC-NPP, obtained at 4.8% conversion in the bulk polymerization of TAIC with 0.05 mol/L DMAIB at 60 °C, and for (---) linear poly(St).

previous paper[43] concerned with the characterization of ideal NPPs, we have schematically illustrated the effect of intermolecular cross-linking followed by intramolecular cross-linking on the molecular size shrinkage as the correlations of $\langle S^2\rangle_z^{1/2}$ versus $M_w$. This illustration was extended to Figure 5 that roughly depicts the correlation of $[\eta]$ versus $M_w$ for different types of polymers, including (A) linear polymer, (B) ideal NPP or branched polymer, (C) branched polymer with loop structures formed through intramolecular cross-linking,[44] and (D) dendritic NPP. Thus, the intrinsic viscosity is expected to be quite low when the TAIC-NPP structure is core–shell-type dendritic.

The resulting TAIC-NPPs were characterized by SEC–MALLS–viscometry as follows. Figure 6 shows the RI-monitored SEC curve and the correlation of $M_w$ versus elution volume of TAIC-NPP obtained at 4.8% conversion in the bulk polymerization of TAIC with 0.05 mol/L DMAIB at 60 °C, along with a dotted line showing linear poly(St) by way of comparison. The SEC curve of TAIC-NPP was broadened toward the higher-molecular-weight side as a reflection of intermolecular cross-linking. The correlation curve of $M_w$ versus elution volume was cited above for TAIC-NPP. Figure 7 shows the correlations of $[\eta]$ versus elution volume. The correlation line for TAIC-NPP shifted drastically downward compared with that for poly(St). This result strongly supports the idea that the structure of TAIC-NPP is dendritic, as it is well-known that the most striking feature of dendritic polymers is a low viscosity.[45] Then the correlation of $[\eta]$ versus $M_w$ was plotted in Figure 8. The correlation line for TAIC-NPP obtained at 4.8% conversion appears at much lower sites compared with the plot for a linear poly(St) as a reflection of its dendritic structure. Similarly, the $[\eta]$ values of the resulting TAIC-NPPs obtained at dilutions of 1/5 and 1/10 were examined; the correlation lines were a bit lower with dilution but they were essentially identical, regardless of the dilution in the polymerization of TAIC. This reflects the almost total lack of intramolecular cross-linking, leading to a loop structure formation that induces a decrease of viscosity.

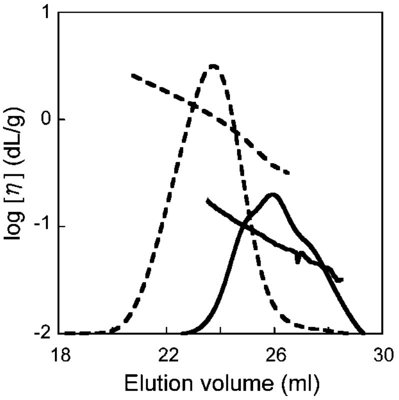

**Figure 7.** RI-monitored SEC curve and correlation of $[\eta]$ vs elution volume (see Figure 6).

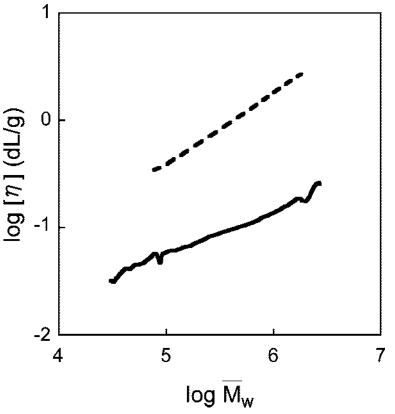

**Figure 8.** Double logarithmic plot of $[\eta]$ vs $M_w$ (see Figure 6).

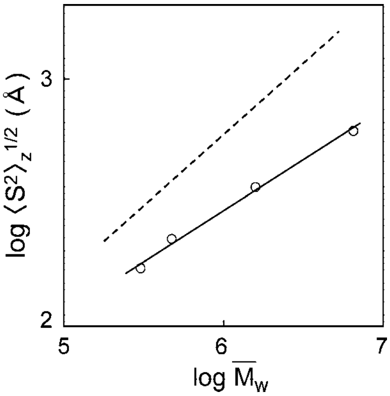

**Figure 9.** Double logarithmic plot of $\langle S^2\rangle_z^{1/2}$ vs $M_w$ for (—) TAIC-NPPS obtained in bulk (see Figure 6) and for (---) linear poly(St).

The core–shell-type dendritic NPP formation was confirmed by light scattering measurement, providing $\langle S^2\rangle_z^{1/2}$ and $A_2$. Since dendritic NPPs are highly shrunken molecules having a much lower interaction with the solvent as compared with a linear polymer of the same molecular weight, the molecular size shrinkage and lowered interaction force would be reflected as the lowering of $\langle S^2\rangle_z^{1/2}$ and $A_2$, respectively. Figure 9 shows a double logarithmic plot of $\langle S^2\rangle_z^{1/2}$ versus $M_w$ for TAIC-NPPs

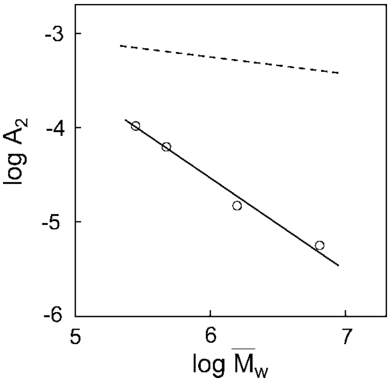

**Figure 10.** Double logarithmic plot of $A_2$ vs $M_w$ (see Figure 9).

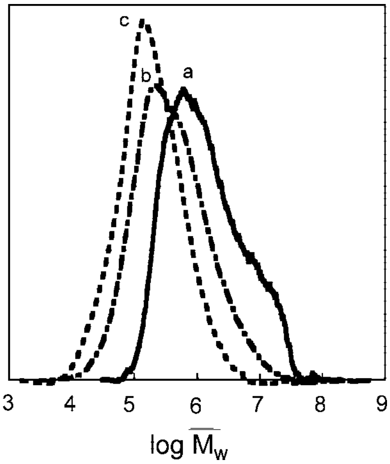

**Figure 11.** Variation of MWD curves of sols with conversion: (a) 12.9%, (b) 14.0%, and (c) 15.7% conversion (see Figure 6).

obtained in bulk (see Figure 6). The radius of gyration was almost constant regardless of the dilution in the polymerization of TAIC. The dendritic NPP formation was also reflected as a lower $A_2$ as shown in Figure 10. The low $A_2$ value, less than $10^{-5}$ mol cm$^3$ g$^{-2}$, may support core—shell-type dendritic NPP formation.[35,45−49]

**Growth of Network Structure with the Progress of Polymerization beyond the Gel Point.** As described above, no microgelation was observed until the gel-point conversion even in the solution polymerization of TAIC. Therefore, we pursued the process of growth of the resulting cross-linked polymer with the progress of polymerization beyond the gel-point conversion because quasi-microgelation proceeded rapidly beyond the gel point in the bulk polymerization of DAP.[15] Figure 11 shows the variation of molecular-weight distribution (MWD) curves of sols with conversion in the bulk polymerization of TAIC with 0.05 mol/L DMAIB at 60 °C, although the gel point was 12.4%. With the progress of polymerization beyond the gel point, the MWD curve of sol shifted toward a lower molecular weight and its shape became sharper. This result suggests that the higher molecular weight fraction was rapidly incorporated into the gel. On the contrary, the incorporation of sol into gel was quite gradual in the bulk polymerization of DAT (see Figure 12), although the gel point was 24.0%. When quasi-microgelation proceeds rapidly beyond the gel point, as is the case in the bulk polymerization of DAP,[15] the unreacted monomer mainly polymerizes in microspaces among quasi-microgels because the segmental density of the interface among quasi-microgels is low and unreacted monomer molecules can move freely without restriction from the swollen cross-linked polymer. The idea that no quasi-microgelation occurred in the bulk polymerization of TAIC was also supported by the variation of swelling ratios of resulting gels with conversion, as shown in Figure 13. The quasi-microgelation in the polymerization of DAT was reflected in a drastic decrease of the swelling ratio as compared with TAIC polymerization.

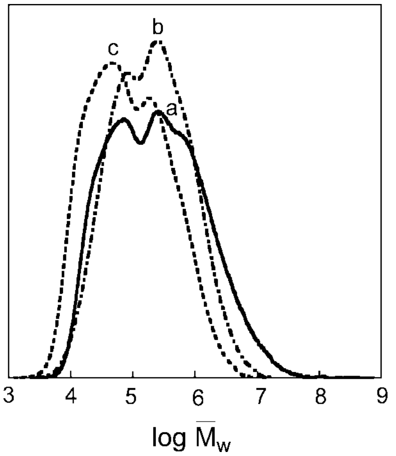

**Figure 12.** Variation of MWD curves of sols with conversion for the bulk polymerization of DAT with 0.05 mol/L DMAIB at 60 °C: (a) 26.2%, (b) 28.9%, and (c) 37.5% conversion.

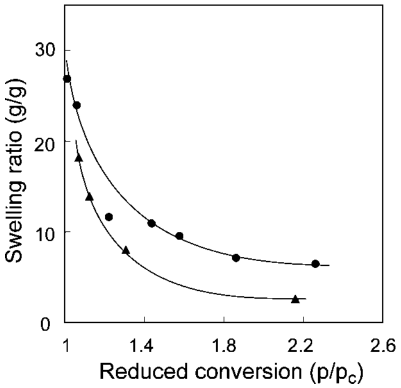

**Figure 13.** Decrease in swelling ratios of resultant gels with the progress of polymerization beyond the gel point in the bulk polymerizations of (●) TAIC (see Figure 6) and (▲) DAT (see Figure 12). The abscissa corresponds to reduced conversion ($p/p_c$), in which $p$ and $p_c$ correspond to conversion and gel point, respectively.

**Origin of Brittleness.** As is evident from the above discussion, the network structure of TAIC resin should be quite homogeneous or never inhomogeneous microgel-like, although TAIC resin was too brittle for practical use. The ordinary explanation that the brittleness of cured resin is caused by the inhomogeneity of network structure does not work for TAIC resin. An alternative explanation for the brittleness of TAIC resins is that the growth of network structure of TAIC resin is insufficient for obtaining appropriate mechanical properties, because the occurrence of intermolecular and intramolecular cross-linking reactions between sterically crowded growing polymer radical and pendant allyl groups belonging to a rigid primary polymer chain would be sterically hindered in the polymerization of TAIC. This imperfection of cross-linking, providing not only insufficient network structure formation but also incorporation of abundant dangling chains into network polymer, could be one of the principal causes of brittleness of cross-linked resins.

Finally, we point out another important aspect of the characteristics of allyl polymerization: In the radical polymerization of allyl monomers, the research objectives will be oligomers or medium-molecular-weight molecules, which are essentially intermediate between low- and high-molecular-weight molecules. Accordingly, allyl polymerization would provide useful information for finding out the inherent phenomena of polymers, not being of real low-molecular-weight molecules, by pursuing the molecular weight dependences of various properties of resulting medium-molecular-weight molecules.[14] In this connection, multiallyl cross-linking polymerization may be presumed to be in between step- and chain-growth cross-linking polymerizations; usually, the primary polymer chain lengths of the NPPs obtained by multiallyl cross-linking polymerization are one-hundredth or less compared with those by common multivinyl cross-linking polymerization. This means that multiallyl cross-linking polymerization not only could be the origin of multivinyl chainwise cross-linking polymerization but also could be close to stepwise cross-linking systems including phenolic resins, amino resins, epoxy resins, alkyd resins, urethane resins, and so on. The extended discussion to common cross-liked resins is in progress for the generalization of our new interpretation of brittleness of cross-linked resins originating in the specific polymerization behavior of TAIC.

## Conclusion

Nonfilled TAIC cured resin obtained directly by polymerization of TAIC monomer was too brittle for practical use. This is also the case with commercially important DAP resins and is due to the inhomogeneity of the cross-linked resins, as evidenced by electron microscopy. As the inhomogenization of the resulting cross-linked polymer to form colloidal particles (quasi-microgelation) proceeded rapidly beyond the gel point, several procedures to improve the brittleness of DAP resins were developed. These procedures, however, did not succeed in improving the toughness of TAIC resins. This clearly demonstrates the difference in the network structures of TAIC and DAP resins. Thus, the polymerization of TAIC would not always provide formation of colloidal particles but instead introduced a rather homogeneous network, since the primary polymer chain of TAIC resin would be much more rigid than with DAP, due to very bulky side chains. That is, the complete loss of flexibility of the polymer chain would not satisfy the prerequisite for the formation of quasi-microgels as colloidal particles in the cross-linking polymerization of TAIC.

The specific gelation behavior of TAIC was investigated in detail in solution polymerization, where intramolecular cross-linking should be enhanced. The correlation between brittleness and network structure of TAIC resins was then further discussed, especially focusing on the characterization of resulting TAIC-NPPs by SEC−MALLS−viscometry. The structure of branched TAIC-NPP is dendritic. This finding was supported by correlations of both $[\eta]$ versus $M_w$ and $\langle S^2 \rangle_z^{1/2}$ versus $M_w$ for TAIC-NPPs. Finally, we pursued the growth process of the resulting cross-linked polymer with the progress of polymerization beyond the gel-point conversion because quasi-microgelation proceeded rapidly beyond the gel point in the bulk polymerization of DAP. The idea that there was no quasi-microgelation in the bulk polymerization of TAIC was also supported by the variation of swelling ratios of resulting gels with conversion.

As will be evident from the above discussion, the network structure of TAIC resin is rather homogeneous or never inhomogeneous microgel-like. The ordinary explanation that the brittleness of cured resin is caused by the inhomogeneity of network structure does not appear to be the true explanation for TAIC resin's extreme brittleness. So, we proposed an alternative explanation for its brittleness: that the growth of network structure of TAIC resin is insufficient because the occurrence of intermolecular and intramolecular cross-linking reactions between sterically crowded growing polymer radical and pendant allyl groups belonging to the rigid primary polymer chain would be sterically hindered in the polymerization of TAIC.

**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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MA800974S