ELSEVIER

Polymer 41 (2000) 3883–3886

polymer

Polymer Communication

Nonterminal units effect on the cyclopolymerization of triallyl isocyanurate

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Received 16 July 1999; received in revised form 8 September 1999; accepted 16 September 1999

Abstract

Cyclopolymerization of triallyl isocyanurate (TAIC) as compared with its isomer triallyl cyanurate (TAC) is discussed in terms of the nonterminal units effect caused by the sterically bulky isocyanurate side groups. Thus, the monomer concentration dependence of the initial residual unsaturation is not explained by considering an ordinary cyclopolymerization mechanism, although TAC polymerization obeyed the mechanism. The effect of the forced introduction of bulkier noncyclic units into the polymer chain on the cyclopolymerizability of TAIC was explored by the copolymerization with allyl dibenzyl isocyanurate, resulting in the enhanced cyclization in conformity with our expectation.

Keywords: Triallyl isocyanurate; Cyclopolymerization; Nonterminal units effect

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1. Introduction

We have been concerned with the elucidation of the specific polymerization behavior of triallyl isocyanurate (TAIC) [1–5], especially focusing our attention on the steric effect. Thus, it was found by chance that in the comparison of the polymerization behaviors of TAIC and its isomer triallyl cyanurate (TAC), the primary chain length of the TAIC polymer was quite high compared with TAC polymerization. This was ascribed to the reduced monomer chain transfer due to the steric effect by the bulky isocyanurate side groups on transition state formation [1]. This steric effect was further discussed by both the copolymerization with allyl benzoate and the telomerization in the presence of CBr_4 [2], by the polymerization of diallyl alkyl isocyanurates [3], by the polymerization and copolymerization of trimethallyl isocyanurate and trimethallyl cyanurate [4], and by the copolymerization with sterically unhindered monomers [5]; in particular, in the last two papers [4,5], the steric effect on the reactivity of growing polymer radicals is discussed in terms of the sequence length dependence of the sterically bulky TAIC units.

Here it should be recalled that in the attempt to find out the reason why gelation occurred much earlier for TAIC polymerization compared with TAC, the cyclopolymerizabilities of TAIC and TAC were explored [1]. That is, they are related to the amount of unreacted pendant allyl groups in the resulting primary chains responsible for the crosslinking reaction and TAIC showed a higher cyclopolymerizability than TAC as opposed to the promoted gelation in the bulk polymerization of TAIC. The ratio of the rate constant for the unimolecular cyclization reaction to that for the bimolecular propagation of the uncyclized radical, K_c, was evaluated to be 3.0 and 0.53 mol/l for TAIC and TAC, respectively, by using the kinetic equation derived for the cyclopolymerization of triallyl citrate [6]. As the inspection of molecular models of TAIC and TAC monomers is not always in conformity with the above results, the high cyclopolymerizability of TAIC could be related to the steric effect on the transition state formation on reaction at the sterically crowded, terminal reaction site of growing polymer radicals caused by the sequential, bulky TAIC units [4,5].

This article deals with the cyclopolymerization of TAIC in order to explore in more detail the specific cyclopolymerizability of TAIC as compared with TAC as the above result was observed only by the bulk polymerization.

2. Experimental

TAIC, TAC and allyl dibenzyl isocyanurate (ADBIC) were supplied by Nippon Kasei Chemical Co., Ltd. The

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PII: S0032-3861(99)00676-X

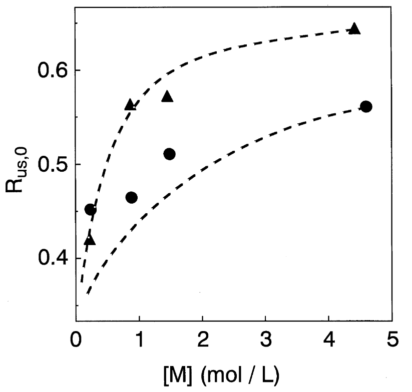

Fig. 1. Dependence of $R_{us,0}$ on monomer concentration for the solution polymerizations of (●) TAIC and (▲) TAC in benzene using 0.05 mol/l of AIBN at 60°C. Dotted lines are calculated according to Eq. (4) using the K_c values of 3.0 and 0.53 mol/l as estimated from the bulk polymerization results of TAIC and TAC, respectively.

former two monomers were purified by vacuum distillation under nitrogen. ADBIC (m.p. 97°C) was recrystallized from methanol. 2,2′-Azobisisobutyronitrile (AIBN) as initiator and benzene as solvent were purified by conventional methods.

Polymerizations were carried out in ampoules as described previously [7]. After the desired time, the reaction mixture was poured into a large amount of hexane for TAC, or chilled methanol for TAIC, to precipitate each polymer. The purification of the polymer was done by repeated reprecipitation from a tetrahydrofuran–precipitant system in order to remove a low-molecular-weight fraction.

The unreacted pendant allyl groups of the polymers obtained as high-molecular-weight fractions were calculated from the iodine value determined by the Wijs method [8].

3. Results and discussion

3.1. Monomer concentration dependence of cyclopolymerizability

Polymerizations were carried out in benzene using 0.05 mol/l of AIBN at 60°C. Fig. 1 shows the dependence of the initial residual unsaturation, $R_{us,0}$, on monomer concentration for the polymerizations of TAIC and TAC; here $R_{us,0}$ was determined by extrapolation of the conversion dependence of R_{us} to zero conversion. In the early stage of polymerization, crosslinking should be negligible and, therefore, $R_{us,0}$ must be 0.667 if no cyclization reaction occurs. Conversely, it reaches zero in an infinitely diluted solution if the bicyclo-intramolecular cyclization reaction occurs completely. On the contrary, in the absence of the bicyclo-intramolecular cyclization, $R_{us,0}$ approaches 0.333, assuming that the intramolecular cyclization occurs only in the same monomer unit as a consecutive cyclization, not with the pendant allyl groups belonging to nonterminal units as a nonconsecutive cyclization leading to a larger ring size formation.

The cyclopolymerization behaviors of TAIC and TAC may fall on the cases of the absence of the bicyclo-intramolecular cyclization, expected from the molecular model, and the occurrence of the nonconsecutive intramolecular addition reaction. Here, it is worth noting that in the polymerizations of diallyl terephthalate [9,10] and triallyl citrate [6], the latter nonconsecutive addition occurred significantly because the corresponding growing polymer radicals have abundant pendant allyl groups to undergo nonconsecutive cyclization as are the cases of TAIC and TAC polymerizations.

As can be seen in Fig. 1, $R_{us,0}$ increased with increasing monomer concentration as a result of reduced occurrence of cyclization. Here it should be noted that the results of monomer concentration dependence of $R_{us,0}$ for the polymerization of TAIC are not explained by considering an ordinary cyclopolymerization mechanism, obeying the following propagation reactions:

$$\mathrm{M}\cdot + \mathrm{M} \rightarrow \mathrm{M}\cdot \qquad 3k_p[\mathrm{M}\cdot][\mathrm{M}] \tag{1}$$

$$\mathrm{M}\cdot \rightarrow \mathrm{M}_c\cdot \qquad 2k_c[\mathrm{M}\cdot] \tag{2}$$

$$\mathrm{M}_c\cdot + \mathrm{M} \rightarrow \mathrm{M}\cdot \qquad 3k_{cp}[\mathrm{M}_c\cdot][\mathrm{M}] \tag{3}$$

Here it is assumed that the three allyl groups of TAIC behave equivalently and that the possibility of a bicyclo-intramolecular cyclization accompanying the formation of a bicyclic ring is negligible as mentioned above.

The dotted lines in Fig. 1 are calculated according to the following equation derived from the above cyclopolymerization mechanism [6]:

$$R_{us,0} = (6[\mathrm{M}] + 2K_c)/(9[\mathrm{M}] + 6K_c) \tag{4}$$

where K_c $(= k_c/k_p)$ values of 3.0 and 0.53 mol/l as estimated from the bulk polymerization results of TAIC and TAC, respectively, are employed. In TAIC polymerization, the experimental $R_{us,0}$ values deviated clearly from the calculated, dotted lines with decreasing monomer concentration as a reflection of reduced cyclopolymerizability, while TAC polymerization obeyed an ordinary cyclopolymerization mechanism.

In this connection, the reduced cyclopolymerizability of TAIC with a decrease in monomer concentration was tentatively evaluated as $K_c = 3.0$, 2.3 and 1.9 mol/l for bulk, 1/2 dilution and 1/3 dilution, respectively. Apparently, the K_c value depended on monomer concentration. This may be ascribed to the decreased rate constant for the unimolecular cyclization reaction, k_c, or the increased rate constant for the bimolecular propagation, k_p, of the uncyclized radical with decreased monomer concentration. TAIC cyclopolymerization would fall on the latter case because the sequence length dependence of steric effect on the reactivity of the growing TAIC radical was found [4,5], in which the steric

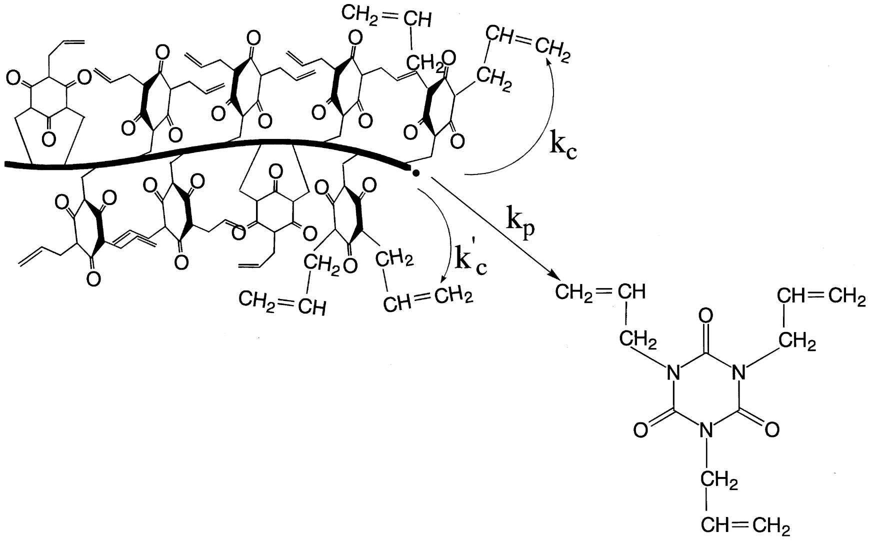

Fig. 2. Consecutive, k_c, and nonconsecutive, k'_c, cyclization reactions of growing TAIC uncyclized radical.

effect is related to the one on the transition state formation on reaction at the sterically crowded, terminal reaction site of growing polymer radical caused by the sequential, bulky TAIC units. Thus, in the cyclopolymerization of TAIC, the following two types of intermolecular and intramolecular reactions for uncyclized TAIC radical will be given as an alternative expression of Eqs. (1) and (2):

$$\sim \mathrm{M_c}\text{–}(\mathrm{M})_n\text{–}\mathrm{M}\cdot + \mathrm{M} \rightarrow \mathrm{M}\cdot \qquad 3k_\mathrm{p}[\mathrm{M}\cdot][\mathrm{M}] \tag{5}$$

$$\sim \mathrm{M_c}\text{–}(\mathrm{M})_n\text{–}\mathrm{M}\cdot \rightarrow \mathrm{M_c}\cdot \qquad 2k_\mathrm{c}[\mathrm{M}\cdot] \tag{6}$$

Here k_p will decrease with an increase in the number of sequential noncyclic units n, whereas k_c should be independent of n. As a reflection of this kind of steric hindrance, the incorporation reaction (Eq. (6)) of cyclic units into the TAIC polymer chain would be enhanced as an opposite reflection of the suppressed incorporation reaction (Eq. (5)) of bulky, noncyclic units. This may be the reason why TAIC polymerization does not obey an ordinary cyclopolymerization mechanism and the K_c value decreases with decreased monomer concentration.

Results similar to TAIC polymerization were reported by Fukuda et al. [11] in the cyclopolymerizations of *N*-alkyl-*N*-allylacrylamides including methyl, butyl and octyl as alkyl groups: the anomalous monomer concentration dependence of noncyclic units in the resulting polymers was interpreted by considering the rotational isomers of the monomer around the C(=O)–N bond and by assuming that the C(=O)–*N-trans* allyl isomer was exclusively cyclized to give a five-membered ring, although we re-evaluated their results in conjunction with the nonterminal units effect on the cyclopolymerization of *N*-benzyl-*N*-allylacrylamide [12].

3.2. Enhanced cyclization by copolymerization with ADBIC

As mentioned above, the deviation of the monomer concentration dependence of $R_{\mathrm{us},0}$ from an ordinary cyclopolymerization mechanism in the polymerization of TAIC became remarkable at a lower monomer concentration. In other words, the incorporation of cyclic units into the polymer chain would reduce the steric effect caused by the sequential, bulky noncyclic units and then the suppressed reactivity for the intermolecular propagation of growing polymer radicals would be weakened to lead the increase of the k_p value, with K_c becoming smaller to provide the deviation of $R_{\mathrm{us},0}$ to be higher than the calculated ones.

On the contrary, the forced introduction of noncyclic units into the polymer chain may induce a relatively enhanced consecutive cyclization reaction, k_c, in the same monomer unit as a reflection of the reduced k_p value, although a nonconsecutive cyclization reaction, k'_c may be inversely reduced. Both consecutive and nonconsecutive cyclization reactions are depicted in Fig. 2, although the latter cyclization involving the intramolecular reactions with allyl groups belonging to a penultimate, pen-penultimate, or so on, is simply exemplified as only a cyclization reaction of growing polymer radical with the pendant allyl groups belonging to the penultimate unit.

Thus, TAIC was copolymerized with ADBIC, a compound, in which two allyl groups of TAIC are replaced by saturated benzyl groups, corresponding to the forced introduction of sterically bulkier side groups into growing polymer radical. Copolymerization was carried out at a dilution of 1/2 in benzene at 60°C. For TAIC/ADBIC (1/1) copolymerization, the $R_{\mathrm{us},0}$ value was obtained to be 0.465; thus the K_c value was estimated to be 3.3 mol/l as compared with 2.3 mol/l for TAIC homopolymerization. The cyclopolymerizability of TAIC was obviously enhanced by the introduction of sterically bulky ADBIC units into the polymer chain.

Here it should be noted that the K_c value for TAIC/ADBIC copolymerization was evaluated according to our previous work [13,14]. Thus, the reactions, Eqs. (7)–(13), can be given as the propagation reactions for cyclocopolymerization if the occurrence of the bicyclo-intramolecular the propagation reaction is negligible

$$M_1\cdot + M_1 \rightarrow M_1\cdot \qquad 3k_{11}[M_1\cdot][M_1] \tag{7}$$

$$M_1\cdot + M_2 \rightarrow M_2\cdot \qquad k_{12}[M_1\cdot][M_2] \tag{8}$$

$$M_1\cdot \rightarrow M_c\cdot \qquad 2k_c[M_1\cdot] \tag{9}$$

$$M_c\cdot + M_1 \rightarrow M_1\cdot \qquad 3k_{c1}[M_c\cdot][M_1] \tag{10}$$

$$M_c\cdot + M_2 \rightarrow M_2\cdot \qquad k_{c2}[M_c\cdot][M_2] \tag{11}$$

$$M_2\cdot + M_1 \rightarrow M_1\cdot \qquad 3k_{21}[M_2\cdot][M_1] \tag{12}$$

$$M_2\cdot + M_2 \rightarrow M_2\cdot \qquad k_{22}[M_2\cdot][M_2] \tag{13}$$

where M_1 is TAIC; M_2, ADBIC and M_c, the cyclized radical formed by the intramolecular cyclization of $M_1\cdot$. On the basis of the seven propagation reactions presented above, the following reaction was derived [13,14]

$$\{(2 - 3R_{us,0})/(3R_{us,0} - 1)\}\{3[M_1]\}$$

$$= 2K_c - (1/r_1)\{(2 - 3R_{us,0})/(3R_{us,0} - 1)\}[M_2] \tag{14}$$

where $r_1 = k_{11}/k_{12}$ and $K_c = k_c/k_{11}$. By assuming $r_1 = 1$ as an equal reactivity of the allyl group belonging to both TAIC and ADBIC monomers, we can calculate the K_c values for TAIC/ADBIC copolymerization.

Finally, the enhanced cyclopolymerizability of TAIC by the introduction of sterically bulky ADBIC units into the polymer chain was extended to the copolymerization of TAC with ADBIC. The copolymerization was carried out at a dilution of 1/2 in benzene at 60°C. K_c was estimated to be 1.2 mol/l as compared with 0.53 mol/l for TAC homopolymerization as a reflection of enhanced cyclization in line with the above discussion.

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