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## Cyclic Acetal-Photosensitized Polymerization. V. Photopolymerization of Styrene Sensitized by the System of 1,3-Dioxolane and $\alpha$ , $\alpha'$ -Azobisisobutyronitrile

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#### ABSTRACT

The photopolymerization of styrene sensitized by 1,3dioxolane in the presence of  $\alpha, \alpha'$ -azobisisobutyronitrile was carried out in benzene solution at 40° C. The initiation ability of the vinyl polymerization of DO was compared with that of AIBN.

#### INTRODUCTION

It is known that the active hydrogen between two alkoxyl groups in cyclic acetals is abstracted as a radical. We reported that an ester radical generated by photoirradiation of 1,3-dioxolane (DO) could initiate polymerization of vinyl monomers [1]. In this experiment, the photopolymerization of styrene (St) sensitized by DO in the presence of  $\alpha, \alpha'$ -azobisisobutyronitrile(AIBN) was carried out. The decomposition of DO induced by the isobutyronitrile radical generated

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by photoirradiation of AIBN was also investigated, and the initiation ability of DO compared with that of AIBN.

#### EXPERIMENTAL

DO was prepared by the method described in a previous paper [1]. St, AIBN, and benzene were purified by the usual methods.

The procedures for the photodecomposition of DO in the presence of AIBN and the photopolymerization of St in the DO-AIBN system were the same as those reported in the previous paper [1].

The intrinsic viscosity of the resulting polymer was measured in benzene at  $30^{\circ}$  C by using an Ubbelohde viscometer.

#### **RESULTS AND DISCUSSION**

With the concentrations of St and AIBN kept at 2.62 mole/liter and  $6.55 \times 10^{-3}$  mole/liter, respectively, the photopolymerization of St was carried out in the presence of DO in the range of 0-10.2 mole/liter. The results are shown in Table 1. Under these conditions, the polymerization rate R ppr increased slightly, and the degree of polymerization  $\overline{P}_{n}$  and nitrogen content of the resulting polymer

DO (mole/liter)	$R_{ppr} \times 10^{-5}$ (mole/liter-sec)	Polymer			
		C (%)	H (%)	N (%)	$\overline{P}_n^{b}$
0	1.17	91.85	7.74	0.41	130
1.31	1.19	91.82	7.70	0.37	116
2.91	1.22	91,81	7.69	0.27	112
5.82	1.26	91.67	7.69	0.26	106
8.73	1.31	91,60	7.65	0.20	101
10 <b>.2</b>	1.34	91.64	7.63	0.10	1 <b>02</b>

TABLE 1. Photopolymerization of St in the DO-AIBN System<sup>a</sup>

<sup>a</sup>Polymerization conditions: [St] = 2.62 mole/liter; [AIBN] = 6.55 mole/liter; 40° C.

<sup>b</sup>This value was calculated by using the equation [2]:  $[\eta] = 1.0 \times 10^{-4} \overline{M}_n^{0.74}$ .

[St] (mole/liter)	[DO]/[St]	$R_{ppr} \times 10^{-5}$ (mole/liter-sec)	[η] (dl/g)	<u>P</u> n <sup>b</sup>
6.98	0.417	4.06	0.254	382
5.24	1.11	2.83	0.194	<b>2</b> 66
4.36	1.67	2.40	0.162	209
3.49	2.50	1.75	0.132	158

TABLE 2. Bulk Photopolymerization of St in the DO-AIBN System<sup>a</sup>

<sup>a</sup>Polymerization conditions: [AIBN] =  $6.55 \times 10^{-3}$  mole/liter;  $40^{\circ}$ C.

<sup>b</sup>This value was calculated from  $[\eta]$  by using the equation [2]:  $[\eta] = 1.0 \times 10^{-4} \overline{M}_{n}^{0.74}$ .

decreased with increasing DO concentration. The active hydrogen of DO may be abstracted by the isobutyronitrile radical generated by the photoirradiation onto the system, i.e., the decomposition of DO may be induced by the nitrile radical.

The results of bulk photopolymerization of St in the DO-AIBN system are shown in Table 2. The chain-transfer constant of the styryl radical to DO was estimated as  $2.0 \times 10^{-3}$  from Table 2.

The reaction orders under various conditions are summarized in Table 3. It was presumed that they depended on the concentration of reactants in the feed and then DO decomposed in concert with AIBN.

[ DO ]	[AIBN]	[ St]	Order <sup>b</sup>		
(mole/liter)	(mole/liter)	(mole/liter)	m	n	1
1.46-8.73	$1.32 \times 10^{-4}$	2.62	0.19	_	_
4.37	$0.656 - 3.28 \times 10^{-4}$	2.62		0.17	-
1.31	$1.64 - 16.4  imes 10^{-3}$	2.62	-	0.30	-
4.37	$1.32 \times 10^{-4}$	0.873-5.24	-		1.2
1.31	$6.55 imes10^{-3}$	0.873-5.24	-	-	1.3
0	0	0.873-5.24	-	-	1.5

TABLE 3. Reaction Order a

<sup>a</sup>Polymerization was carried out in benzene at 30°C.

<sup>b</sup>Exponents in equation:  $R_p = \text{const.} [DO]^m [AIBN]^n [St]^1$ .

The formate radical and the nitrile radical obtained from the mechanism shown in Eqs. (1)-(5) could initiate the polymerization of vinyl monomers.

$$\begin{array}{c} \overset{c}{} \overset{c}{} \overset{c}{} \overset{c}{} \overset{c}{} \overset{h}{} \overset{h}{} \overset{\nu}{} \overset{c}{} \overset{c}{} \overset{h}{} \overset{h}{} \overset{\nu}{} \overset{c}{} \overset{c}{} \overset{c}{} \overset{h}{} \overset{h}{} \overset{\nu}{} \overset{c}{} \overset{c}{} \overset{c}{} \overset{h}{} \overset{h}{} \overset{h}{} \overset{\nu}{} \overset{c}{} \overset{c}{} \overset{c}{} \overset{h}{} \overset$$

$$H_{2} \begin{pmatrix} CH_{2} & F_{2} \\ 0 & CH_{2} \end{pmatrix} H \begin{pmatrix} CH_{2} & F_{2} \\ 0 & CH_{2} \end{pmatrix} H \begin{pmatrix} CH_{2} & F_{2} \\ 0 & CH_{2} \end{pmatrix}$$
(2)

$$HC \xrightarrow{0} CH_{2} \xrightarrow{0} H-C \xrightarrow{0} OCH_{2}CH_{2}$$
(3)

$$CH_{3}CN \xrightarrow{CH_{3}} + H_{2}C \xrightarrow{O-CH_{2}} - CH_{3}CH \xrightarrow{CH_{3}} + HC \xrightarrow{O-CH_{2}} - CH_{2}$$
(4)

$$H = C_{OCH_2CH_2}^{O} + H_2C_{OCH_2}^{O} + H_2C_{OCH_2}^{O} + HC_{OCH_2CH_3}^{O} + HC_{OCH_2}^{O} + HC_{OC$$

# Accordingly, the polymerization scheme can be written as shown in Eqs. (6)-(14).

$$I \xrightarrow{k_{dI}} 2R \cdot$$
 (6)

$$S \xrightarrow{k} S + H$$
 (7)

$$\mathbf{R} \cdot + \mathbf{S} \xrightarrow{\mathbf{k}_{tr1}} \mathbf{R} + \mathbf{S} \cdot \tag{7}$$

$$s \xrightarrow{k_{Iso}} E$$
. (8)

$$\mathbf{R} \cdot + \mathbf{M} \xrightarrow{\mathbf{k}_{ir}} \mathbf{M} \cdot$$
(9)

.

1-

$$\mathbf{E}^{\bullet} + \mathbf{M} \xrightarrow{\mathbf{K}_{ie}} \mathbf{M}^{\bullet}$$
(10)

$$M + M \xrightarrow{k_i} 2M$$
 (11)

$$\mathbf{M} \cdot + \mathbf{M} \xrightarrow{\mathbf{p}} \mathbf{M} \cdot$$
(12)

$$\mathbf{M} \cdot + \mathbf{S} \xrightarrow{\mathbf{K}_{\mathrm{tr}2}} \mathbf{P} + \mathbf{S} \cdot \tag{14}$$

Here I is AIBN, S is the cyclic acetal, R is isobutyronitrile, M is St, P denotes the polymer, R is isobutyronitrile radical, S is the acetal radical, E is the ester radical, and M is the styryl radical.

If a steady state is assumed for the different types of radical, the rate of polymerization  $R_{ppr}$  in the presence of DO and AIBN can be written as Eq. (15).

$$R_{ppr} = k_{p} \left[ M \cdot \right] \left[ M \right]$$
$$= k_{p} \left( \frac{2k_{i} \left[ M \right] + 2k_{dI} \left[ I \right] + k_{ds} \left[ S \right]}{k_{t}} \right)^{0.5} \left[ M \right]$$
(15)

On the other hand, the rate of polymerization in the absence of DO and AIBN  $(R_{pab})$  is given by Eq. (16):

$$R_{pab} = k_p (2k_i/k_t)^{0.5} [M]^{1.5}$$
(16)

On subtraction of the square of Eq. (16) from the square of Eq. (15), Eq. (17) is obtained:

$$R_{ppr}^{2} - R_{pab}^{2} = (k_{p}^{2}/k_{t})(2k_{dI}[I] + k_{ds}[S])[M]^{2}$$
(17)



FIG. 1. Plots of  $(R_{ppr}^2 - R_{pab}^2)$  vs. [S] or [I]: ( $\circ$ ) [M] = 2.62 mole/liter, [I] = 1.32 × 10<sup>-4</sup> mole/liter; ( $\bullet$ ) [M] = 2.62 mole/liter, [S] = 4.37 mole/liter, in benzene at 40° C.



FIG. 2. Plots of  $(R_{ppr}^2 - R_{pab}^2)$  vs.  $[M]^2$ . [S] = 4.37 mole/liter,  $[I] = 1.32 \times 10^{-4}$  mole/liter, in benzene at 40° C.

The relationships among  $(R_{ppr}^2 - R_{pab}^2)$ , [S] or [I], and [M]<sup>2</sup> are plotted in Figs. 1 and 2; there are the good linear relationships, predicted by Eq. (17). The values of  $k_p^2 k_{ds}^2 / k_t$  and  $2k_p^2 k_{dI}^2 / k_t$  were estimated to be  $3.7 \times 10^{-13}$  liter/mole-sec,  $6.68 \times 10^{-9}$  liter/molesec from the slope and intercept of these straight lines, respectively. Thus, the  $k_{ds}^2 / k_{dI}^2$  value was calculated to be  $0.92 \times 10^{-4}$  by combining these values. It was therefore concluded that the initiation ability of the polymerization of DO is no smaller than that of AIBN on the photopolymerization of St.

#### ACKNOWLEDGMENT

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