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### SOLVENT EFFECT ON GELATION IN THE RADICAL POLYMERIZATION OF TRIALLYL ISOCYANURATE

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## NOTE

# SOLVENT EFFECT ON GELATION IN THE RADICAL POLYMERIZATION OF TRIALLYL ISOCYANURATE

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Key Words: Triallyl Isocyanurate, Triallyl Cyanurate, Gelation, Solvent Effect

## ABSTRACT

Radical solution polymerization of triallyl isocyanurate was conducted in methyl benzoate or hexyl benzoate as good or poor solvent, respectively, using AIBN as initiator at 60°C. An increased rate of polymerization, enlarged primary chain length, and promoted gelation were observed in the poor solvent. The actual gel point was compared with the theoretical one; the discrepancy

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between these points was great, although no substantial solvent effect was detected. These results are discussed in comparison with the results obtained from the polymerizations of its isomer triallyl cyanurate and diallyl terephthalate, a typical diallyl ester. The swelling ratio of the gel obtained just beyond the gel point was quite high, suggesting no microgelation up to the gel point conversion even in the solution polymerization.

## INTRODUCTION

For a long time, the network formation mechanism and the fine structure of cured resins have been controversial problems because of the complexity of the reactions involved and the insolubility of the products. In particular, the free-radical crosslinking polymerization and copolymerization of multivinyl compounds are the problem cases. Since the pioneering theoretical and experimental works of Flory and Stockmayer [1, 2] and Walling [3], many papers have been published. Dusek [4] reviewed the network formation by chain crosslinking (co)polymerization, especially emphasizing the importance of cyclization leading to the formation of microgel-like particles. Dotson *et al.* [5,6] tested the predictions of classical Flory-Stockmayer's theory for the establishment of a network by free-radical crosslinking polymerization. Zhu *et al.* [7] summarized their studies on the elucidation of the crosslinking mechanism and kinetics, the characterization of network microstructures, and the development of kinetic gelation models. Recently, Tobita [8] reported the molecular weight distribution formed through chain-length-dependent crosslinking reactions in free-radical vinyl/divinyl copolymerization by using Monte Carlo simulations. Also, Funke *et al.* [9] reviewed microgels as intramolecularly crosslinked macromolecules with a globular structure in the crosslinking polymerization of unsaturated monomers. Although several factors, including cyclization, reduced reactivity of pendant vinyl groups of the prepolymer, intramolecular crosslinking, microgelation, and thermodynamic excluded volume effect have been proposed in order to interpret the observed discrepancy from theory for each polymerization system, it still seems that a more comprehensive study is required for a full understanding of network formation processes.

We have extensively investigated the free-radical polymerization of a variety of symmetrical or asymmetrical divinyl compounds including diallyl dicarboxylates [10], dimethacrylate [11], bis(allyl fumarate)s [12], and allyl unsaturated carboxylates [13] in terms of cyclopolymerization and gelation,

although our research goal is aimed at the elucidation of the crosslinking reaction mechanism and the control of network formation in order to molecular-design three-dimensional vinyl-type polymers with high performance and high functionality. Thus, we recently reviewed the mechanistic discussion of the three-dimensional network formation in the radical polymerization of multivinyl compounds, based on the experimental results obtained mainly in our laboratory [14].

Here we deal with the solvent effect on gelation in the radical polymerization of triallyl isocyanurate (TAIC) because in our previous studies the specific polymerization behavior of TAIC was compared with its isomer triallyl cyanurate (TAC), especially focusing our attention on the steric effect of growing polymer radical having sequential, bulky TAIC units [15-19]. Thus, the primary chain of poly(TAIC) having bulky side-chains is rigid and, therefore, the intermolecular and/or intramolecular crosslinking reactions may be suppressed as compared with the polymerization of diallyl terephthalate (DAT), a typical diallyl ester, in which the primary chain is flexible [20].

## EXPERIMENTAL

TAIC and TAC, supplied by Nippon Kasei Chemical Co., Ltd., and DAT, supplied by Daiso Co., Ltd., as monomers, and methyl benzoate (MeBz) and hexyl benzoate (HxBz) as solvents, were purified by vacuum distillation under nitrogen. 2,2'-Azobisisobutyronitrile (AIBN) as initiator was purified by recrystallization from methanol.

Polymerizations were carried out in ampoules as described previously [21]. After the desired time, the reaction mixture was poured into a large amount of hexane for TAC, or chilled methanol for TAIC and DAT, to precipitate the polymer. The purification of the polymer was done by reprecipitation from a benzene-precipitant system. The gel fraction of polymer obtained at conversions beyond the gel point was isolated by extracting the sol fractions with benzene.

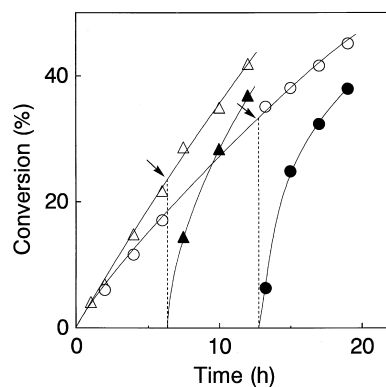
GPC-LALLS measurements were carried out as described previously [15].

## RESULTS AND DISCUSSION

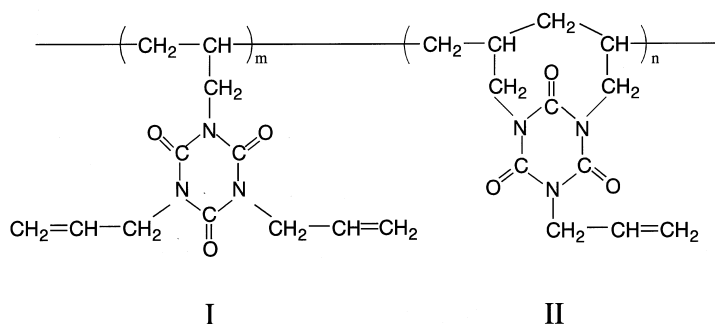
Solution polymerizations of TAIC were conducted in MeBz or HxBz at a dilution of monomer to solvent 1/2 (v/v) using 0.1 mol/L of AIBN at 60°C. We

have chosen MeBz and HxBz as good and poor solvent, respectively. The solvent power for poly(TAIC) was tentatively checked by the measurement of swelling ratio of the gel obtained just beyond the gel point in the bulk polymerization of TAIC, giving the values of 50, 47, 47, 46, 39, 34, or 32 ml/g for MeBz, dioxane, ethyl benzoate, benzene, ethyl acetate, propyl benzoate, or HxBz, respectively. Figure 1 shows the conversion-time curves; the rate of polymerization was higher in the poor solvent. The percentages of gel polymers are also plotted in Figure 1. The time at which gel starts to form was determined by extrapolating the gel formation curve to zero percentage. Then, the conversion at which gel starts to form, i.e., the gel point, was estimated to be 33.6 and 26.3% for the solution polymerizations in MeBz and HxBz, respectively. Gelation was obviously promoted in the poor solvent. It is noteworthy that no Trommsdorff effect [22] was observed, even beyond the gel point. This may be due to chain transfer from the growing polymer radical to the monomer (called degradative chain transfer [23]), which is significant in the polymerization of allyl compounds.

Prior to a detailed discussion about gelation, we should refer to the structure of the primary chain; the TAIC units incorporated into the polymer chain may have basically three different types of structures, including the uncyclized



**Figure 1.** Conversion-time curves for the solution polymerization of TAIC in (○, ●) MeBz and (△, ▲) HxBz. Open and full symbols correspond to total and gel polymers, respectively. (↓) Gel point.



**Figure 2.** Structures of uncyclized (I) and cyclized (II) TAIC units.

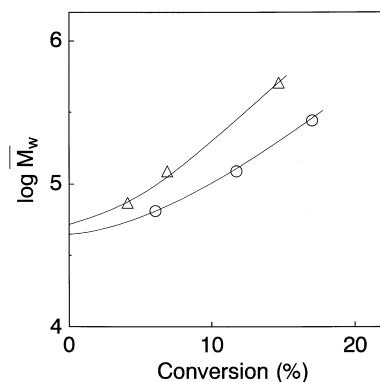
(I), the cyclized (II), or both structures I and II, as are depicted in Figure 2. However, the formation of a bicyclic ring was not observed experimentally [19] as it would be also expected from the inspection of a molecular model. So, every TAIC unit in the primary chain has more than one pendant, unreacted allyl groups useful for crosslinking reaction. These groups belonging to the same TAIC unit can not be used up for connecting three bulky, rigid primary chains, because of the steric crowding; thus TAIC would behave practically like a non-cyclopolymerizable divinyl monomer.

Then, the theoretical gel point was tentatively calculated according to the following Gordon's equation [24] derived for the polymerization of a divinyl monomer:

$$(1 - b_c) = 1 - \left[ \frac{r(\overline{P}_w - 3) - 1}{r(\overline{P}_w - 3) + 1} \right]^2$$

where  $(1 - b_c)$  is the conversion of the monomer at the gel point,  $r$  is the fraction of monomer units having pendant double bond in the polymer, and  $\overline{P}_w$  is the weight-average number of divinyl monomer units per primary chain.

Now, we need to estimate both  $r$  and  $\overline{P}_w$  values. The  $r$  value was assumed to be unity, because every TAIC unit in the primary chain can be useful for producing one crosslink between primary chains. Figure 3 shows the conversion dependence of weight-average molecular weight,  $\overline{M}_w$ , of the prepolymer determined by GPC-LALLS; the prepolymer of a higher  $\overline{M}_w$  value was obtained in the poor solvent. The primary chain length  $\overline{P}_w$  values. The  $r$  value was assumed to



**Figure 3.** Dependence of  $\bar{M}_w$  on conversion for the solution polymerizations of TAIC in (○) MeBz and (Δ) HxBz.

be unity, because every TAIC unit in the was then estimated by the extrapolation of the curves, shown in Figure 3, to zero conversion.

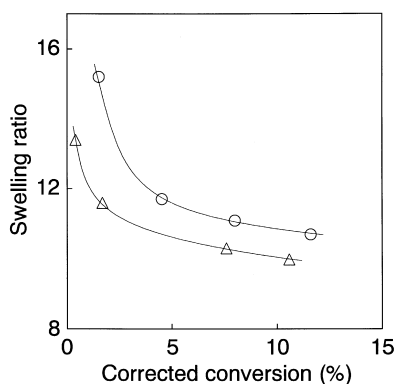
Table 1 summarizes a comparison of the actual gel points with the theoretical ones for the solution polymerizations, along with the result of the bulk polymerization [15]. The actual gel point was quite delayed from that predicted by theory for each polymerization system and especially, in the case of solution polymerization. For a comparison, the bulk and MeBz solution polymerizations of TAC and DAT were conducted similarly and the results obtained are also shown in Table 1. Clearly, these revealed that the actual gel points of TAIC and TAC were greatly delayed as compared to DAT, probably being due to the rigidity of primary chain, although no such difference between TAIC and TAC was observed. In this connection, the steric effect on the reactivity of growing polymer radical having sequential bulky TAIC units was reflected as solvent effect causing an increased rate of polymerization, an enlarged primary chain length and a promoted gelation, in the poor solvent. The terminal reacting site of growing polymer radical would be more sterically crowded in this solvent.

Finally, the swelling ratios of resulting gels for the solution polymerizations of TAIC and TAC in MeBz were plotted against conversion as shown in Figure 4; the swelling ratio decreased with the progress of gelation for both polymerizations, although TAIC gels showed higher swellability than TAC, probably due to the higher rigidity of TAIC polymer chain. Here it should be noted that

TABLE 1. Comparison of Actual and Theoretical Gel Points in the Solution Polymerizations of TAIC, TAC, and DAT<sup>a)</sup>

Monomer	Solvent	$R_p \times 10^5$ (mol/L · s)	$\bar{P}_w$	Gel point (%)	$\frac{\text{Actual G.P.}}{\text{Theoretical G.P.}}$
TAIC	MeBz	1.27	168	33.6	28
"	HxBz	1.73	211	26.3	28
"	None <sup>b)</sup>	3.40	280	12.4	17
TAC	MeBz	1.41	142	46.2	33
"	None <sup>b)</sup>	3.20	133	21.3	14
DAT <sup>c)</sup>	MeBz	--	45	47.2	8.8 <sup>d)</sup>
"	None	--	50	24.0	5.4 <sup>d)</sup>

a)  $[\text{Monomer}]/[\text{Solvent}] = 1/2$  (v/v);  $[\text{AIBN}] = 0.1$  mol/L;  $60^\circ\text{C}$ . b) In bulk;  $[\text{AIBN}] = 0.05$  mol/L. c)  $[\text{BPO}] = 0.1$  mol/L. d) The  $r$  values were estimated according to the cyclopolymerization mechanism ( $r = 2[M]/(2[M] + K_c)$ ), using  $K_c = 0.6$  mol/L [14].



**Figure 4.** Decrease of the swelling ration with the progress of polymerization beyond the gel point conversion for the solution polymerization of (O) TAIC and (Δ) TAC in MeBz. Conversion in abscissa is corrected such as the corresponding gel points are zero% of conversion.



the swelling ratio of the resulting gel just beyond the gel point is quite high; this suggests no occurrence of microgelation up to the gel point conversion, even in the solution polymerization, although no microgelation was observed in the bulk polymerization of diallyl phthalate [25]. This result is considered reasonable because a locally enhanced occurrence of intramolecular crosslinking should be required for microgelation [14] but the rigidity of TAIC polymer chain caused by the bulky side-chains would suppress the intramolecular crosslinking reaction.

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