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Cyclic Acetal-Photosensitized Polymerization. 9. Photopolymerization of Triallylidene Sorbitol

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Cyclic Acetal-Photosensitized Polymerization.
9. Photopolymerization of Triallylidene Sorbitol

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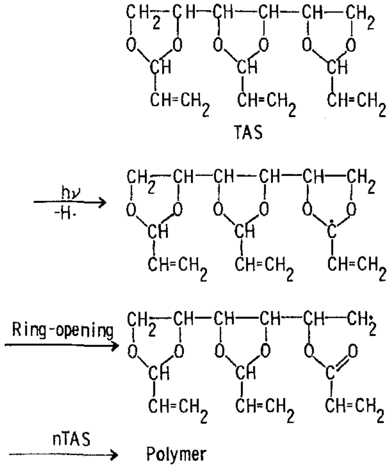
ABSTRACT

The photopolymerization of triallylidene sorbitol (TAS) was carried out in benzene at 40° C without the usual initiator. The polymerization of TAS was found to be initiated with the ester radical generated via the acetal radical from TAS by means of photoirradiation. The rate of polymerization and the molecular weight of polymer were small due to the degradative chain transfer. It was kinetically investigated from the standpoints of the degradative chain transfer by the allylidene group and the cyclization by three double bonds. The following results were obtained: (1) The relation between the rate of polymerization, R_p, the monomer concentration, $[M]$, could be expressed by $[M]/R_p = (A[M] + B)/(3[M] + C)$, where A, B, and C were constant; (2) the ratio of the rate constant of unimolecular cyclization to the total rate constant of bimolecular propagation and the chain transfer of uncyclized radical was estimated to be 3.0 mol/dm^3. A small amount of cyclopolymerization took place.

INTRODUCTION

In a previous paper [1] we reported that diallylidene pentaerythritol (DAPE), which is a divinyl compound containing two cyclic acetal groups, could be polymerized by means of photoirradiation without an ordinary radical initiator to give oligomer. The vinyl polymerization of DAPE was proposed to be initiated by the ester radical generated through an acetal radical by means of photoirradiation onto DAPE. Accordingly, it was expected that the polymerization of triallylidene sorbitol (TAS), which was the trivinyl compound containing three cyclic acetal groups, could be initiated by means of photoirradiation, as shown in the following scheme:



In the present paper the photopolymerization of TAS without the ordinary radical initiator is investigated and kinetically discussed from the standpoints of the degradative chain transfer by the allylidene group and the cyclization by three double bonds. The kinetic equations are applied by the modification of those derived in the photopolymerization of DAPE.

EXPERIMENTAL

Materials

TAS was prepared from D-sorbitol and acrolein by the method of Fisher and Smith [2], bp 194-196°C/8 mmHg (lit. bp 149-151°C/0.9 mmHg). Found: C, 60.82%; H, 6.88%; bromine value (BV), 159; molecular weight ($\overline{M}_n$), 296. Calculated for $C_{15}H_{20}O_6$: C, 60.80%; H, 6.80%; BV, 161; $\overline{M}_n$, 296.

Benzene was purified by the usual method.

Procedures

Photopolymerization was carried out by the same procedure reported in a previous paper [3]. The polymer was precipitated by petroleum ether and followed by centrifuging. The conversion of the polymer was less than 10%. The rate of polymerization was determined by measurement of the weight of polymer.

The isomerization rate was determined by measurement of the saponification value (SV) of the reaction mixture.

Characterization of Polymer

The identification of polymer was carried out by measurements of IR and ^{1}H-NMR spectra and by elemental analysis. The residual unsaturation (R_{us}) and the degree of esterification (E_s) of the polymer were estimated by measurement of BV and SV of polymer, respectively, according to a previous paper [3]. The molecular weight of polymer was measured by means of a vapor-pressure osmometer at 37° C, using benzene as the solvent.

RESULTS AND DISCUSSION

Photopolymerization of TAS

The polymerization of TAS was carried out under different monomer concentrations in benzene at 40° C. The results are given in Table 1, in which the values of BV, R_{us}, SV, E_s, and $\overline{M}_n$ of the polymer are estimated by extrapolating to zero for conversion by means of photoirradiation. TAS was found to be able to polymerize without the ordinary initiator. However, the rate of polymerization of TAS and the molecular weight of the polymer were small. Thus the polymer obtained was concluded to be the oligomer which is hereinafter described as the polymer.

Structure of Polymer

IR spectra of the monomer and polymer of TAS are shown in Fig. 1. Four peaks at 1200-1040 cm^{-1} are assigned to the cyclic acetal group, and those at 1641, 990, and 910 cm^{-1} to the vinyl group. The band at 1735 cm^{-1}, assigned to the carbonyl group in the polymer, was not recognized in the monomer, and the peaks of the cyclic acetal and the vinyl group in the polymer are smaller than those in the monomer.

The ^{1}H-NMR spectrum of TAS polymer compared with that of TAS

TABLE 1. Photopolymerization of TAS at 40°C in Benzene

[M] (mol/dm^3)	$R_p \times 10^8$ (mol dm^{-3} s^{-1})	Polymer				
		BV^a	R_{us}^{a}	SV^a	E_s^{a}	M_n^{a}
1.69	2.12	65.81	0.414	12.9	0.068	1206
1.35	1.49	61.22	0.385	15.9	0.084	1068
1.01	0.964	52.79	0.332	17.1	0.090	995
0.844	0.751	49.29	0.310	18.2	0.096	921
0.675	0.543	42.77	0.269	20.2	0.106	890

[a] The values were estimated by extrapolating to zero for conversion.

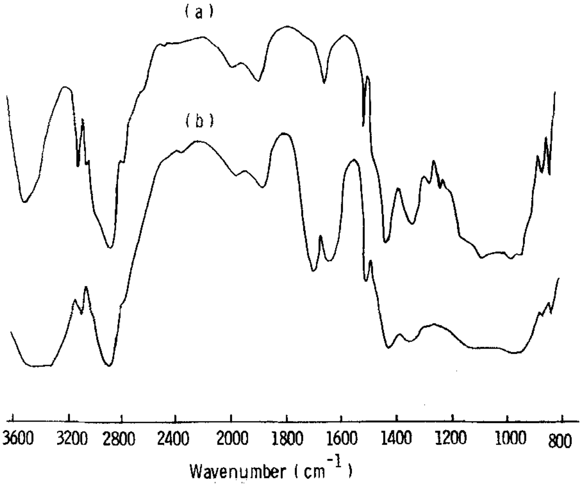


FIG. 1. IR spectra of (a) monomer and (b) polymer of TAS.

monomer is shown in Fig. 2. In the monomer spectrum the peaks at 3.6-4.2 ppm and 4.9-5.7 ppm are attributed to the protons of the cyclic acetal and the allylidene groups, respectively. These bands in the polymer are smaller than those in the monomer. In the polymer spectrum, the absorptions assigned to the protons of the methine-methylene group obtained from the polymerization of the vinyl group and the new bands of the allylidene group appear at 0.9-1.8 ppm and 6.6-7.3 ppm, respectively.

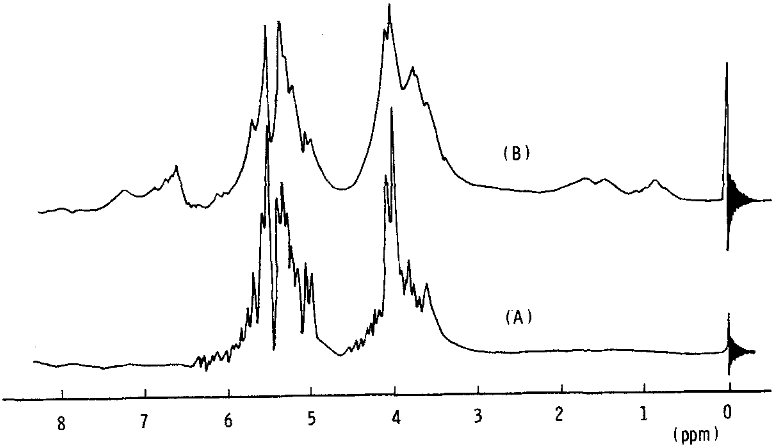


FIG. 2. ^{1}H-NMR spectra of (A) monomer and (B) polymer. Solvent $CDCl_3$, reference TMS, temperature 25°C.

Moreover, from the results of elemental analysis, the composition of the polymer was found to be same as that of the monomer.

It was therefore presumed that the polymer having the ester unit as an end group consisted mainly of the vinyl propagating unit.

Kinetic of Photopolymerization

The initial polymerization of TAS is kinetically treated in a similar manner to that proposed in a previous paper [1], including chain transfer and cyclization. The kinetic equations are derived by assuming the following reaction scheme:

Decomposition	$M \xrightarrow{h\nu} S\cdot$	k_d
Isomerization	$S\cdot \longrightarrow R\cdot$	k_{iso}
Initiation	$R\cdot + M \longrightarrow M\cdot$	k_i
Cyclization	$M\cdot \longrightarrow M_c\cdot$	k_c
Propagation	$M\cdot + M \longrightarrow M\cdot$	k_p
	$M_c\cdot + M \longrightarrow M\cdot$	k_{cp}

(1)

(continued)

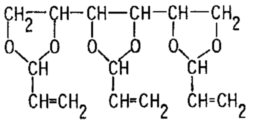
$$\begin{array}{lll} & R\cdot + M \longrightarrow R' + S\cdot & k_{trr} \\ \text{Chain transfer} & M\cdot + M \longrightarrow P + S\cdot & k_{trm} \\ & M_c\cdot + M \longrightarrow P + S\cdot & k_{trmc} \\ \text{Stabilization} & S\cdot \longrightarrow M^* & k_{ts} \end{array} \qquad (1)$$

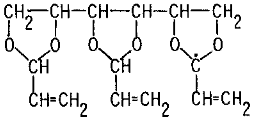
where R' is an ester and P is a polymer.

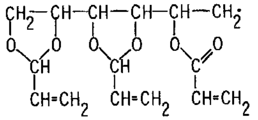
Proof of Radical Mechanism

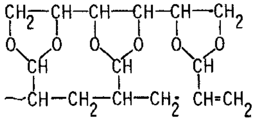
The ESR spectrum of the reaction mixture at -160° C is shown in Fig. 3. A symmetrical absorption of about 20 gauss appeared at g = 2.0038. The existence of a relatively stable radical was found. Thus the polymerization may proceed through a radical mechanism.

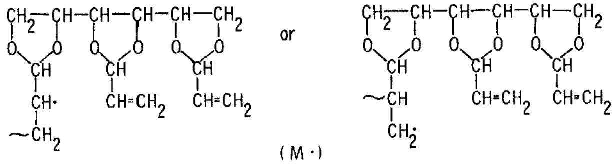
M, S·, R·, M·, M_c·, and M* have the structures


(M)

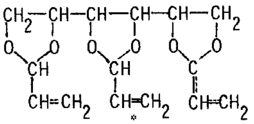

(S·)


(R·)


(Mc·)



(M·)


(M*)

where H· denotes a hydrogen radical.

The following equations can be derived by assuming steady-state conditions.

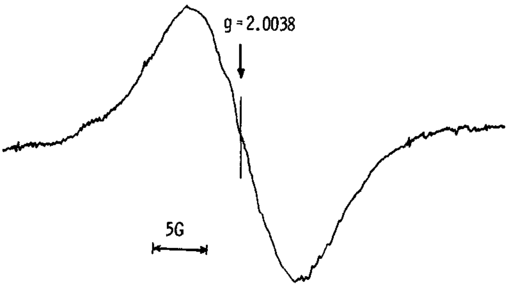


FIG. 3. ESR spectrum of reaction mixture at -160° C in benzene.

$$[\mathrm{S}\cdot] = \frac{3k_d}{k_{ts}}[\mathrm{M}] \tag{2}$$

$$[\mathrm{R}\cdot] = \frac{k_{iso}k_d}{(k_i + k_{trr})k_{ts}} \tag{3}$$

$$[\mathrm{M}\cdot] = \left\{\frac{k_d k_i}{k_c k_{trmc} + 3k_{trm}(k_{cp} + k_{trmc})[\mathrm{M}]}\right\}\left\{\frac{3k_{iso}(k_{cp} + k_{trmc})}{k_{ts}(k_i + k_{trr})}\right\}[\mathrm{M}] \tag{4}$$

$$[\mathrm{M_c}\cdot] = \left\{\frac{k_c k_{iso} k_d k_i}{3k_{trm}(k_{cp} + k_{trmc})[\mathrm{M}] + k_c k_{trmc}}\right\}\left\{\frac{1}{k_{ts}(k_i + k_{trr})}\right\} \tag{5}$$

Equations (2)-(5) are rewritten as Eqs. (6)-(8):

$$[\mathrm{R}\cdot] = \frac{\gamma_i}{k_i} \tag{6}$$

$$[\mathrm{M}\cdot] = \frac{3\gamma_i[\mathrm{M}]}{k_c\beta_{trmc} + 3k_{trm}[\mathrm{M}]} \tag{7}$$

$$[\mathrm{M_c}\cdot] = \frac{\gamma_i\alpha_c}{\alpha_c k_{trmc} + 3k_{trmc}\alpha_{trm}[\mathrm{M}]/\beta_{trmc}} \tag{8}$$

where

$$\gamma_i = \frac{k_{iso}k_dk_i}{k_{ts}(k_i + k_{trr})}$$

$$\alpha_c = \frac{k_c}{k_p + k_{trm}}$$

$$\alpha_{trm} = \frac{k_{trm}}{k_p + k_{trm}} \tag{9}$$

$$\beta_{trmc} = \frac{k_{trmc}}{k_{cp} + k_{trmc}}$$

The Rate of Isomerization

The rate of isomerization, R_{iso}, is given by

$$R_{iso} = k_{iso}[S\cdot]$$

$$= \frac{3k_dk_{iso}}{k_{ts}}[M] \tag{10}$$

The Rate of Polymerization

The rate of polymerization, R_p, is given by

$$R_p = d[M]_{eff}/dt$$

$$= 3\gamma_i \left\{\frac{3[M] + \alpha_c}{3\,\alpha_{trm}[M] + \alpha_c\beta_{trmc}}\right\}[M] \tag{11}$$

Equation (11) can be written as

$$R_p = \left\{\frac{3[M] + \alpha_c}{3\,\alpha[M] + \alpha_c\beta}\right\}[M] \tag{12}$$

which, on rearrangement, gives

$$\frac{[M]}{R_p} = \frac{\alpha_c(\beta - \alpha)}{3[M] + \alpha_c} + \alpha \tag{13}$$

where

$$\left.\begin{aligned} \alpha &= \frac{\alpha_{trm}}{3\gamma_i} \\ \beta &= \frac{\beta_{trmc}}{3\gamma_i} \end{aligned}\right\} \tag{14}$$

The Residual Unsaturation

The rate of formation of pendent double bonds in the polymer is given by

$$\begin{aligned} 3d[m]/dt &= 3k_i[R\cdot][M] + 3k_p[M\cdot][M] + 3k_{cp}[M_c\cdot][M] - k_c[M\cdot] \\ &= \left\{\frac{3[M]}{3\,\alpha[M] + \alpha_c\beta}\right\}[M] \end{aligned} \tag{15}$$

By the combination of Eqs. (12) and (15), the residual unsaturation of polymer, R_{us}, is

$$\begin{aligned} 3R_{us}/2 &= 3d[m]/d[M]_{eff} \\ &= \frac{3[M]}{3[M] + \alpha_c} \end{aligned} \tag{16}$$

which, on rearrangement, gives

$$\frac{2}{3R_{us}} - 1 = \frac{\alpha_c}{3[M]} \tag{17}$$

Degree of Esterification

The rate of the formation of ester in polymer is shown by

$$3d[e]/dt = 3k_i[R\cdot][M]$$
$$= 3\gamma_i[M] \tag{18}$$

By the combination of Eqs. (11) and (18), the degree of esterification of polymer, E_s, can be written as

$$3E_s = 3d[e]/d[M]_{eff}$$
$$= 3\gamma_i[M]/R_p \tag{19}$$

Application of Derived Equation

First, the photoirradiation onto TAS was carried out in benzene at 40°C. By measuring SV of the reaction mixture, the first-reaction plots for the isomerization of TAS to the ester are made. As shown in Fig. 4, a good straight line was obtained. Therefore, Eq. (10) was found to be valid; R_{iso} was proportional to the first power of the concentration of TAS.

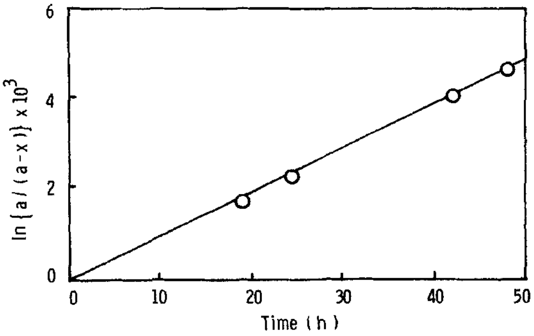


FIG. 4. First-order reaction plots in the isomerization of TAS to ester, with a = the initial monomer concentration (1.01 mol/dm^3) and x = the reacted monomer concentration.

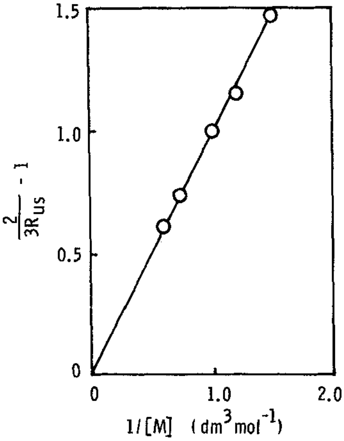


FIG. 5. Plots of $(2/3R_{us} - 1)$ vs $1/[M]$.

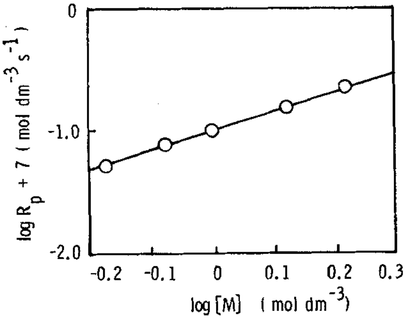


FIG. 6. Plots of log R_p vs log $[M]$ at 40°C.

As can be seen from Table 1, the residual unsaturation decreased with a decrease of monomer concentration; there was a tendency to cyclize. The plots of $(2/3R_{us} - 1)$ vs $1/[M]$ are shown in Fig. 5. The straight line through the point of origin was obtained, as predicted by Eq. (17). From the slope, the α_c value was calculated to be 3.0 mol/dm^3; a little cyclization took place.

Plots of log R_p vs log $[M]$ are shown in Fig. 6. From this figure it was found that the rate of polymerization was proportional to the 1.8 power of the concentration of TAS.

By using the α_c values obtained above, plots of $[M]/R_p$ vs

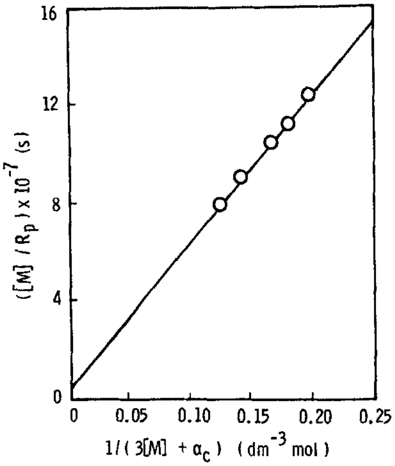


FIG. 7. Plots of $[M]/R_p$ vs $1/(3[M]$ at $\alpha_c)$.

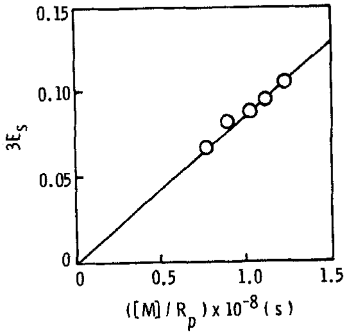


FIG. 8. Plots of $3E_s$ vs $[M]/R_p$.

$1/(3[M] + \alpha_c)$ according to Eq. (13) are shown in Fig. 7. There was the good linear relationship. From the intercept of the ordinate at the zero point and from the slope of the straight line, the values of α and β were estimated to be 2.9×10^6 and 2.1×10^8 s, respectively.

Plots of $3E_s$ vs $[M]/R_p$ are shown in Fig. 8. A straight line through the point of origin was obtained, as predicted by Eq. (19). From the slope of the straight line, the γ_i value could be estimated.

TABLE 2. Parameters of TAS Compared with DAPE

Monomer	γ_i (s^{-1})	α_{trm}	β_{trmc}	α_c (mol/dm^3)
TAS	2.9×10^{-10}	2.5×10^{-3}	0.18	3.0
DAPE	1.4×10^{-9}	1.4×10^{-3}	0.14	1.1

The values of α_{trm} and β_{trmc} for TAS, obtained by applying α, β, and γ_i to Eq. (14), were compared with those for DAPE (Table 2).

It was found the values of α_{trm} and β_{trmc} for TAS were larger than those for DAPE. Consequently, the degradative chain transfer was found to occur more readily on TAS than on DAPE.

On the other hand, the α_c value for TAS was larger than that for DAPE; the triallylidene compound was cyclized more easily than the diallylidene compound. The difference in steric hindrance between tri- and diallylidene cyclic acetals may contribute to such a tendency.

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