Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Ouchi, Tatsuro and Komatsu, Yuji(1977) 'Cyclic Acetal-Photosensitized Polymerization. V. Photopolymerization of Styrene Sensitized by the System of 1,3-Dioxolane and α,α'-Azobisisobutyronitrile', Journal of Macromolecular Science, Part A, 11: 3, 483 — 489

To link to this Article: DOI: 10.1080/00222337708061283

URL: http://dx.doi.org/10.1080/00222337708061283

J. MACROMOL. SCI.–CHEM., A11(3), pp. 483-489 (1977)

Cyclic Acetal-Photosensitized Polymerization. V. Photopolymerization of Styrene Sensitized by the System of 1,3-Dioxolane and α,α′-Azobisisobutyronitrile

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ABSTRACT

The photopolymerization of styrene sensitized by 1,3-dioxolane in the presence of α,α′-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 α,α′-azobisisobutyronitrile(AIBN) was carried out. The decomposition of DO induced by the isobutyronitrile radical generated 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° C by using an Ubbelohde viscometer.

RESULTS AND DISCUSSION

With the concentrations of St and AIBN kept at 2.62 mole/liter and 6.55×10^{-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 $\bar{P}_n$ and nitrogen content of the resulting polymer

TABLE 1. Photopolymerization of St in the DO-AIBN System[a]

DO (mole/liter)	$R_{ppr} \times 10^{-5}$ (mole/liter-sec)	Polymer			
		C (%)	H (%)	N (%)	$\bar{P}_n$[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
10.2	1.34	91.64	7.63	0.10	102

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

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

TABLE 2. Bulk Photopolymerization of St in the DO-AIBN System[a]

[St] (mole/liter)	[DO]/[St]	$R_{ppr} \times 10^{-5}$ (mole/liter-sec)	[η] (dl/g)	$\overline{P}_n$[b]
6.98	0.417	4.06	0.254	382
5.24	1.11	2.83	0.194	266
4.36	1.67	2.40	0.162	209
3.49	2.50	1.75	0.132	158

[a] Polymerization conditions: [AIBN] = 6.55×10^{-3} mole/liter; 40° C.

[b] This value was calculated from [η] 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 2.0×10^{-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.

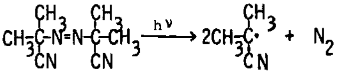
TABLE 3. Reaction Order [a]

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

[a] Polymerization was carried out in benzene at 30° C.

[b] Exponents in equation: $R_p = \text{const.}\,[DO]^m[AIBN]^n[St]^l$.

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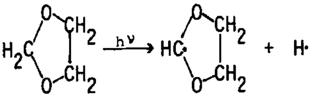
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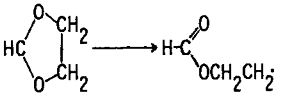
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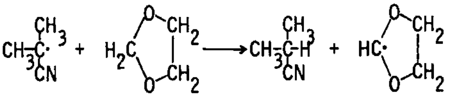
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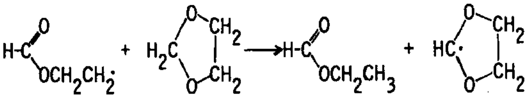
(5)

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

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

$$S \xrightarrow{k_{ds}} S\cdot + H\cdot \qquad (7)$$

$$R\cdot + S \xrightarrow{k_{trI}} R + S\cdot \qquad (7)$$

$$S\cdot \xrightarrow{k_{Iso}} E\cdot \qquad (8)$$

$$R\cdot + M \xrightarrow{k_{ir}} M\cdot \qquad (9)$$

$$E\cdot + M \xrightarrow{k_{ie}} M\cdot \tag{10}$$

$$M + M \xrightarrow{k_i} 2M\cdot \tag{11}$$

$$M\cdot + M \xrightarrow{k_p} M\cdot \tag{12}$$

$$M\cdot + M\cdot \xrightarrow{k_t} P \tag{13}$$

$$M\cdot + S \xrightarrow{k_{tr2}} P + S\cdot \tag{14}$$

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).

$$R_{ppr} = k_p[M\cdot][M]$$

$$= k_p\left(\frac{2k_i[M] + 2k_{dI}[I] + k_{ds}[S]}{k_t}\right)^{0.5}[M] \tag{15}$$

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

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

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

$$R_{ppr}^2 - R_{pab}^2 = (k_p^2/k_t)(2k_{dI}[I] + k_{ds}[S])[M]^2 \tag{17}$$

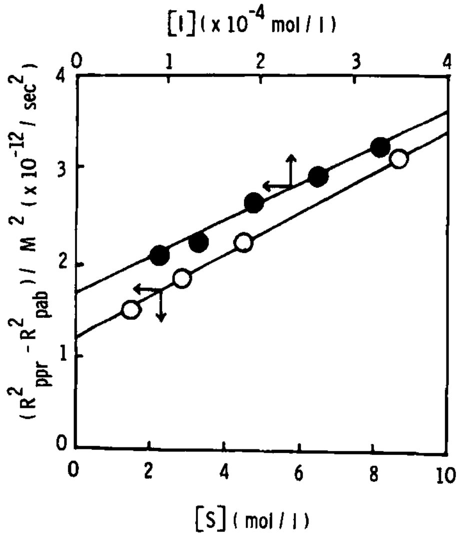

FIG. 1. Plots of (R_{ppr}^2 - R_{pab}^2) vs. [S] or [I]: (○) [M] = 2.62 mole/liter, [I] = 1.32 × 10^{-4} mole/liter; (●) [M] = 2.62 mole/liter, [S] = 4.37 mole/liter, in benzene at 40° C.

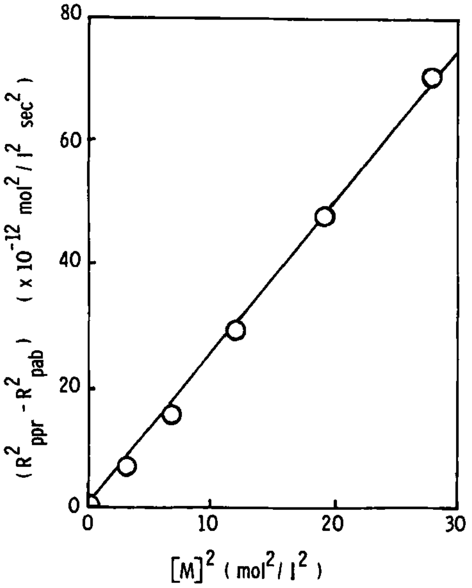

FIG. 2. Plots of (R_{ppr}^2 - R_{pab}^2) vs. $[M]^2$. [S] = 4.37 mole/liter, [I] = 1.32 × 10^{-4} mole/liter, in benzene at 40° C.

The relationships among $(R_{ppr}{}^2 - R_{pab}{}^2)$, [S] or [I], and $[M]^2$ are plotted in Figs. 1 and 2; there are the good linear relationships, predicted by Eq. (17). The values of $k_p{}^2k_{ds}/k_t$ and $2k_p{}^2k_{dI}/k_t$ were estimated to be 3.7×10^{-13} liter/mole-sec, 6.68×10^{-9} liter/mole-sec from the slope and intercept of these straight lines, respectively. Thus, the k_{ds}/k_{dI} value was calculated to be 0.92×10^{-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

The authors are grateful to Prof. Dr. M. Imoto for advice.

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Accepted by editor July 14, 1976
Received for publication July 21, 1976