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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
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To cite this Article Asakura, Jun-Ichi , Matsubara, Yoshio , Yoshihara, Masakuni and Maeshima, Toshihisa(1980) 'Photopolymerization of β-Allyloxypropionaldehyde', Journal of Macromolecular Science, Part A, 14: 6, 803 — 812
To link to this Article: DOI: 10.1080/00222338008068112
URL: http://dx.doi.org/10.1080/00222338008068112

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J. MACROMOL. SCI.–CHEM., A14(6), pp. 803-812 (1980)

Photopolymerization of β-Allyloxypropionaldehyde

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ABSTRACT

Homo- and copolymerizations of β-allyloxypropionaldehyde (I) have been carried out by photoirradiation at 12-13°C in degassed glass ampules. The number-average molecular weights of the homopolymers of I obtained in a few reaction conditions were determined by means of gel-permeation chromatography. I initiated and/or accelerated the photopolymerizations of such vinyl monomers as methyl methacrylate and vinyl acetate. Photocopolymerizabilities of I with styrene (St) and acrylonitrile (AN) were also investigated, and the copolymerization parameters were obtained as follows: for the St-I system, $r_1 = 12$, $r_2 = 0.01$; for the AN-I system, $r_1 = 5.2$, $r_2 = 0.01$.

INTRODUCTION

Previously, the authors reported the results of polymerizations of β-allyloxypropionaldehyde (I) with radical, cationic, and anionic catalysts [1]. Although several other studies [2, 3] on the radical

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and ionic polymerizations of olefins bearing aldehyde group have been reported, very few investigations [4, 5] have been reported on their photopolymerizations. I has an absorption band at 280 nm due to the aldehyde group and hence photoirradiation is expected to cause the polymerization of I.

This paper is concerned with the results of the homo- and copolymerizations of I by photoexcitation.

EXPERIMENTAL

Materials

β-Allyloxypropionaldehyde (I) was prepared according to the previous method [1], bp 55°C/14 mm Hg.

Methyl methacrylate (MMA), vinyl acetate (VAc), styrene (St), and acrylonitrile (AN) were purified by conventional methods.

Solvents were purified by ordinary methods.

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Polymerizations

Photopolymerization was carried out at 12-13°C in a degassed glass ampoule which was set up at a distance of 5.5 cm from the light source (high pressure 400-W mercury lamp).

The homopolymer of I was purified in the following manner. Thus, the reaction mixture was poured into petroleum ether to give two layers. The petroleum ether layer was separated and the residue was distilled under reduced pressure to give the homopolymer of I. No polymer was detected in the petroleum ether layer by means of GPC analysis.

Photocopolymerizations of I with MMA and VAc were carried out in benzene at 12-13°C, and methanol was used as a precipitation reagent.

Polymer Characterizations

GPC measurements of the polymers were done with THF as the solvent. Solvent flow rates were 1 ml/min. The columns used throughout totalled 16 ft in length (Shimazu SG-1, 1, 2,2).

The infrared spectra reported in this paper were taken with a Yanagimoto LSG-25 infrared spectrometer.

The number-average molecular weights of the polymers were determined by vapor-pressure osmometry with benzene as a solvent at 40.5°C with a Hitachi Perkin-Elmer Model 105 apparatus.

The compositions of copolymers were determined by elemental analysis.

TABLE 1. Photopolymerization of I[a]

Run No.	I (ml)	Solvent (ml)	Time (hr)	Conversion (%)	Conversion rate (%/hr)
A-1	20	-	10	7.1	0.71
A-2	20	-	50	37.2	0.74
A-3[b]	10	-	50	-	-
A-4	10	Benzene (10)	10	20.3	2.03
A-5	10	Benzene (10)	24	54.9	2.29
A-6	10	Ethanol (10)	24	8.3	0.35

[a] At distance of 5.5 cm from 400-W high-pressure mercury lamp at 12°C.

[b] Thermal polymerization at 60°C.

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RESULTS AND DISCUSSION

Homopolymerization

Table 1 summarizes the results of the photopolymerization of I. The homopolymer of I was found to be obtained by the photoactivation but not by the thermal activation. The polymer was soluble in such organic solvents as alcohol, n-hexane, ether, benzene, and DMF. Polymerization rates in benzene were found to be larger than those in other solvents, suggesting that the photoexcitation of benzene also might be of some importance in accelerating the polymerization of I.

Figure 1 shows typical GPC curves of the homopolymers in which four or five peaks were observed. It is interesting to note that, with an increase of the reaction time, species of lower molecular weight tended to decrease in the intensity and the species of higher molecular weight tended to increase (A-1 vs. A-2 and A-4 vs. A-5). These observations suggest that the oligomers produced initially reacted with each other to produce the higher polymers.

Figure 2 shows IR spectra of the homopolymers. In every case, there were observed absorption bands at 1724 cm^{-1} due to the aldehyde group, at 1645 and 990 cm^{-1} due to the terminal vinyl group, and at 1100 cm^{-1} due to the ether group of I.

Though sufficient data were not available to deduce the polymerization mechanism of I, the photopolymerization of I is considered to proceed via a radical process. If this hypothesis is valid, I will initiate and/or accelerate the photopolymerization of other vinyl monomers. Therefore, the effects of I on the photopolymerizations of

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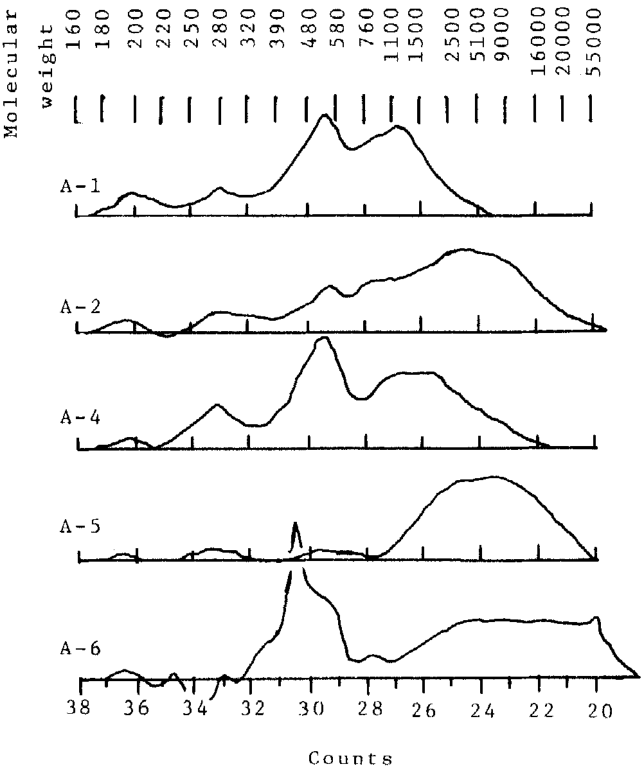

FIG. 1. Gel-permeation chromatography of the products obtained by the photopolymerization of I. Column, SG-1, 1, 2, 2 (16 ft) in THF at 15°C.

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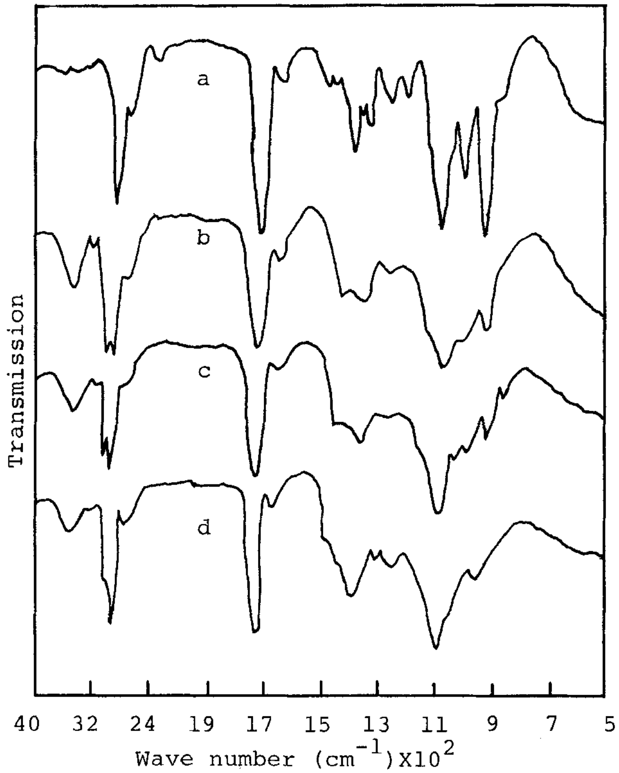

FIG. 2. Infrared spectra of the products obtained by the photopolymerization of I: (a) monomer; (b) run A-1; (c) run A-4; (d) run A-6.

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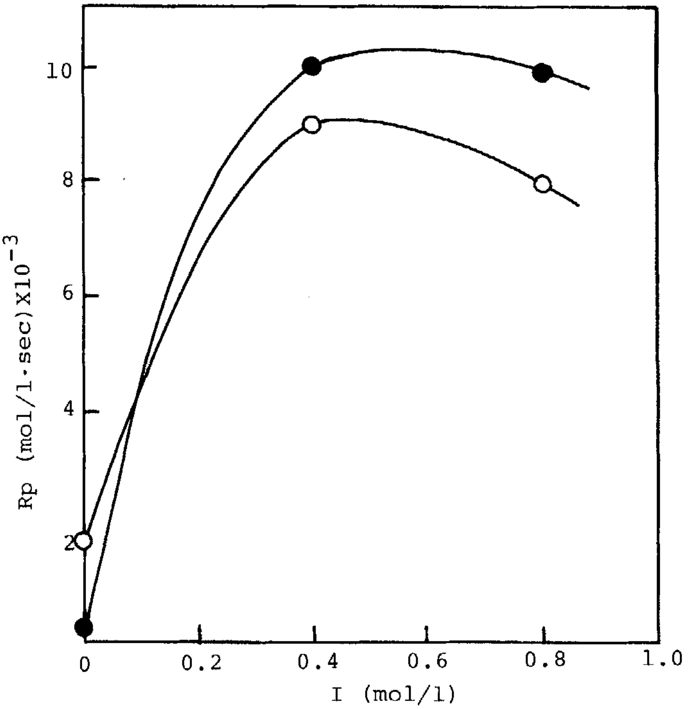

FIG. 3. Effect of I on the photopolymerization of MMA and VAc: (○) MMA-I system, [MMA] = 4 mole/liter in benzene; (●) VAc-I system, [VAc] = 4 mole/liter in benzene.

MMA, VAc, St, and AN were studied. Both the elemental analysis and the IR spectra of the polymers revealed that the homopolymerization of I took place for I-MMA and I-VAc systems and that the usual copolymerizations took place in the cases of the I-St and I-AN systems. As is clearly seen in Fig. 3, sharp increases of the polymerization rates of MMA and VAc were observed with addition of a small amount of I.

However, with the increase of the concentration of the additive I, the polymerization rates were found to be almost constant or slightly decreased. This fact may be caused by the degradative chain transfer of I. Actually, the chain-transfer constant of I was determined to be the rather large value of 3.5×10^{-3} [1].

Copolymerization

Photocopolymerization of I(M_2) with St in benzene and with AN in DMF was carried out; the results are shown in Figs. 4 and 5. In every

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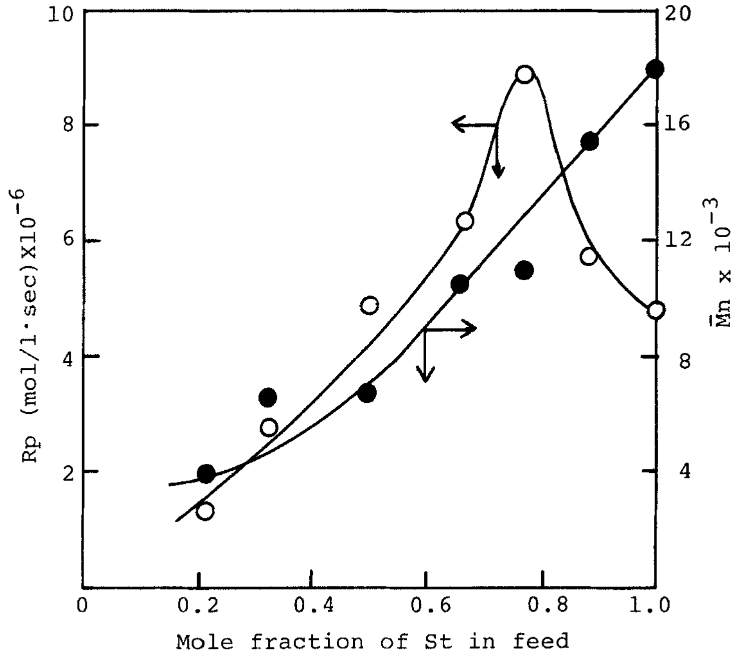

FIG. 4. Dependence of (○) R_p and (●) $\overline{M}_n$ on the monomer composition in the photocopolymerization of I with St; [I] + [St] = 4.5 mole/liter in benzene at 15°C.

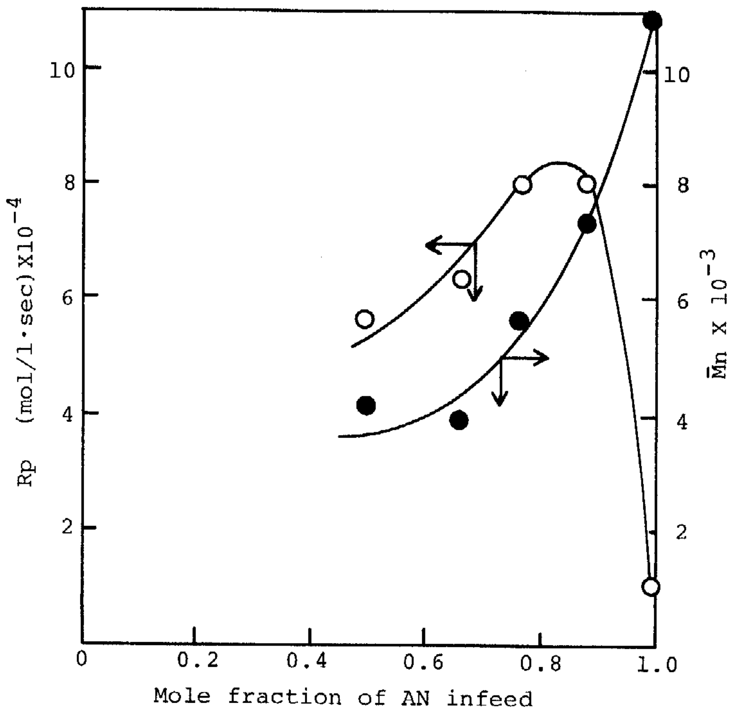

FIG. 5. Dependence of (○) R_p and (●) $\overline{M}_n$ on the monomer composition in the photocopolymerization of I with AN; [I] + [AN] = 4.5 mole/liter in DMF at 15°C.

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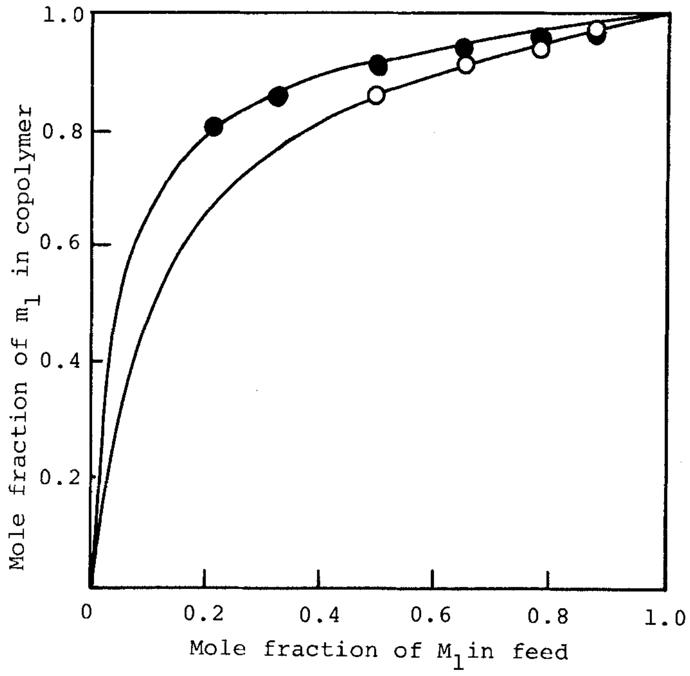

FIG. 6. Copolymerization composition curves for the photocopolymerization of I (M_2) with St and AN: (○) I-St system; (●) I-AN system.

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case, optimum rates of copolymerization were observed at a M_1 mole fraction of 0.8 in monomer feed. These observations are also explained by taking account of the initiation ability and the chain-transfer ability of I. Namely, an increase of I in the monomer feed results in acceleration of the copolymerization due to the photoexcitation of I. However, when the concentration of I in the monomer feed is too high to initiate the polymerization, the chain-transfer reaction of I will predominate to decrease the copolymerization rate.

This hypothesis seems partly supported by the fact that the number-average molecular weight of the copolymer was decreased with the increase of M_1 concentration in the monomer feed.

The monomer-copolymer composition curves are shown in Fig. 6. I was found to have only weak photocopolymerizability with AN and St. It is noted that the monomer reactivity ratios in the I-AN system (r_1 = 5.2, r_2 = 0.01) were almost equal to those obtained by using AIBN (r_1 = 5.0, r_2 = 0.015) [1], clearly indicating that the photopolymerization of I proceeds via radical process.

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Accepted by editor May 23, 1979
Received for publication June 20, 1979

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