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Cyclic Acetal-Photosensitized Polymerization. IV. Photopolymerization of Styrene in the Presence of 1,3:2,4:5,6-Trimethylene-D-Sorbitol

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ABSTRACT

Styrene(St) was polymerized in benzene solution in the presence of 1,3:2,4:5,6-trimethylene-D-sorbitol(TCA) by means of photoirradiation of system at 30° C. It was found that the polymerization was depressed by the addition of TCA and then proceeded through a radical mechanism. The chain-transfer constant of the styryl radical to TCA was estimated to be 0.16. Accordingly, the photopolymerization of St in the presence of TCA is studied kinetically with regard to chain transfer and termination.

INTRODUCTION

In previous papers [1, 2], the photopolymerization of styrene(St) was investigated in the presence of such mono- and dicyclic acetal compounds as 1,3-dioxolane (DO) and 2,4,8,10-tetraspiro-[5,5]-undecane (TU). It was found that the monoester radicals generated by photoirradiation can initiate the polymerization of vinyl compounds. Moreover, it is known [2] that the ability to promote polymerization of vinyl monomers for TU compounds is twice as large as that for DO compounds.

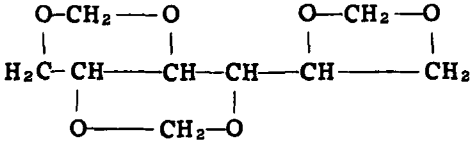
In this experiment, the photopolymerization of St in the presence of 1,3:2,4:5,6-trimethylene-D-sorbitol (TCA) was carried out. Against our expectation, the photopolymerization of St was depressed by the addition of TCA. We will discuss our results from the standpoints of chain transfer and termination.

EXPERIMENTAL

Materials

TCA was prepared by the concentration of 37%-formalin with D-sorbitol by using sulfuric acid as a catalyst according to the method of Ness [3].

Other materials were purified in the usual manner.



TCA

Procedures

The photopolymerization of St and the photoirradiation onto TCA were carried out at 30° C in the same manner as reported in the previous papers [1, 2]. In the present experiment, a 500-W high-pressure mercury vapor lamp was used instead of a 300-W lamp. The rate of polymerization was determined gravimetrically, and the determination of decomposition rate of TCA was carried out by the same method as reported in the previous papers [1].

Analysis of Polymer

The chemical composition of the polymer obtained was determined by elemental analysis.

The viscosity of the obtained polymer was measured in benzene solution at 30° C in an Ubbelohde viscometer. By assuming that the polymer behaved as well as the homopolymer of St, the apparent number-average molecular weight ($\overline{M}_n$) was calculated from the intrinsic viscosity ($[\eta]$) of the polymer by using the equation [4]:

$$[\eta] = 1.0 \times 10^{-4} \overline{M}_n^{0.74}$$

RESULTS AND DISCUSSION

Photodecomposition

The photoirradiation onto TCA was carried out at the concentration of 1.31 mole/liter with the use of benzene as a solvent at 30° C.

Thin-layer chromatography showed the reaction mixture to consist of many components. Two components other than TCA can be isolated by using benzene as the developing solvent.

Infrared spectra before and after the photoirradiation onto TCA are shown in Fig. 1. In the infrared spectrum of fraction I, the four absorption bands in the range of 1200-1040 cm^{-1} due to the cyclic acetal decreased and new peaks at 1070 cm^{-1} (C–O–C), 1650 cm^{-1} (C=C), and 3440 cm^{-1} (OH) appeared. In fraction II, new peaks at 1720 and 1180 cm^{-1} (C=O) increased. It can be considered that TCA is rearranged to the corresponding ether compounds by means of photoirradiation.

In ESR spectrum of the reaction mixture, absorptions appeared in the neighborhood of 2 G. It is presumed that on photoirradiation of TCA, the hydrogen on carbon 2 or 3 is also abstracted as a radical rather than the active hydrogen between two alkoxy groups.

Accordingly a photochemical rearrangement is considered to proceed through two radical routes.

The decomposition rate in the presence of St was proportional to the first power of the concentration of TCA. The molar rate constant k_d' of decomposition for TCA was obtained as 1.17×10^{-7} sec^{-1}; this value is larger than the rate constants obtained by using DO and TU compounds.

Accordingly, it was expected that the methylene radicals generated could initiate the polymerization of vinyl compounds.

Kinetics of Polymerization

The dependence of TCA and St concentration on the rate of photopolymerization is plotted in Figs. 2 and 3. It was found from the

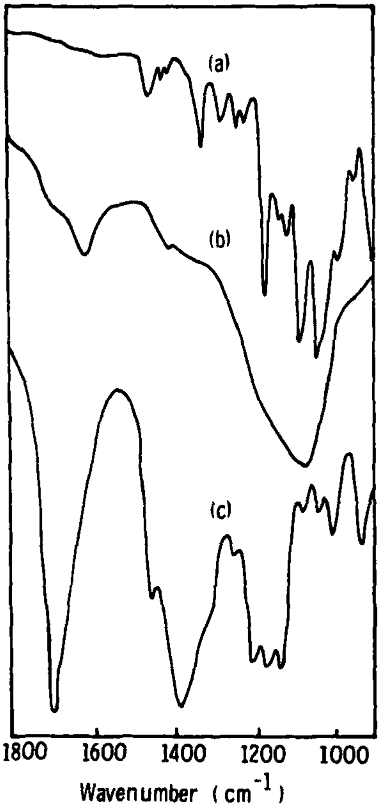
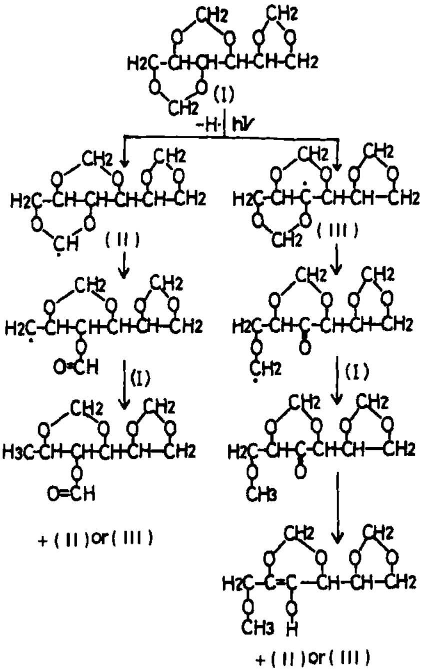


FIG. 1. IR spectra of (a) TCA; (b) fraction I; (c) fraction II.

slopes of these straight lines that the polymerization rate was proportional to the -0.19 power of TCA concentration and the 1.77 power of St concentration. Accordingly, the polymerization rate (R_p) in the presence of TCA could be expressed by Eq. (1).

$$R_p = \text{const.}\ [\text{TCA}]^{-0.19}\ [\text{St}]^{1.77} \qquad (1)$$

Figure 2 shows that the rate of photopolymerization of St decreases with an increase in TCA concentration. It was considered that TCA



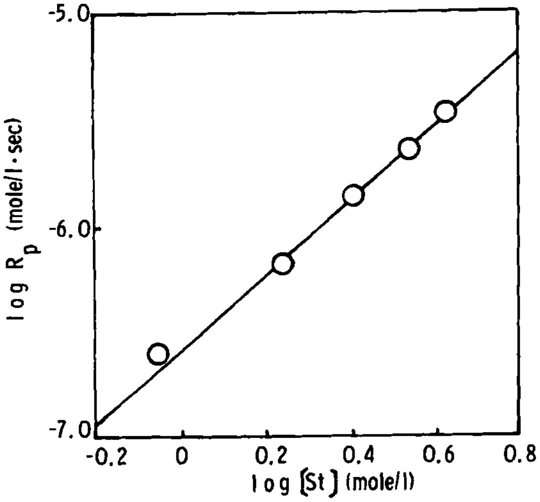


FIG. 2. Effect of TCA concentration on the rate of polymerization at 30° C. [St] = 2.62 mole/liter in benzene.

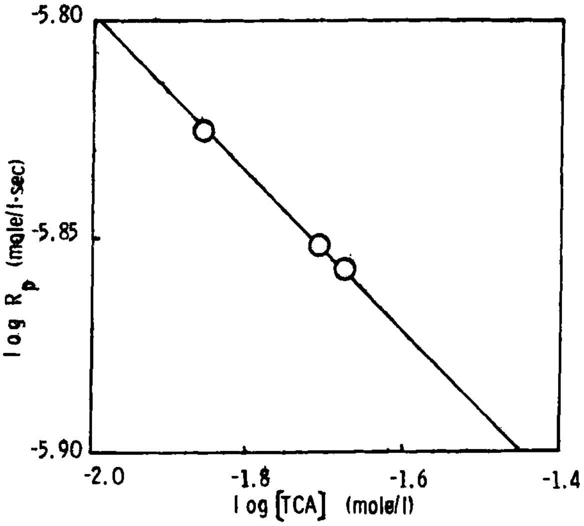


FIG. 3. Effect of St concentration on the rate of polymerization at 30° C. [St] = 2.62 mole/liter in benzene.

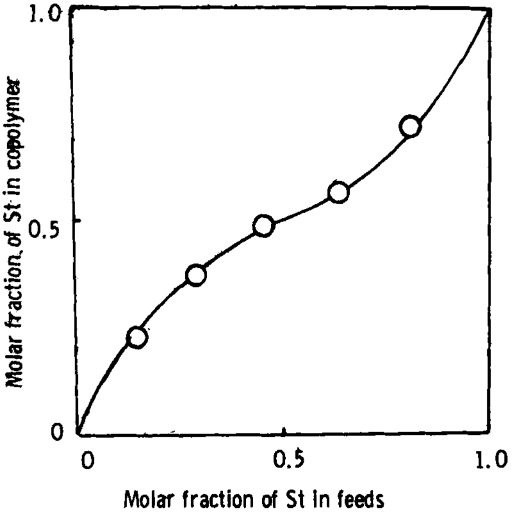


FIG. 4. Copolymerization of St with MMA in the presence of TCA. [St + MMA] = 2.62 mole/liter; [TCA] = 1.30×10^{-2} mole/liter; in benzene; 30° C; 4 hr.

acted as the chain-transfer agent or the terminator rather than the accelerator.

It was found that the molecular weight of the resulting polymer decreased and the oxygen content in the polymer increased with increasing TCA concentration. The chain-transfer constant to TCA was estimated to be 0.16; this was somewhat larger than the values of DO and TU compounds [1, 2]. It was recognized that TCA played an important role as chain-transfer agent, chiefly through abstraction of the active hydrogen atoms.

On the other hand, the polymerization proceeded through a radical mechanism, as shown in Fig. 4.

On the basis of the above views, a polymerization scheme can be written:

Decomposition of sensitizer:

$$S \xrightarrow{k_d} S\cdot + H\cdot$$

Isomerization:

$$S\cdot \xrightarrow{k_{iso}} R\cdot$$

Initiation:

$$2M \xrightarrow{k_i} 2M\cdot$$

Propagation:

$$M\cdot + M \xrightarrow{k_p} M\cdot$$

Chain transfer:

$$M\cdot + S \xrightarrow{k_{trs}} P + S\cdot$$

Termination:

$$M\cdot + M\cdot \xrightarrow{k_t} P$$

$$M\cdot + R\cdot \xrightarrow{k_t} P$$

$$R\cdot + R\cdot \xrightarrow{k_t} D$$

Here S is the sensitizer, M is the vinyl monomer, P is the polymer, D is the dimer of TCA, S• is an acetal radical, H• is a hydrogen radical, R• is the ester or ether radical, and M• is the propagating radical.

Therefore, the rate of photopolymerization can be written as in Eq. (2).

$$R_p = \frac{2k_i k_p [M]^2}{k_{trs}[S] + \sqrt{2k_i k_t [M] + k_d k_t [S]}} \tag{2}$$

Equation (1) can be satisfied with Eq. (2).

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