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Polymerization of Diallyl Alkyl Isocyanurates

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NOTE

POLYMERIZATION OF DIALLYL ALKYL ISOCYANURATES

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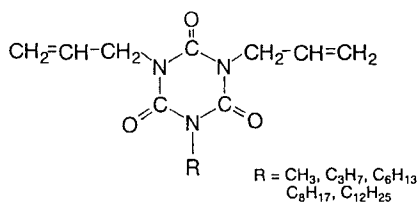
ABSTRACT

Polymerizations of several diallyl alkyl isocyanurates were investigated to explore in more detail the steric effect observed in the polymerization of triallyl isocyanurate [3, 5], as compared to its isomer triallyl cyanurate, by changing alkyl groups from methyl, propyl, hexyl, and octyl up to lauryl. The rate of polymerization, the gel point, the cyclization constant, and the primary chain length were evaluated. For example, the primary chain length increased with an increase in the bulkiness of the alkyl group as expected, although in the polymerization of diallyl lauryl isocyanurate it decreased as a reflection of reduced rate of propagation due to the enhanced steric effect arising from a very bulky lauryl group.

INTRODUCTION

In our continuing studies concerned with the free-radical polymerization of multiallyl compounds [1, 2], the polymerization of triallyl isocyanurate (TAIC) and its isomer triallyl cyanurate, commercially important as crosslinking agents, were

compared in detail [3]. We found, by chance, that in the polymerization of TAIC, gelation was promoted and the primary chain length of resulting TAIC polymers was quite high because of the reduction of monomer chain transfer characteristic in the polymerization of allyl compounds [4]. This may be attributed to a steric effect in an interaction between growing polymer radical and allylic hydrogens for the formation of the transition state of monomer chain transfer, suggesting the possibility of chain length enlargement in allyl polymerization [5]. In order to explore in more detail this kind of the steric effect, the present note deals with the polymerization of several diallyl alkyl isocyanurates having various alkyl groups as depicted:



Diallyl alkyl isocyanurate

EXPERIMENTAL

TAIC and diallyl alkyl isocyanurates, including diallyl methyl isocyanurate (DAMIC), diallyl propyl isocyanurate (DAPIC), diallyl hexyl isocyanurate (DAHIC), diallyl octyl isocyanurate (DAOIC), and diallyl lauryl isocyanurate (DALIC), were supplied by Nippon Kasei Chemical Co. They were purified by vacuum distillation under nitrogen (DAMIC: b.p. 100°C/3.4×10⁻²mmHg; DAPIC: b.p. 88°C/2.0×10⁻²mmHg; DAHIC: b.p. 108°C/1.3×10⁻²mmHg; DAOIC: b.p. 128°C/1.1×10⁻²mmHg; DALIC: bp 159°C/1.1×10⁻²mmHg), and also checked by ¹H-NMR spectroscopy. 2,2'-Azobisisobutyronitrile (AIBN), as an initiator, was purified by recrystallization from methanol.

Polymerization, sol-gel separation, determination of the unreacted pendant allyl groups of the polymers, and GPC-LALLS measurements were carried out as described previously [3].

RESULTS AND DISCUSSION

The polymerizations of DAMIC, DAPIC, DAHIC, DAOIC, and DALIC were conducted in bulk using 0.05 mol/L of AIBN at 60°C. The conversion-time

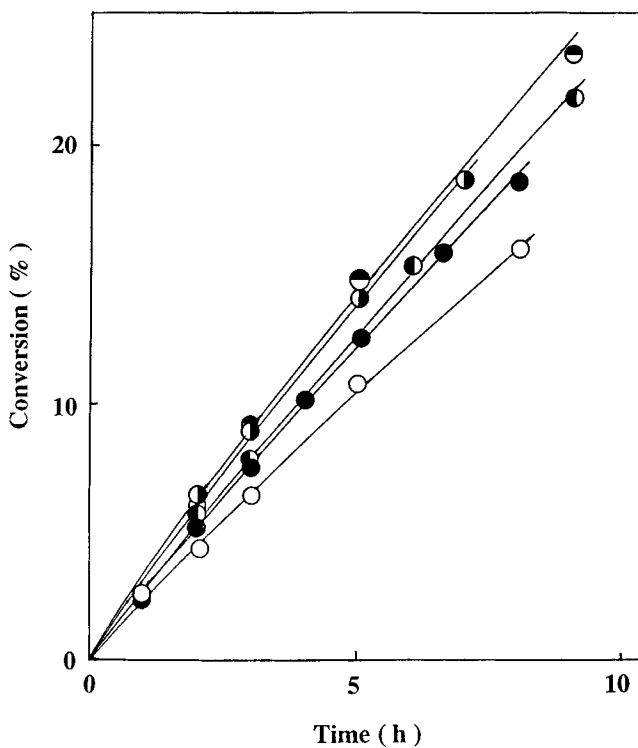


Figure 1. Conversion-time curves for the bulk polymerization of (○) DAMIC, (●) DAPIC, (○) DAHIC, (○) DAOIC, and (●) DALIC using 0.05 mol/L of AIBN at 60°C.

curves are shown in Figure 1. No Trommsdorff effect [6] was observed, even beyond the gel point conversion shown later; this may be due to chain transfer from the growing polymer radical to the monomer (called degradative chain transfer [4]), which is significant in the polymerization of allyl compounds, i.e., the allylic monomer radical plays an important role in the termination reaction. From each slope of the curves, the overall rate of polymerization, R_p , was estimated to be 3.6, 3.1, 2.9, 2.1, and 2.2 $\times 10^{-5}$ mol/L s for DAMIC, DAPIC, DAHIC, DAOIC, and DALIC, respectively, which are comparable to the value of 3.2 $\times 10^{-5}$ mol/L s for TAIC.

The gel point, the conversion at which gel starts to form, was also estimated to be 15, 14, 18, 21, and 24% for DAMIC, DAPIC, DAHIC, DAOIC, and DALIC, respectively, compared to 12.4% for TAIC polymerization. In this

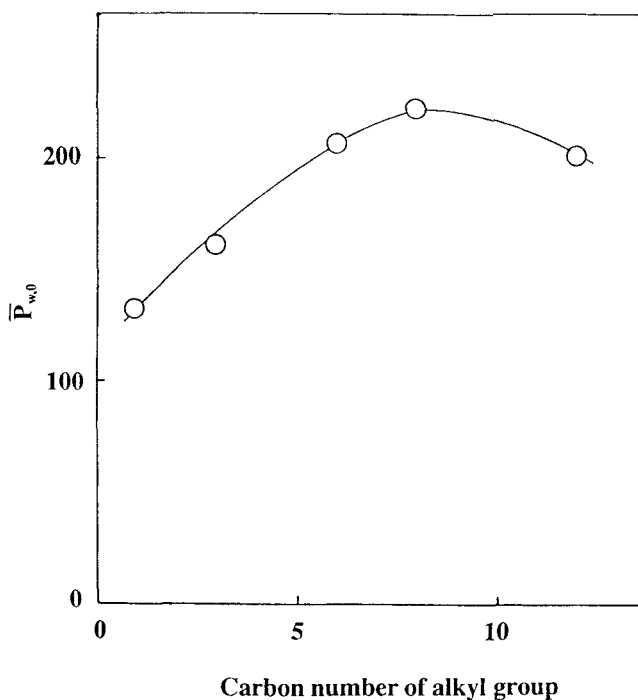


Figure 2. Correlation of the primary chain length with the carbon number of alkyl group for the bulk polymerizations of diallyl alkyl isocyanurates.

connection, gelled polymers were usually obtained at above 20% conversion for the polymerizations of diallyl dicarboxylates [1]. The gelation of diallyl alkyl isocyanurates, especially including DAMIC and DAPIC, occurred only at a bit higher conversion compared to TAIC as a triallyl compound, but their differences were small considering the remarkably reduced content of pendant allyl groups useful for crosslinking in the polymerizations of diallyl alkyl isocyanurates as diallyl compounds. Although two main factors are theoretically operative for gelation [7], the more significant contribution of the high primary chain length than the content of pendant allyl groups to the promoted gelation is suggested. This is in agreement with our previous discussion on the TAIC polymerization [3]. Moreover, the delay of gelation was enhanced with the bulkiness of alkyl group, especially including octyl and lauryl groups, as a reflection of steric effect on the intermolecular crosslinking reaction between growing polymer radical and pendant double bonds of prepolymer.

The initial residual unsaturations, $R_{us,0}$, obtained by extrapolation of the conversion dependence of R_{us} to zero conversion, were 0.394, 0.379, 0.382, 0.379, and 0.384 for DAMIC, DAPIC, DAHIC, DAOIC, and DALIC, respectively. In the early stage of polymerization, crosslinking should be negligible and, therefore, the deviation of $R_{us,0}$ from 0.5, the value which would correspond to no occurrence of cyclization and crosslinking reactions, may be ascribed predominantly to intramolecular cyclization. Thus, the cyclization constant, K_C , the ratio of the rate constant for the unimolecular cyclization reaction to that for the bimolecular propagation of the uncyclized radical, was evaluated to be 2.9, 2.7, 2.4, 2.1, and 1.8 mol/L for DAMIC, DAPIC, DAHIC, DAOIC, and DALIC, respectively [8].

Finally, the initial weight-average degree of polymerization, $\bar{P}_{w,0}$, as the primary chain length, was determined by extrapolation of the conversion dependence of the weight-average molecular weight measured by GPC-LALLS to zero conversion and then, $\bar{P}_{w,0}$ was plotted against the carbon number of alkyl group as shown in Figure 2. The primary chain length increased with an increase in the bulkiness of alkyl group as expected, although in the polymerization of DALIC it decreased as a reflection of reduced rate of propagation due to the enhanced steric effect arising from a very bulky lauryl group.

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