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Further discussion of steric effect on the radical polymerization of triallyl isocyanurate as compared with its isomer triallyl cyanurate: polymerization and copolymerization of corresponding trimethallyl compounds

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Abstract

As part of our continuing studies concerned with the radical polymerization of multiallyl compounds, the polymerization behavior of triallyl isocyanurate (TAIC) was compared in detail with those of its isomer triallyl cyanurate (TAC). It was found by chance that the primary chain length of the TAIC polymer obtained was quite high compared with TAC polymerization. This is ascribed to the reduced occurrence of monomer chain transfer characteristic of the polymerization of allyl compounds due to the steric effect on transition state formation by the bulky side-chain group, providing an interesting example of reaction control in radical polymerization. In order to discuss in more detail this kind of the specific polymerization behavior of TAIC, this work deals with the polymerization and copolymerization of corresponding trimethallyl compounds including trimethallyl isocyanurate (TMAIC) and trimethallyl cyanurate (TMAC) having additional allylic hydrogens as α-methyl group in which no steric hindrance may occur for the transition state formation of monomer chain transfer reaction. TMAIC showed almost no homopolymerizability, while only slightly reduced polymerizability was observed for TMAC as compared with TAC. Specificity of TAIC polymerization was almost lost by copolymerizing about 20 mol% of TAC or TMAC. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

In our previous articles [1, 2], the polymerization behaviors of triallyl isocyanurate (TAIC) and its isomer triallyl cyanurate (TAC) were compared in detail; gelation was quite promoted in the polymerization of TAIC, mainly being due to the enlarged primary chain length of the TAIC polymer because of the reduced monomer chain transfer [3] characteristic of the polymerization of allyl compounds. This interesting enlargement of the primary chain length in the polymerization of TAIC, especially by considering that TAIC is a typical allyl compound, was then discussed from the standpoint of a steric effect on the transition state formation of monomer chain transfer [2], i.e. by the copolymerization with allyl benzoate (ABz) in which the steric hindrance is reduced with an increase in the proportion of ABz in the feed and in addition, by the telomerization in the presence of CBr_4 in which the monomer chain transfer is replaced by transfer to CBr_4.

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In the present article, the steric effect on the radical polymerization of TAIC is further discussed by the polymerization and copolymerization of corresponding trimethallyl compounds including trimethallyl isocyanurate (TMAIC) and trimethallyl cyanurate (TMAC):

{Structural Formulae of
TAIC, TMAIC, TAC and TMAC}.

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 growing polymer radical and the allylic hydrogens responsible for monomer chain transfer compared with TAC and, moreover, this effect may be enhanced by the polar adjacent carbonyl groups. Thus, an interaction between growing polymer radical and allylic hydrogens for formation of the transition state of monomer chain transfer is sterically hindered as a reflection of the following fact that 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 leading to increased chain length. We may extend our discussion of this steric effect to the polymerization of TMAIC and its copolymerization with TAIC as follows: TMAIC has additional allylic hydrogens as α-methyl group in which no steric hindrance may occur for 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, whereas 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. Thus, for monomer chain transfer reaction, the rate constant $k_{\mathrm{tr,m}}$ (TMAIC) is larger than $k_{\mathrm{tr,m}}$ (TAIC), while for propagation reaction, the rate constant k_{p} (TMAIC) is smaller than k_{p}(TAIC).

Here it should be noted that we have found almost no difference in the reactivity between allyl and methallyl esters as reported previously [4–6], although the rate and degree of polymerization in the polymerization of methallyl acetate were quite diminished with temperature compared with allyl acetate, especially above the ceiling temperature for a head-to-tail propagation [7]. In this connection, the polymerization behavior of TMAC is also interesting as compared to TAC.

2. Experimental

TAIC, TMAIC, TAC and TMAC were supplied by Nippon Kasei Chemical Co. Ltd. ABz was supplied by Daiso Co. Ltd. These monomers and propyl benzoate as solvent were purified by vacuum distillation under nitrogen, except that TMAIC (mp. 84°C) was recrystallized from methanol.

2,2′-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) as initiators were purified by conventional methods. Polymerization, sol-gel separation and GPC measurements were conducted as described previously [1].

3. Results and discussion

3.1. Homopolymerization of TMAIC and TMAC

The polymerization of TMAC was conducted in bulk using 0.05 mol/l of AIBN at 60°C. The conversion–time curve is shown in Fig. 1 along with the polymerizations of TAIC and TAC for comparison. The overall rate of polymerization of TMAC was estimated to be 2.1×10^{-5} mol/l s, being lower than the value of 3.2×10^{-5} mol/l s for TAC, although almost no polymerization was observed for the solution polymerization of TMAIC in propyl benzoate under similar polymerization conditions. As a further attempt to examine the polymerizability of TMAIC in more detail, it was undertaken to polymerize TMAIC at a dilution of 2/3 in propyl benzoate under more severe

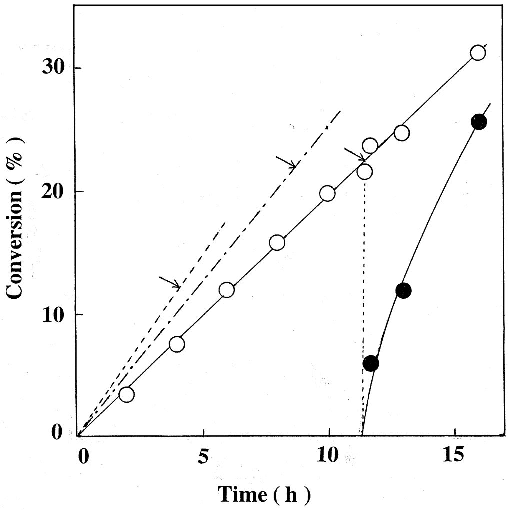


Fig. 1. Conversion–time curve for the bulk polymerization of (○,●) TMAC as compared with (----) TAIC and (–·–) TAC polymerizations, using 0.05 mol/l of AIBN at 60°C. Closed symbols correspond to gel polymers and arrows indicate gel points.

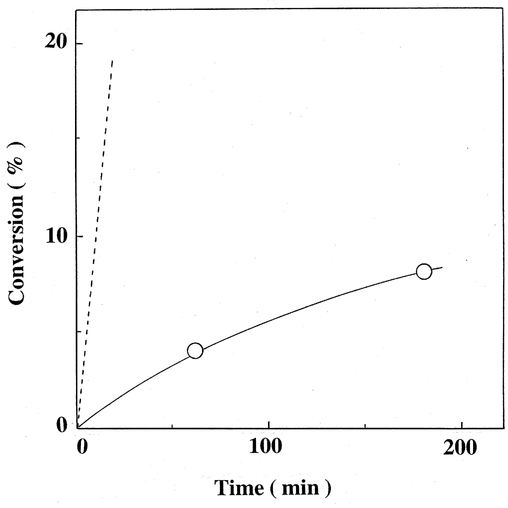


Fig. 2. Conversion–time curve for the solution polymerization of (○) TMAIC as compared with (----) TAIC, using 0.1 mol/l of BPO at 80°C.

polymerization conditions of higher initiator concentration and higher temperature, i.e. using 0.1 mol/l of BPO at 80°C. Fig. 2 shows the conversion–time curve along with TAIC polymerization for comparison; the rate of polymerization of TMAIC was lower than 1/16 of that of TAIC and very low-molecular-weight polymer ($P_n \fallingdotseq 10$) was only obtained.

The percentage of gel polymer is also plotted in Fig.1. The conversion at which gel starts to form, i.e. the gel point, was 22.5% for TMAC compared with 21.3% for TAC polymerization. Here it should be noted that no Trommsdorff effect [8] was observed, even beyond the gel point, being due to degradative chain transfer from the growing polymer radical to the monomer [3], which is significant in the polymerization of allyl compounds.

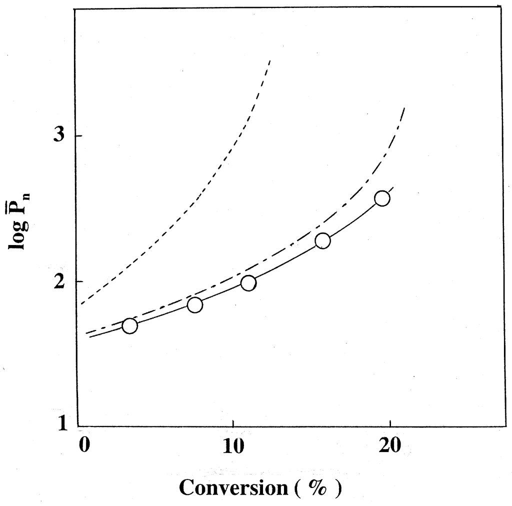


Fig. 3. Dependence of $\bar{P}_n$ on conversion (see Fig. 1).

Fig. 3 shows the dependence of the number-average degree of polymerization measured by GPC on conversion; interestingly, the initial degree of polymerization as primary chain length was almost equivalent for both TMAC and TAC polymerizations.

3.2. Copolymerization of TAIC with TAC, TMAC and TMAIC

In order to explore the specific polymerization behavior of TAIC in more detail, TAIC was copolymerized in bulk with TAC, TMAC and TMAIC using 0.05 mol/l of AIBN at 60°C. Fig. 4 shows the dependence of the overall rate of polymerization on monomer composition in the feed. The rate of polymerization decreased with an increase in the proportion of each comonomer according to the following features, respectively: (1) in the case of the copolymerization with TAC, it decreased markedly until *ca* 20 mol% of TAC and then it increased rather slightly; (2) with TMAC, it decreased markedly until *ca* 20 mol% of TMAC and then its decreasing tendency became gradual; (3) with TMAIC, it decreased drastically.

In Fig. 5, the initial degree of polymerization of the copolymer obtained was plotted against monomer composition in the feed. Thus, the primary chain length decreased markedly with an increase in the proportion of each comonomer according to the following features, respectively: (1) by the copolymerizations

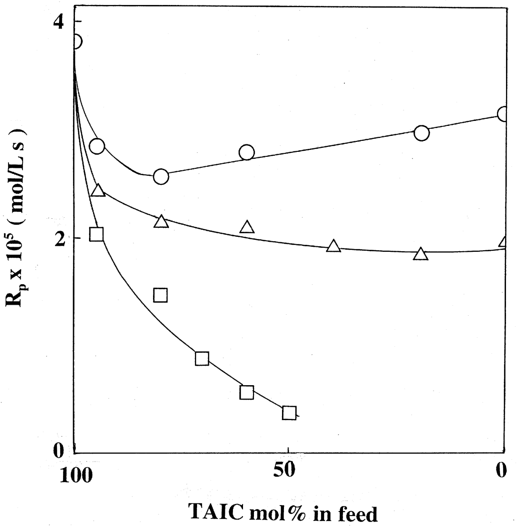


Fig. 4. Dependence of R_p on monomer composition for the bulk copolymerizations of TAIC with (○) TAC, (△) TMAC, and (□) TMAIC using 0.05 mol/l of AIBN at 60°C.

with TAC and TMAC, both cases showed a similar tendency, decreasing markedly until *ca* 20 mol% of comonomer and then becoming gradually constant; (2) with TMAIC, it decreased drastically.

3.3. Copolymerization of TAIC and TMAIC with ABz

Finally, TMAIC was copolymerized with ABz in comparison with the previous result for the copolymerization of TAIC with ABz [2], in which the primary chain length decreased markedly with an increase in the mole fraction of ABz and the difference between TAIC and TAC copolymerizations was reduced until almost no difference was observed above 50 mol% of ABz. Fig. 6 shows the result obtained; a reversed tendency was observed for the copolymerization of TMAIC with ABz.

3.4. Mechanistic discussion

It is well known that in the radical polymerization of allyl compounds, only low molecular weight polymers are obtainable because of degradative chain transfer [3], characteristic of allyl polymerization. Thus the key factor for controlling molecular weights of the resulting polymers is the ratio of the rate constant of monomer chain transfer reaction, $k_{tr,m}$, to that of propagation reaction, k_p , the former reaction being essentially termination.

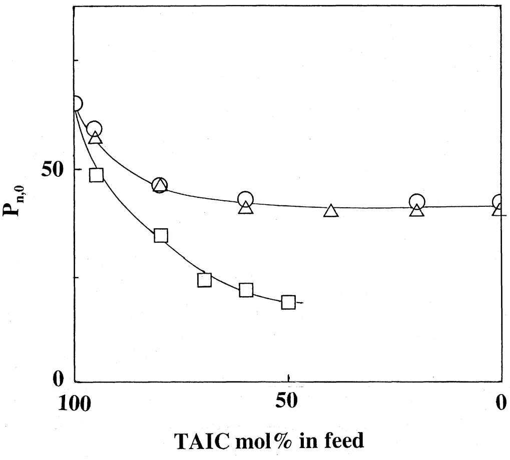
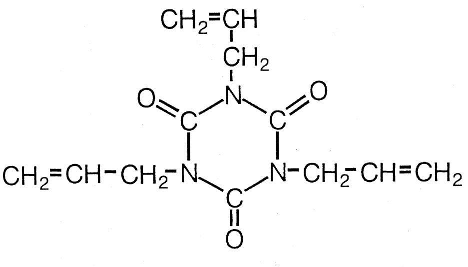
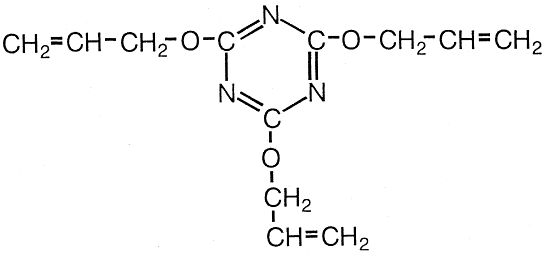


Fig. 5. Dependence of $\bar{P}_{n,0}$ on monomer composition (see Fig. 4).

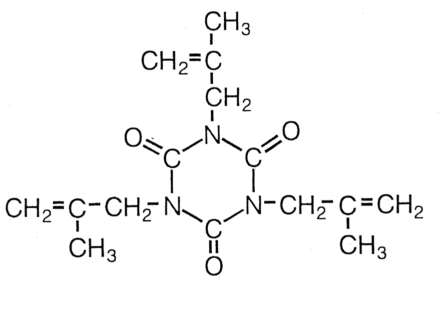
The polymerizability of TMAIC was drastically reduced as compared with TAIC; this may be ascribed to both an enlarged monomer chain transfer constant $k_{tr,m}$ (TMAIC) and a reduced propagation rate constant k_p (TMAIC) compared with the values of $k_{tr,m}$ *(TAIC) and* k_p (TAIC), whereas the polymerizability of TMAC was almost similar to that of TAC since a steric crowding for both growing polymer radical and the allylic hydrogens responsible for monomer chain



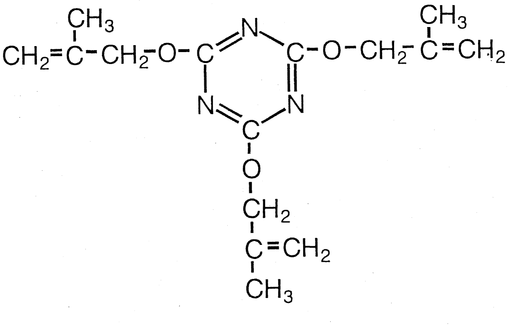
Triallyl isocyanurate (TAIC)



Triallyl cyanurate (TAC)



Trimethallyl isocyanurate (TMAIC)



Trimethallyl cyanurate (TMAC)

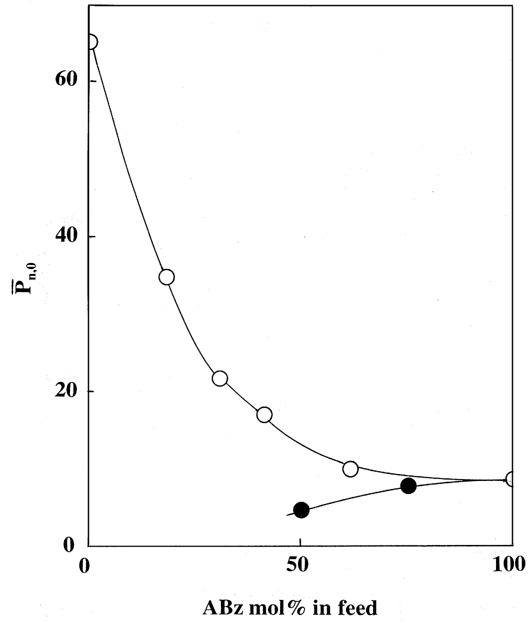


Fig. 6. Dependence of $\bar{P}_{n,0}$ on monomer composition for the copolymerization of (○) TAIC and (●) TMAIC with ABz.

transfer is much less compared with TAIC and TMAIC.

In the copolymerization of TAIC with TAC and TMAC, both rate and degree of polymerization decreased markedly with an increase in the proportion of comonomer, especially until *ca* 20 mol%, suggesting sequence length dependence of steric effect on the reactivity of growing TAIC radical, as we will discuss in more detail elsewhere. In the copolymerization with TMAIC, the promoted monomer chain transfer and reduced propagation are demonstrated again.

The copolymerization result with ABz also suggests the release of steric crowding of growing polymer radical leading to the recovery of propagation in conformity with the above discussion.

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