

Further Discussion of Correlation between Brittleness and Network Structure of Triallyl Isocyanurate Resins

Akira MATSUMOTO*, Tomoya MATSUDA*, Chikaomi HIRAO*, Hiroyuki AOTA*,
Yoshihiro TAKAYAMA** and Hiroyuki TORIDOME**

(Received October 2, 2006)

Abstract

Attempts to improve the toughness of triallyl isocyanurate (TAIC) resins were unsuccessful using the procedures developed for diallyl phthalate (DAP) resins as typical allyl resins by considering microinhomogenization of the DAP resin during polymerization beyond the gel-point conversion. This demonstrates the difference in network structure of TAIC and DAP resins. The structure of branched TAIC prepolymer was characterized as dendritic by SEC-MALLS-viscometry. Thus, an alternative explanation for the brittleness of TAIC resins is provided: the insufficient growth of the network structure of TAIC resin because of steric hindrance on the crosslinking reaction between sterically crowded growing polymer radical and pendant allyl groups belonging to the rigid primary polymer chain.

1. Introduction

Triallyl isocyanurate (TAIC) is commercially important both as a crosslinking agent with comonomers and for the post-curing of preformed polymers, such as olefin copolymers, in electrical insulations^{1, 2)}. In addition, it has found another application as a crosslinking agent for unsaturated polyester resins. However, in the direct preparation of non-filled TAIC cured resin from TAIC monomer, the resulting material was too brittle for practical use. This is also the case with the commercially important diallyl phthalate (DAP) resins³⁾ and may be due to the rigidity of structural units, particularly crosslinked units, as well as to the inhomogeneity of the cured resins. Although Erath and Robinson⁴⁾, using electron microscopy, observed the DAP cured resin directly as the agglomerate of colloidal particles, our detailed investigation⁵⁾ to clarify the process of growth of the resulting crosslinked polymer with the progress of polymerization beyond the gel-point conversion clearly demonstrated that no microgelation occurred up to the gel point in the bulk polymerization of DAP. Thus, the formation of colloidal particles observed by electron microscopy⁴⁾ should be induced during the polymerization process beyond the gel point. The inhomogenization of the resulting crosslinked polymer, i.e., 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. In other words, the occurrence of intramolecular crosslinking

*Department of Applied Chemistry

**Nippon Kasei Chemical Co., Ltd.

inside the highly swollen crosslinked polymer produced just beyond the gel point would be enhanced with the progress of gelation. Moreover, intramolecular crosslinking may tend to occur locally. Thus, the segmental density of the interface among quasi-microgels would be low and unreacted monomer molecules can move freely without restriction from the swollen crosslinked polymer.

Therefore, the previous investigation⁵⁾ of the microinhomogenization of the crosslinked polymer during polymerization beyond the gel point in the bulk polymerization of DAP was extended to the microinhomogeneous copolymerization of DAP with comonomers accompanied by the formation of quasi-microgel and, moreover, macrogel with the intention of improving the mechanical properties of DAP resins^{6, 7)}. First, three kinds of glycol bis(allyl phthalate)s were crosslinked with DAP, and the resulting crosslinked products were evaluated for the elucidation of correlations between mechanical properties and crosslinkers⁶⁾. That is, DAP resins with improved flexibility were successfully obtained by introducing flexible crosslinked units on the surface of the quasi-microgel. DAP was co-cured in bulk with vinyl monomers having long-chain alkyl groups, including lauryl methacrylate (LMA)⁷⁾. Thus, for the DAP/LMA copolymerization process leading to colloidal particle formation, the prepolymers of high LMA content initially obtained cannot be compatible with DAP-enriched polymer chains which increase rapidly with the progress of polymerization. Therefore, they may exist predominantly in the spaces between colloidal particles and act as flexible crosslinkers of colloidal particles to form the resins.

On the basis of the above procedures, with which the flexibility of DAP resins had been successfully improved, we attempted to improve the mechanical properties of TAIC resins, especially its toughness.

Firstly, TAIC was co-cured with LMA. Although the addition of 20 mol% of LMA to DAP resin clearly improved the flexibility of the resulting resin⁷⁾, the addition effect of LMA on the modification of TAIC resin was unsatisfactory; only a very brittle resin was obtained.

Secondly, the modification procedure that had been successful for DAP resins⁸⁾ and which was based on the idea of interpenetrating polymer network (IPN) formation⁹⁾ was applied. Thus, the curing processes in various monomethacrylate/dimethacrylate/DAP systems were examined⁸⁾, in which monomethacrylate/dimethacrylate copolymer network is formed as a first network during the early stage of polymerization. Thereafter, the polymerization of DAP proceeds, in the presence of the first network, to form IPN. As a result, enhancement of strength was induced by the first network of moderate crosslink density. DAP was then replaced by TAIC, keeping the same curing conditions that had been useful for the improvement of DAP resin. This resulted in an unsuccessful addition effect of TAIC on the modification of DAP resin, clearly indicating a decrease in tensile strength with an increase in the mole fraction of TAIC.

Thirdly, TAIC was co-cured with allyl benzoate (ABz), since the rigid TAIC polymer chain¹⁰⁾ would become more flexible with incorporation of ABz units into the polymer chain and the crosslink density would decrease. Unfortunately, however, only brittle materials were obtained.

Finally, the effect of primary polymer chain length on the mechanical properties was examined, since the primary polymer chain length of TAIC resin is relatively large^{10, 11)} for an allyl monomer. Thus, TAIC was co-cured with trimethylallyl isocyanurate to reduce the

primary polymer chain length¹²⁾, since microgelation would be enhanced with an increase in the primary polymer chain length¹³⁾. Nevertheless, once again, no improvement of toughness of the TAIC resins resulted.

The above-mentioned unsuccessful results for the 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 the agglomerate of colloidal particles^{4, 5)}, the polymerization of TAIC may not always provide the formation of colloidal particles. Instead, polymerization introduces a 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 Fig. 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 crosslinking polymerization of TAIC. This is because the locally-enhanced occurrence of intramolecular crosslinking reaction would be required for microgelation¹⁴⁾.

Thus, the present article is concerned with further discussion of the correlation between brittleness and network structure in TAIC resins, especially focusing on the characterization of resultant crosslinked polymer precursors or TAIC prepolymers using size-exclusion chromatography (SEC) with both multiangle laser light scattering (MALLS) and viscosity detectors, providing the correlation of intrinsic viscosity versus molecular weight of fractionated samples. In addition, the polymerization process beyond the gel-point conversion was pursued, in terms of the elucidation of the crosslinking mechanism.

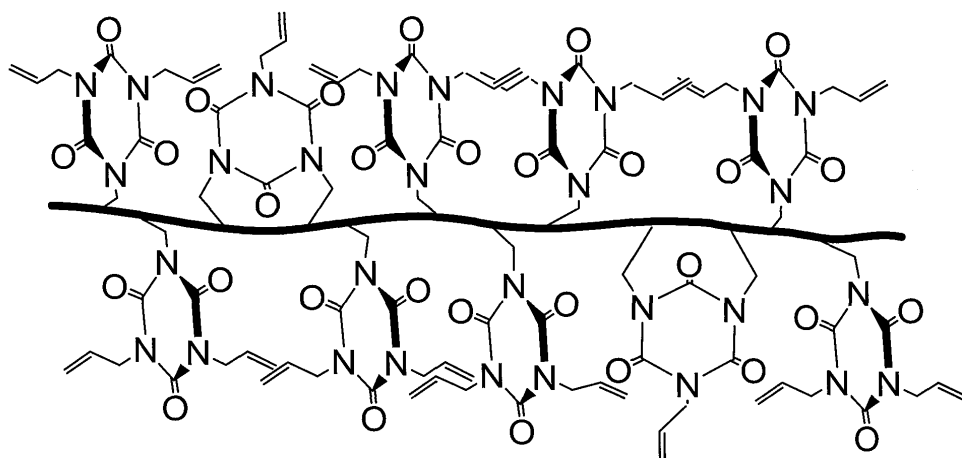


Fig. 1 Rigid poly(TAIC) chain with bulky side chains.

2. Experimental

TAIC, supplied by Nippon Kasei Chemical Co., Ltd., and diallyl terephthalate (DAT), supplied by Daiso Co., Ltd., as monomers, and methyl benzoate (MBz) as a solvent, were purified by vacuum distillation under nitrogen. As initiators 2,2'-azobisisobutyronitrile (AIBN) and dimethyl 2,2'-azobisisobutyrate (DMAIB) were purified by recrystallization from methanol.

Polymerization was carried out in a glass ampule containing suitable amounts of monomers, AIBN or DMAIB, and MBz. The ampule was degassed 3 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°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 extracting the sol fraction with THF.

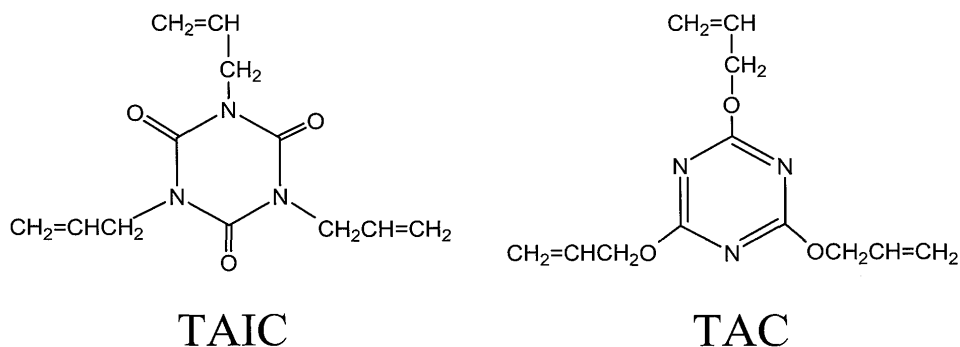
The weight-average molecular weights (M_w) and the r.m.s. radii of gyration ($\langle S^2 \rangle_z^{1/2}$) of the resulting polymers were measured by light scattering (LS). The LS measurements were carried out in THF at 30°C with an Otsuka Electronics DLS-7000 dynamic light scattering spectrophotometer over the angular range between 30° and 150°, using unpolarized light of a wavelength of 632.8 nm. 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 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 SEC-MALLS-viscosity 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- μ L flow cell. A Wyatt ViscoStar (Wyatt Technology Corp.) was employed as the viscometer.

3. Results and Discussion

3.1 Steric effect on the polymerization of TAIC

In our continuing studies of the radical polymerization of multiallyl monomers^{15,16}, the polymerization behavior of TAIC and its isomer triallyl cyanurate (TAC) was explored in detail¹¹, since only a few basic studies of the polymerization of both monomers have been published^{17, 18}. Gelation occurred at quite a low conversion in the polymerization of TAIC as compared to that of TAC. The cyclopolymerizability of TAIC was greater than that of TAC; the unreacted pendant double bonds responsible for crosslinking of poly(TAIC) were less abundant than those of poly(TAC) 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 gelation¹⁹, was precisely estimated. The primary polymer chain length of poly(TAIC) was formed to be quite high, 2.3 times greater than that of poly(TAC), clearly 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 elsewhere¹⁰. In allyl polymerization, the monomer chain transfer constant, $C_m (= k_{tr,m}/k_p)$, (i.e., the ratio of the rate constant of monomer chain transfer to that of propagation of the growing polymer radical) will determine the degree of polymerization²⁰. The k_p values are not expected to be different for TAIC and TAC because the reactivity ratios of both monomers toward styrene, methyl methacrylate and vinyl acetate are essentially equivalent¹⁸, while $k_{tr,m}$ for TAIC should be smaller than that for TAC. This reduction in monomer chain transfer may result from steric hindrance, as indicated in the following structural formulae of TAIC and TAC:



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 β -site from the isocyanuric ring, whereas the propagation reaction occurs through attack of the growing polymer radical at the γ -site vinyl methylene carbon. This results in the reduced transfer to monomer.

The steric effect on the polymerization of TAIC was discussed in detail from different viewpoints. Firstly, polymerizations of several diallyl alkyl isocyanurates were investigated by changing alkyl groups from methyl to lauryl²¹. Secondly, TAIC was copolymerized with allyl benzoate (ABz) in which steric hindrance is reduced with increase in the proportion of ABz in the feed¹⁰. Thirdly, 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 ¹⁰. Fourthly, the polymerization and copolymerization of corresponding trimethallyl monomers were carried out¹². Notably, trimethallyl isocyanurate has additional allylic hydrogens as α -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 α -methyl group which are located at the δ -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 α -methyl group. Fifthly, the high cyclopolymerizability of TAIC could be related to the steric effect on the transition state formation in the reaction at the sterically crowded, terminal reaction site of growing polymer radical caused by the sequential, bulky TAIC units, i.e., the non-terminal units effect on the cyclopolymerization of TAIC²². As is discussed above, the sequence length dependence of steric effect on the reactivity of the growing TAIC radical was suggested. Finally, we attempted to explore in more detail this novel sequence length dependence of steric effect on the reactivity of growing polymer radical in the copolymerization of TAIC, a bulky monomer, with sterically unhindered monomers²³.

3.2 Microgel formation through intramolecular crosslinking

We have been concerned with the elucidation of the crosslinking reaction mechanism and the control of network formation in free-radical crosslinking polymerization and copolymerization of multivinyl monomers, especially including multiallyl monomers, in order to molecularly design three-dimensional vinyl-type network polymers¹⁴). 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 crosslinking, 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 crosslinking reaction between growing polymer radical and prepolymer, especially at high molecular weight. Beyond the theoretical gel point, a secondary factor is the intramolecular crosslinking which becomes progressively important with conversion. The latter leads to the restriction of segmental motion of the prepolymer and, moreover, imposes steric hindrance, i.e., shielding effect [24] or steric excluded volume effect, inducing reduced reactivity of the prepolymer as a tertiary factor.

As a further illustration of this tertiary factor leading to reduced reactivity of pendant double bonds in the prepolymer, intramolecular crosslinking tends to occur locally because the formation of the crosslink 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 crosslinking. Thus, the locally-enhanced occurrence of intramolecular crosslinking accompanied by microsineresis could lead to the formation of a microgel^{13, 25-27}), having a highly crosslinked microdomain which may induce microphase inversion. Here, the microgel is conceived of as consisting of both core and shell parts of high and low crosslink 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. 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.

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 the numerous reports about microgel formation that were published on the homopolymerization of common multivinyl monomers and their copolymerization with common monovinyl monomers²⁸⁻³²). 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, for occurrence of a monomer chain transfer is quite remarkable²⁰). 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 polymerization³³. 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 cases where the primary polymer chain lengths were adjusted to be comparable.

Thus, the network formation through multiallyl polymerization or common multivinyl oligomerization apparently seems to be quite different from common multivinyl polymerization in the absence of a chain transfer agent. As is depicted in Fig. 2, only oligomeric linear or loop-structured prepolymer is formed to generate the core of network polymer at an early stage of polymerization. This is completely different from the case of common multivinyl polymerization, where high-molecular-weight swollen polymer particle is formed³⁴⁻³⁶. Here it should be noted that no gel effect³⁷ was observed in multiallyl polymerization or common multivinyl oligomerization. The key reaction responsible for the gel effect is an intramolecular crosslinking that leads to the complication of the prepolymer structure sterically influencing the intermolecular crosslinkability of pendant vinyl groups; the steric effect is more remarkable for the vinyl groups located at the inner part of branched prepolymer molecule. Such complexity of prepolymer structure induced by intramolecular crosslinking leads not only to reduced occurrence of intermolecular crosslinking, but also to almost no occurrence

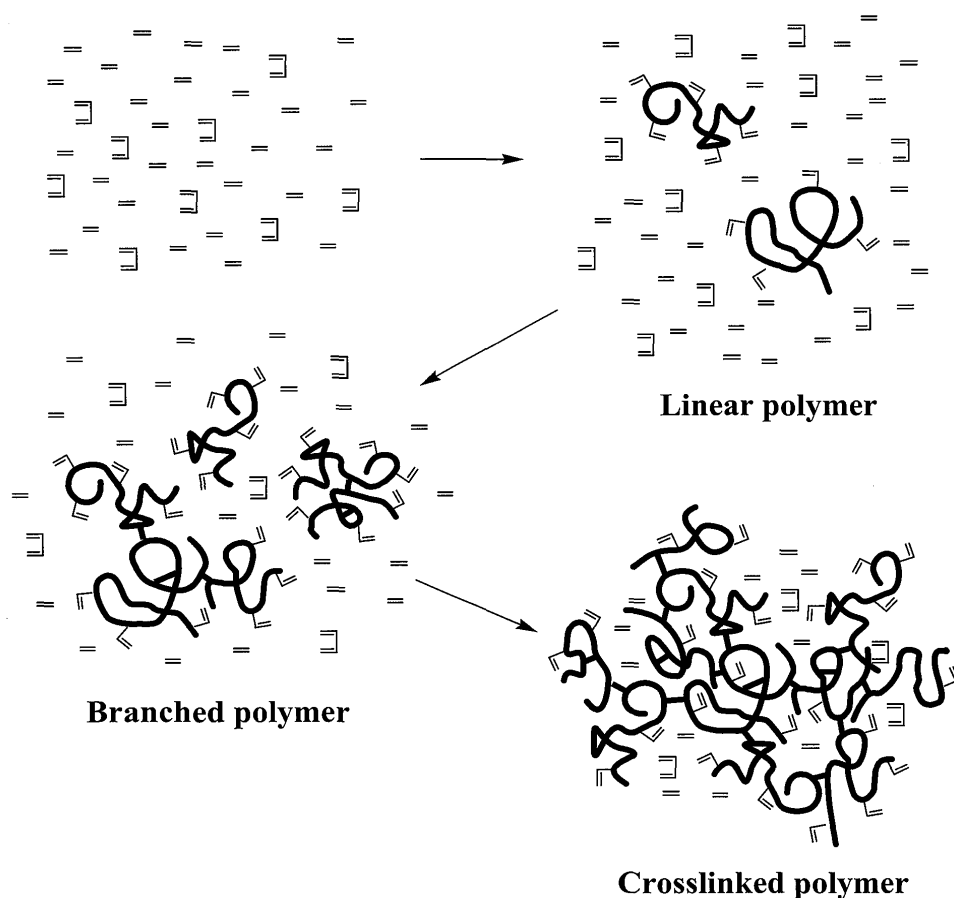


Fig. 2 A rough sketch of network formation processes in the free-radical crosslinking monoallyl/diallyl copolymerization.

or inhibition of the bimolecular termination between sterically crowded growing polymer radicals^{38, 39}. 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 crosslinking is inevitable for the inhomogeneous network structure formation of crosslinked 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, but it is a typical multiallyl monomer, never generating living-type radical, and the complete loss of flexibility of the polymer chain would not satisfy the prerequisite of the locally-enhanced occurrence of intramolecular crosslinking reaction leading to microgelation. Thus, we need to find an alternative explanation for the brittleness of TAIC resins. So, let us now discuss the correlation between brittleness and network structure of TAIC resins, especially focusing on the characterization of resulting crosslinked polymer precursors or TAIC prepolymers by SEC-MALLS-viscometry, providing a correlation of intrinsic viscosity versus molecular weight of fractionated samples.

3.3 Specific gelation behavior in the solution polymerization of TAIC

Our previous article¹¹⁾ is concerned with a detailed discussion of the specific gelation behavior of the bulk polymerization of TAIC. In order to discuss in more detail the intramolecular crosslinking leading to microgelation, the solution polymerizations of TAIC were conducted in MBz at a dilution of 1/4 and 1/9 (v/v) monomer to solvent using 0.1 mol/L of DMAIB at 60°C. Fig. 3 shows the conversion versus time curves at a dilution of 1/4, and the percentage of gel polymers is also plotted. The time at which gel starts to form was determined by extrapolating the gel formation curve to zero percentage. The conversion at

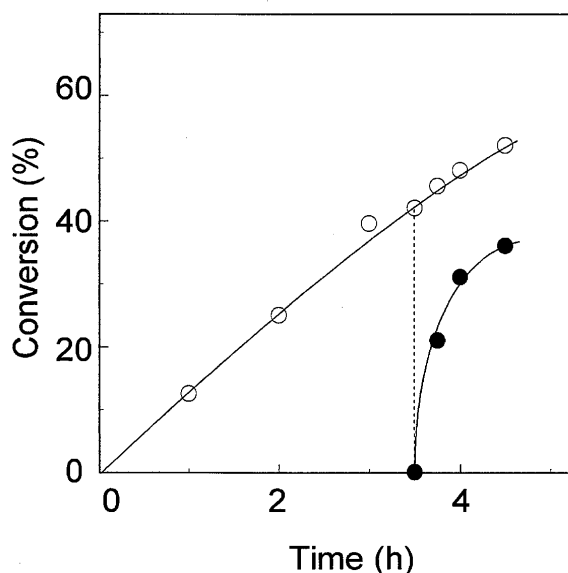


Fig. 3 Conversion versus time curve for the solution polymerization of TAIC in MBz at a dilution of monomer to solvent 1/4 (v/v) using 0.1 mol/L of DMAIB at 60°C. Open and filled symbols correspond to total and gel polymers, respectively.

which gel starts to form, i.e., the gel point, was estimated to be 42.0%. It is noteworthy that no gel effect³⁷⁾ 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 polymer chain show three basic types of structure: uncyclized, monocyclic and bicyclic structures. However, the formation of a bicyclic ring was not observed experimentally²²⁾ as it would also be expected from the inspection of a molecular model. Every TAIC unit in the primary polymer chain has more than one pendant, unreacted allyl group, which is useful for intermolecular crosslinking reaction. Thus TAIC would, in practice, behave like a noncyclopolymerizable divinyl monomer.

The theoretical gel point was then tentatively calculated according to Gordon's equation⁴⁰⁾ derived for the polymerization of a divinyl monomer:

$$(1 - b_c) = 1 - \frac{[r(2P_w - 3) - 1]}{[r(2P_w - 3) + 1]^2}$$

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 is the weight-average number of divinyl monomer units per primary polymer chain.

Now, we need to estimate both r and P_w values. The r value was assumed to be unity, because every TAIC unit in the primary polymer chain can be useful for producing one crosslink between primary polymer chains. Fig. 4 shows the conversion dependence of M_w of the prepolymer determined by LS. The primary polymer chain length P_w was then estimated by extrapolation of the curves to zero conversion. Table 1 summarizes the actual gel points as compared with theoretical ones for the solution polymerizations, along with the result of the bulk polymerization¹¹⁾. The actual gel point was considerably delayed from that predicted by theory for each polymerization system, and, interestingly, the deviation was almost constant regardless of the dilution, although in the polymerization of DAT as a comparison, the

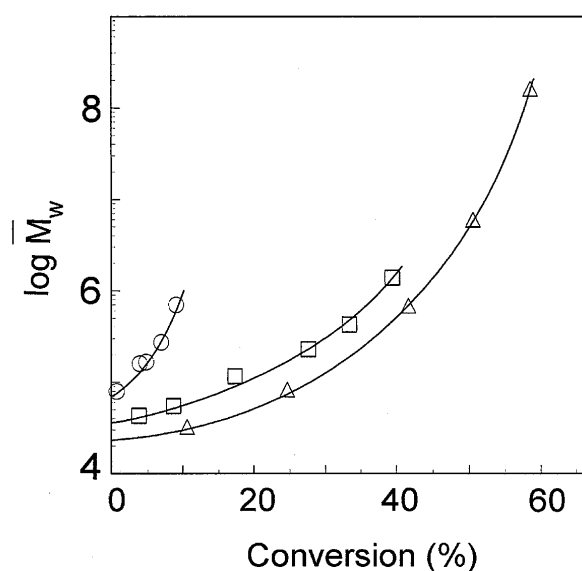


Fig. 4 Dependence of M_w on conversion for the (circles) bulk and (squares, triangles) solution polymerizations of TAIC at dilutions of monomer to solvent 1/4 and 1/9, respectively.

Table 1. Comparison of actual and theoretical gel points in the bulk and solution polymerizations of TAIC and DAT using 0.1 mol/L of DMAIB at 60°C

Monomer	Solvent	$\bar{P}_{w,0}$	Gel point (%)	Actual G.
				Theoretical G. P.
TAIC	None	280	12.4	17
	MeBz ^{a)}	80	42.0	17
	MeBz ^{b)}	48	62.0	15
DAT	None	50	24.0	5.4
	MeBz ^{a)}	32	58.4	7.0
	MeBz ^{b)}	23	> 65.3	> 7.3

a, b) [Monomer]/[Solvent] = (a) 1/4 and (b) 1/9 (v/v).

deviation of actual gel point from theoretical one became greater with dilution. These are in conformity with the complete loss of flexibility of poly(TAIC) chain, which does not satisfy the prerequisite of the locally-enhanced occurrence of intramolecular crosslinking reaction leading to microgelation. Thus, as was expected, no microgelation was observed until the gel-point conversion in the polymerization of TAIC.

3.4 Characterization of TAIC prepolymers by SEC-MALLS-viscometry

As depicted in Fig. 2, the structure of branched TAIC prepolymer is dendritic, with almost no occurrence of intramolecular crosslinking reaction leading to the formation of loop structures. Fig. 5 shows a double logarithmic plot of $\langle S^2 \rangle_z^{1/2}$ versus M_w for the poly(TAIC) prepolymers obtained at a dilution of 1/4 (see Fig. 3), along with a plot for poly(DAT) prepolymers by way of comparison. The higher $\langle S^2 \rangle_z^{1/2}$ value was observed for poly(TAIC) as

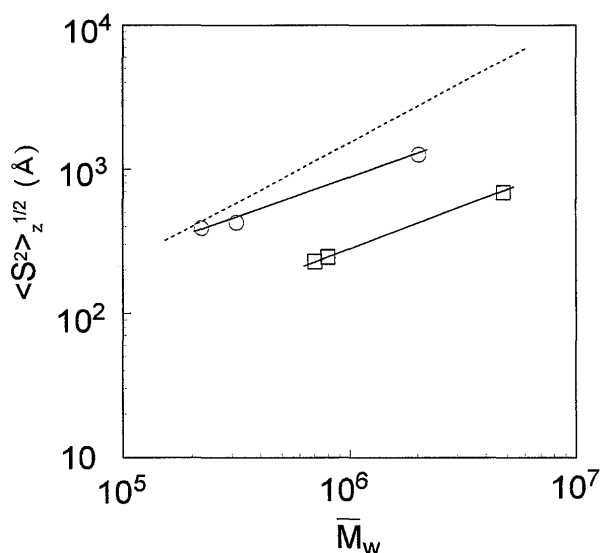


Fig. 5 Double logarithmic plot of $\langle S^2 \rangle_z^{1/2}$ versus M_w for (circles) poly(TAIC) prepolymers obtained at a dilution of 1/4 (see Fig. 3), along with a plot for (squares) poly(DAT) prepolymers. Dotted line corresponds to poly(methyl methacrylate).

a reflection of there being almost no occurrence of intramolecular crosslinking as compared to DAT polymerization. The radius of gyration was almost constant regardless of the dilution in the polymerization of TAIC, although in the polymerization of DAT it decreased with dilution.

Next, we tried to estimate the correlation of $[\eta]$ versus M_w by SEC-MALLS-viscometry. Fig. 6 shows the variation of RI-monitored SEC curves with conversion and the correlation of $[\eta]$ versus elution volume for the bulk polymerization of TAIC, along with a plot for poly(styrene) (poly(St)) by way of comparison. The correlation line shifted more radically downward than that for poly(St), and almost no conversion dependence was observed. These results strongly support the idea that the structure of branched TAIC prepolymer is dendritic. Fig. 7 shows the correlations of $[\eta]$ versus M_w , along with that of poly(St). The correlation lines for poly(TAIC)s obtained at 1.8 and 4.8% conversions appear at much lower levels compared with the plot for a linear poly(St). This must reflect the dendritic structure of branched poly(TAIC). In this connection, the $[\eta]$ value of the resulting polymer was almost constant, regardless of the dilution in the polymerization of TAIC. This reflects the almost total lack of intramolecular crosslinking leading to a loop structure formation that induces a decrease of viscosity.

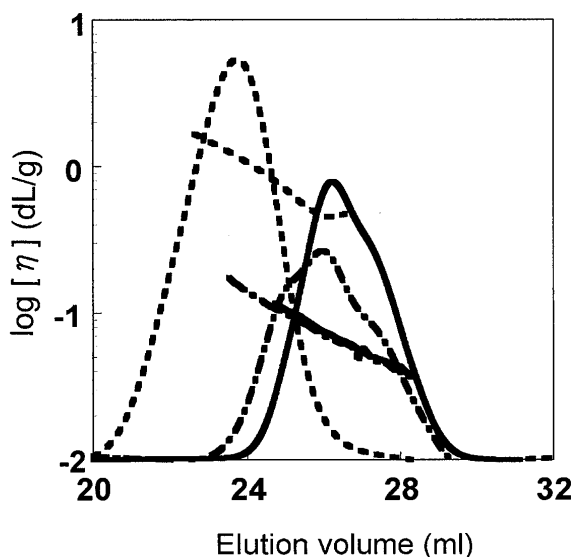


Fig. 6 Variation of RI-monitored SEC curves with conversion and the correlations of $[\eta]$ versus elution volume for bulk polymerization of TAIC using 0.05 mol/L of AIBN at 60°C at (solid line) 1.8 and (broken line) 4.8% conversions, along with a plot for (dotted line) poly(St).

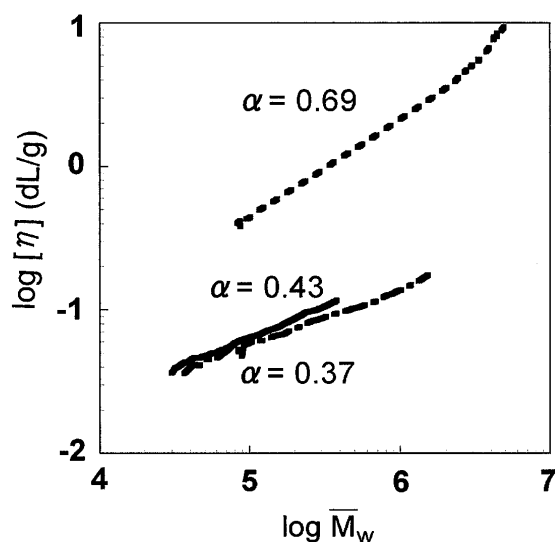


Fig. 7 Correlations of $[\eta]$ versus M_w , along with that of poly(St) (see Fig. 6).

3.5 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. Next, therefore, we pursued the process of growth of the resulting crosslinked 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 DAP⁵⁾. Fig. 8 shows the variation of molecular-weight distribution

(MWD) curves of sols with conversion in the bulk polymerization of TAIC using 0.05 mol/L of AIBN 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 fraction of higher molecular weight was rapidly incorporated into the gel. On the contrary, the incorporation of sol into gel was quite gradual in the bulk polymerization of DAT. When quasi-microgelation proceeds rapidly beyond the gel point, as is the case in the bulk polymerization of DAP⁵⁾, 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 crosslinked 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 Fig. 9. The quasi-microgelation in the polymerization of DAT was reflected in a drastic decrease of the swelling ratio as compared with TAIC polymerization.

As is evident from the above discussion, the network structure of TAIC resin should be quite homogeneous, and never inhomogeneous, 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 crosslinking 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.

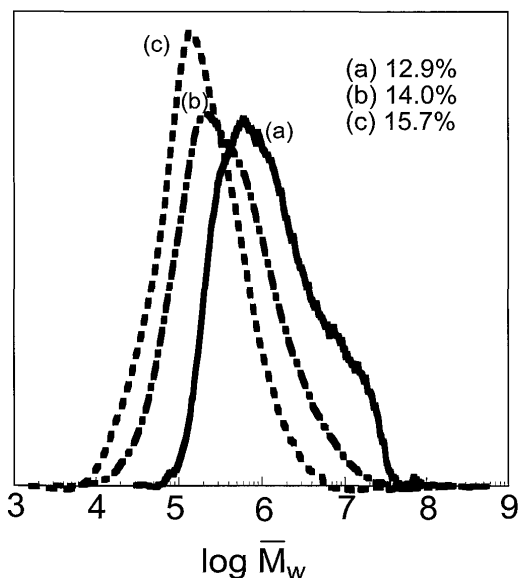


Fig. 8 Variation of MWD curves of sols with conversion in the bulk polymerization of TAIC using 0.05 mol/L of AIBN at 60°C.

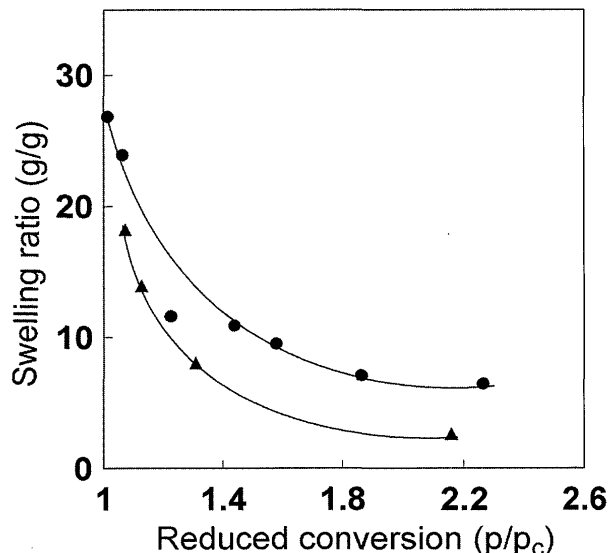


Fig. 9 Decrease in swelling ratios of resultant gels with the progress of polymerization beyond the gel point in the bulk polymerizations of (circles) TAIC and (triangles) DAT (see Fig. 8). Abscissa corresponds to reduced conversion (p/p_c), in which p and p_c correspond to conversion and gel point, respectively.

4. Conclusion

Non-filled TAIC cured resin obtained by direct preparation from TAIC monomer was too brittle for practical use. This is also the case with commercially important DAP resins, and is due both to the rigidity of structural units and to the inhomogeneity of the cured resins, as evidenced by electron microscopy⁴. As the inhomogenization of the resulting crosslinked polymer to form colloidal particles (quasi-microgelation) proceeded rapidly beyond the gel point⁵, several procedures to improve the brittleness of DAP resins were developed⁶⁻⁸. 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 introduce a homogeneous network, since the primary polymer chain of TAIC resin would be much more rigid than with DAP, due to very bulky side-chains^{10-12, 21-23}. 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 crosslinking polymerization of TAIC.

The specific gelation behavior of TAIC was investigated in detail in the solution polymerization where intramolecular crosslinking should be enhanced. No microgelation was observed until the gel-point conversion. This is in conformity with the complete loss of flexibility of poly(TAIC) chain that does not satisfy the prerequisite of the locally-enhanced occurrence of intramolecular crosslinking reaction leading to microgelation. The correlation between brittleness and network structure of TAIC resins was then further discussed, especially focusing on the characterization of resulting TAIC prepolymers by SEC-MALLS-viscometry. The structure of branched TAIC prepolymer is dendritic, with almost no occurrence of intramolecular crosslinking reaction leading to the formation of loop structures. This finding was supported by both correlations of $\langle S^2 \rangle_z^{1/2}$ versus M_w and $[\eta]$ versus M_w for poly(TAIC) prepolymers. Then, finally, we pursued the growth process of the resulting crosslinked 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 DAP⁹. The variation of MWD curves of sols with conversion in the bulk polymerization of TAIC demonstrated that the fraction of a higher molecular weight was rapidly incorporated into the gel. On the contrary, in the bulk polymerization of DAT the incorporation of sol into gel was quite gradual. 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 fairly homogeneous, and never inhomogeneous. 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 crosslinking 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.

References

- 1) C. E. Schildknecht, *Allyl Compounds and Their Polymers*, Wiley, New York (1973), p. 591.
- 2) C. E. Schildknecht, *Encycl. Polym. Sci. Eng.*, Vol. 4, Wiley, New York (1986), p. 779.
- 3) R. C. Laible, *Encycl. Polym. Sci. Technol.*, Vol. 1, Wiley, New York (1964), p. 750.
- 4) E. H. Erath, M. Robinson, *J. Polym. Sci.*, C3, 65 (1963).
- 5) A. Matsumoto, H. Nakajima, and M. Oiwa, *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.)*, 9, 141 (1988).
- 6) A. Matsumoto, K. Aoki, Y. Kukimoto, M. Oiwa, M. Ochi, and M. Shimbo, *J. Polym. Sci. Polym. Lett. Ed.*, 21, 837 (1983).
- 7) A. Matsumoto, K. Aoki, M. Oiwa, M. Ochi, and M. Shimbo, *Polym. Bull.*, 10, 438 (1983).
- 8) A. Matsumoto, T. Toyama, M. Oiwa, and M. Ochi, *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.)*, 12, 61 (1991).
- 9) D. Klempner, L. H. Sperling, *Interpenetrating Polymer Networks*, ACS Adv. Chem. Ser., Vol. 239, American Chemical Society, Washington, DC (1994).
- 10) A. Matsumoto, T. Matsumoto, H. Inoue, M. Oiwa, and H. Saito, *Eur. Polym. J.*, 26, 661 (1990).
- 11) A. Matsumoto, H. Inoue, T. Matsumoto, M. Oiwa, T. Kimura, and H. Saito, *J. Macromol. Sci.*, A26, 1279 (1989).
- 12) A. Matsumoto, F. Hirai, Y. Sumiyama, H. Aota, Y. Takayama, A. Kameyama, and T. Nakanishi, *Eur. Polym. J.*, 35, 195 (1999).
- 13) A. Matsumoto, S. Takahashi, and T. Morita, *Nettowaku Porima (J. Net. Polym. Jpn.)*, 17, 139 (1996).
- 14) A. Matsumoto, *Adv. Polym. Sci.*, 123, 41 (1995).
- 15) M. Oiwa and A. Matsumoto, *Prog. Polym. Sci. Jpn.*, Vol. 4, Kodansha, Tokyo (1974), p. 107.
- 16) A. Matsumoto, *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.)*, 8, 99 (1987).
- 17) M. Oiwa and W. Kawai, *Nippon Kagaku Zasshi*, 76, 107 (1955).
- 18) B. H. Clampitt, D. E. German, and J. R. Galli, *J. Polym. Sci.*, 27, 515 (1958).
- 19) W. H. Stockmayer, *J. Chem. Phys.*, 11, 45 (1943); 12, 125 (1944).
- 20) P. D. Bartlett and R. Altschul, *J. Am. Chem. Soc.*, 67, 812 (1945) (see also p. 816).
- 21) A. Matsumoto, K. Watanabe, T. Matsumoto, H. Aota, M. Hirabayashi, A. Kameyama, and T. Nakanishi, *J. Macromol. Sci., Pure Appl. Chem.*, A35, 1889 (1998).
- 22) A. Matsumoto, K. Watanabe, H. Aota, Y. Takayama, A. Kameyama, and T. Nakanishi, *Polymer*, 41, 3883 (2000).
- 23) A. Matsumoto, H. Yamasaki, M. Katsumoto, H. Aota, Y. Takayama, A. Kameyama, and T. Nakanishi, *Eur. Polym. J.*, 36, 1741 (2000).
- 24) B. T. Storey, *J. Polym. Sci.*, A3, 265 (1965).
- 25) H. Staudinger and E. Husemann, *Chem. Ber.*, 68, 1618 (1935).
- 26) A. Matsumoto, S. Takahashi, and M. Oiwa, *ACS Polym. Prep.*, 31, 149 (1990).
- 27) W. Funke, O. Okay, and B. J. Muller, *Adv. Polym. Sci.*, 136, 139 (1998).
- 28) K. Horie, A. Otagawa, M. Muraoka, and I. Mita, *J. Polym. Sci., Polym. Chem. Ed.*, 13, 445 (1975).
- 29) H. Galina, K. Dusek, Z. Tuzar, M. Bohdanecky, and S. Sokr, *Eur. Polym. J.*, 16, 1043 (1980).
- 30) J. Spevacek and K. Dusek, *J. Polym. Sci., Polym. Phys. Ed.*, 18, 2027 (1980).
- 31) A. C. Shah, I. W. Parsons, and R. N. Haward, *Polymer*, 21, 825 (1980).
- 32) R. Leicht and J. Fuhrmann, *Polym. Bull.*, 4, 141 (1981).
- 33) A. Matsumoto, D. Mitomi, H. Aota, and J. Ikeda, *Polymer*, 41, 1321 (2000).
- 34) C. Walling, *J. Am. Chem. Soc.*, 67, 441 (1945).
- 35) K. Dusek, H. Galina, and J. Mikes, *Polym. Bull.*, 3, 19 (1980).

- 36) K. Dusek and M. Duskova-Smrckova, *Prog. Polym. Sci.*, 25, 1215 (2000).
- 37) E. Trommsdorff, H. Kohle, and P. Lagally, *Makromol. Chem.*, 1, 169 (1948).
- 38) D. T. Landin and C. W. Macosko, *Macromolecules*, 21, 846 (1988).
- 39) S. Zhu and A. E. Hamielec, *Macromolecules*, 22, 3093 (1989).
- 40) M. Gordon, *J. Chem. Phys.*, 22, 610 (1954).