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Cyclic Acetal-Photosensitized Polymerization. VI. Photopolymerization of 2-Vinyl-1,3-dioxolane

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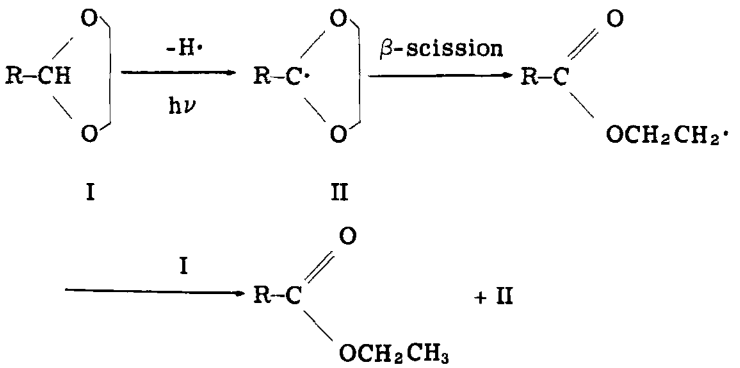
ABSTRACT

The photopolymerization of 2-vinyl-1,3-dioxolane (VDO) was carried out in benzene at 40°C without use of the usual radical initiator. VDO was decomposed by means of photoirradiation to a cyclic acetal radical which transformed instantly into the ester radical by β-scission of dioxolane ring: the vinyl polymerization could be initiated by the ester radical. Because of the degradative chain transfer by allylidene group, the rate of polymerization and the molecular weight of polymer were very small.

INTRODUCTION

Recently we reported that 1,3-dioxolane (DO) compounds were effective for the photopolymerization of vinyl monomers [1]. Since the active hydrogen between two alkoxyl groups in 1,3-DO compounds is abstracted as a radical, they are rearranged to the corresponding esters by means of photoirradiation, as shown in Eq. (1).



(1)

Accordingly, the polymerization of vinyl compounds was initiated by the above ester radical.

The present paper deals with the photopolymerization of 2-vinyl-1,3-dioxolane (VDO), which is vinyl monomer concluding a cyclic acetal group. It was also expected that the ester radicals generated from VDO by means of photoirradiation should attack vinyl groups of VDO and initiate the polymerization.

A number of studies on the polymerization of VDO were reported: the ring-opening polymerization of VDO with cationic catalyst [2, 3] and the radical polymerization of VDO with α,α'-azobisisobutyronitrile by the carbon-carbon double bond addition route [4, 5]. Most of the work on the polymerization of VDO have dealt with the polymerization with the initiator. On the other hand, the polymerization of VDO without the initiator was carried out by γ-ray irradiation [4]; this follows two modes of vinyl and 1,3-hydrogen migration. However, this polymerization has not been kinetically investigated by considering the initiation scheme.

This paper deals with the photopolymerization of VDO without use of radical initiator. The initiation scheme was kinetically studied, and the degradative chain transfer owing to allylidene group was further discussed.

EXPERIMENTAL

Materials

VDO was prepared according to the method of Fischer [6], i.e., by reaction of acrolein with ethylene glycol. After being dried over anhydrous magnesium sulfate, it was purified by fractional distillation in a nitrogen atmosphere; yield 50%; bp 115-117°C (lit. mp 114-116°C).

Solvents were purified by the usual methods.

Procedure

A glass tube (18 cm in diameter) was charged with measured amounts of monomer and benzene, degassed several times with a mercury diffusion pump, and then sealed off in vacuo. The photopolymerization was carried out under the same conditions as reported in a previous paper [1]. After a given period of time, the polymer was separated by pouring into a large amount of cyclohexane and following by centrifuging. The polymer obtained was then washed repeatedly with precipitating agent and dried under vacuum to a constant weight.

The rate of polymerization was determined by measurement of the weight of dried polymer or the bromine value (BV) of the reaction mixture.

On the other hand, the isomerization rate was determined by measurement of the saponification value (SV) of the reaction mixture.

ESR spectra of the reaction mixture were measured with use of a Hitachi Company MPU-3B X-band spectrometer, at room temperature.

Characterization of Polymer

The ester content and the double bond content in polymer were determined from SV and BV of the polymer, respectively. A 0.1-g portion of polymer was saponified with 10 ml of 0.1 $\underline{N}$ alcoholic KOH under reflux for 8 hr. The ester content in polymer was determined by titration of the excess base with 0.1 $\underline{N}$ HCl solution. To the reaction mixture, 10 ml of 5 $\underline{N}$ H_2SO_4 solution and 5 ml of 0.2 $\underline{N}$ KBr-$KBrO_3$ solution were added and then allowed to stand for 3 hr in the dark. After 5 ml of 0.2 $\underline{N}$ KI aqueous solution was added to the mixture, by titration of excess bromine with 0.1 $\underline{N}$ sodium thiosulfate solution the double bond content in polymer was calculated.

The molecular weight ($\overline{M}_n$) was measured by means of a vapor-pressure osmometer (Hewlett-Packard Model-302) at 37°C, using methanol as a solvent.

The infrared spectra were measured with use of a Shimadzu infrared spectrophotometer (Model IR-27 G) with sodium chloride prism.

The proton magnetic resonance (^{1}H) spectrum was obtained at 60 MHz with a Japan Electron Optics, Model JNM 3H60 spectrometer.

RESULTS AND DISCUSSION

Photopolymerization of VDO

The result of the photopolymerization of VDO is shown in Table 1. By means of photoirradiation, VDO was able to polymerize without use of usual radical initiator. The conversion of VDO and the molecular weight of polymer were quite small owing to the degradative chain transfer by allylidene group. The polymer obtained was viscous and soluble in chloroform, acetone, and p-dioxane.

Structure of Polymer

Infrared spectrum of polymer compared with that of monomer is shown in Fig. 1. The band at 1735 cm^{-1} is assigned to the carbonyl group, peaks at 1200-1000 cm^{-1} to the cyclic acetal group, and those at 1650, 990, and 910 cm^{-1} to the vinyl group.

On the other hand, the ^{1}H-NMR spectrum of polymer is shown in Fig. 2; the peaks between 8.2 and 8.7 τ are attributed to methylene and methine groups resulting from the polymerization of vinyl group; the signal of the acetal hydrogen appears at 5.2 τ; the band of 6.0 τ is attributed to methylene group of the cyclic acetal. There is a peak at 6.5 τ representing the protons of the open ester. A wide band is also observable between 3.8 and 4.8 τ, which can be attributed to the hydrogen atoms of vinyl group. Moreover, it was clear from Table 1 that in the initial reaction, the number of double bonds and number of esters in a molecular were nearly equal to 1.0.

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

Therefore, it was concluded that the polymer contained the structure III as a main unit. As the reaction proceeds, the number of double bonds in the molecular became slightly smaller than 1.0 and number of esters in a molecular became slightly larger than 1.0. This change suggests partial reaction of the end double bond and partial ring-opening of pendent cyclic acetal in polymer.

TABLE 1. Photopolymerization of VDO[a]

No.	VDO (mole/ liter)	Time (hr)	Conversion (%)	Polymer						
				$\overline{M}_n$	BV	Double bond content	SV	Ester content	Number of double bond in a molecule	Number of ester in a molecule
1	2.00	41	2.85	462	35.2	0.220	125	0.223	1.02	1.03
2	3.00	41	2.63	508	30.4	0.190	120	0.214	0.965	1.09
3[b]	4.00	41	2.74	434	34.9	0.219	128	0.229	0.951	0.992
4	4.00	60	4.01	460	32.5	0.204	131	0.234	0.937	1.07
5	4.00	80	5.15	492	29.6	0.185	130	0.232	0.911	1.14
6[c]	5.00	41	2.51	465	33.8	0.212	130	0.232	0.983	1.08
7	6.00	41	2.97	490	31.5	0.197	133	0.238	0.966	1.16

[a] Solvent, benzene; temperature, 30 °C.
[b] Calcd for $C_5H_8O_2$: C, 59.98%; H, 8.05%. Found: C, 59.91%; H, 8.09%.
[c] Found: C, 59.62%; H, 8.10%.

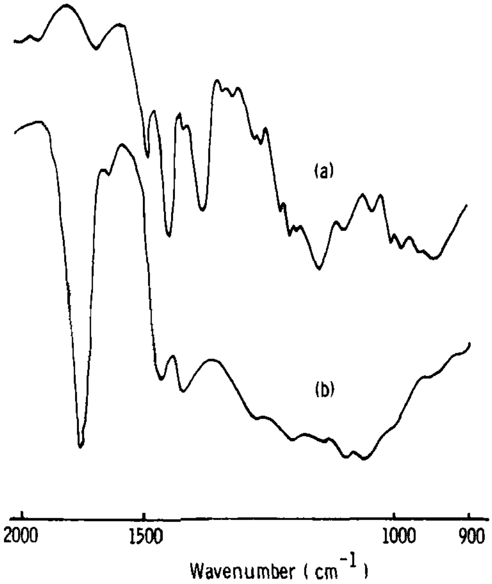


FIG. 1. IR spectra of (a) monomer and (b) polymer.

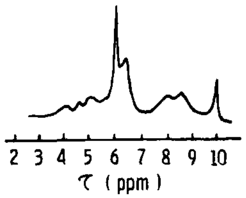
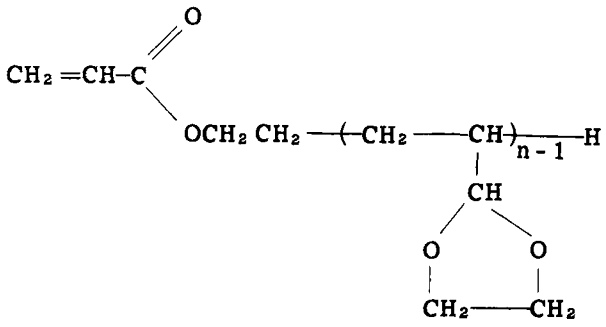


FIG. 2. ^{1}H-NMR-spectrum of polymer. Solvent, $CDCl_3$; temp, 30°C.

Rate of Polymerization

Photopolymerization of VDO was carried out in benzene solution at 40°C. The plots of time vs. conversion obtained by the weight method are shown in Fig. 3. The reasonableness of these plots was checked by measurement of BV of the reaction mixture. Regardless of the concentration of VDO in the feed, the relation between time and



III

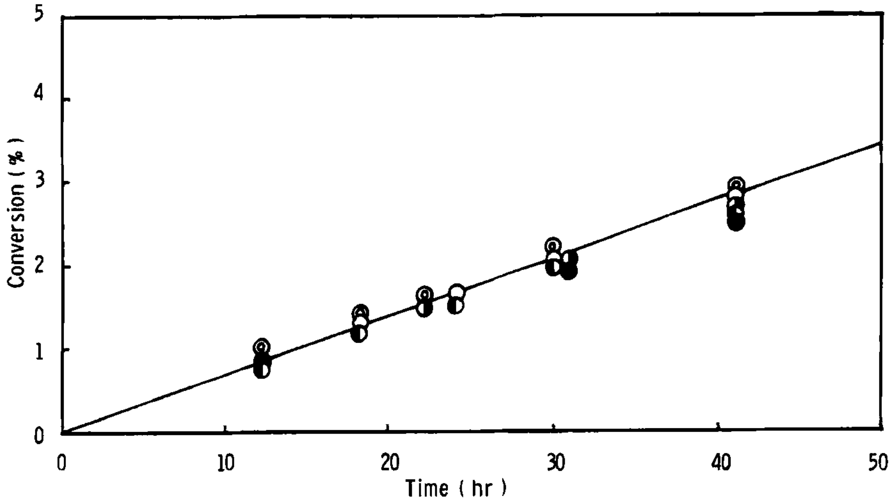


FIG. 3. Plots of conversion vs. time at 40°C: $[VDO]_0$ = 2.00 mole/liter; (◐) 3.00 mole/liter; (◑) 4.00 mole/liter; (●) 5.00 mole/liter; (◎) 6.00 mole/liter.

conversion followed a straight line; the rate of polymerization was expressed by Eq. (2):

$$R_p = k[VDO] \tag{2}$$

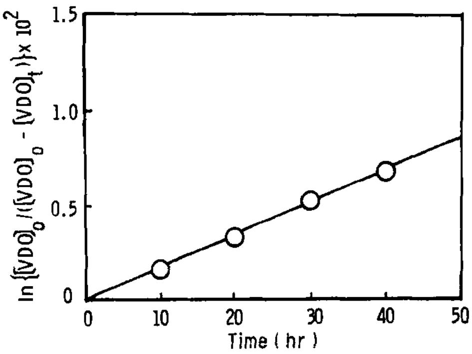


FIG. 4. Plots of ln $\{[VDO]_0/([VDO]_0 - [VDO]_t)\}$ vs. time at 40°C; $[VDO]_0 = 4.00$ mole/liter.

Moreover, the isomerization of VDO was found to follow a first-order reaction as shown in Fig. 4.

Proof of Radical Mechanism

The ESR spectrum of the reaction mixture after photoirradiation is shown in Fig. 5. A sharp symmetric absorption appeared about 2 gauss. The existence of relative stable radical was found. The polymerization may proceed through a radical mechanism.

Kinetics of Photopolymerization

In the initial reaction, the ring-opening of pendent cyclic acetal and the reaction of end double bond were negligible. Therefore, a reaction scheme can be written as shown in Eqs. (3)-(8).

Decomposition:

$$M \xrightarrow{k_d} S\cdot + H\cdot \qquad (3)$$

Isomerization:

$$S\cdot \xrightarrow{k_{iso}} R\cdot \qquad (4)$$

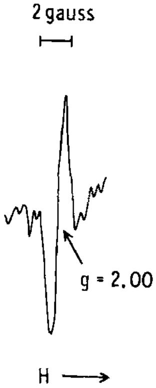


FIG. 5. ESR spectrum of reaction mixture at room temperature.

Initiation:

$$R\cdot + M \xrightarrow{k_i} M\cdot \tag{5}$$

Propagation:

$$M\cdot + M \xrightarrow{k_p} M\cdot \tag{6}$$

Chain Transfer:

$$R\cdot + M \xrightarrow{k_{trr}} R + S\cdot \tag{7a}$$

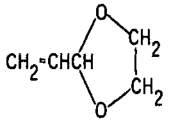
$$M\cdot + M \xrightarrow{k_{trm}} P + S\cdot \tag{7b}$$

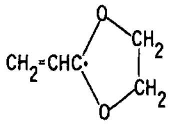
Stabilization:

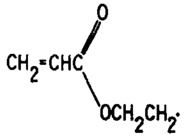
$$S\cdot \xrightarrow{k_{ts}} M^* \tag{8}$$

Here M, $S\cdot$, $R\cdot$, $M\cdot$, and M^* have the structures shown.

In addition, the formation of ethyl acrylate, R, was confirmed by gas chromatography.


(M)


(S·)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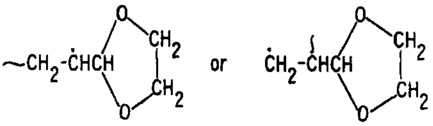
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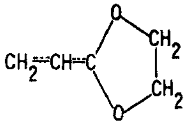
(M*)

By assuming steady-state conditions Eqs. (9)-(11) are derived.

$$[S\cdot] = (k_d/k_{ts})[M] \tag{9}$$

$$[R\cdot] = k_d k_{iso}/k_{ts}(k_{ir} + k_{trr}) \tag{10}$$

$$[M\cdot] = k_d k_{iso} k_i/k_{trm} k_{ts}(k_i + k_{trr}) \tag{11}$$

The rate of isomerization R_{iso} is given by Eq. (12).

$$\begin{aligned} R_{iso} &= k_{iso}[S\cdot] \\ &= (k_d k_{iso}/k_{ts})[M] \end{aligned} \tag{12}$$

The rate of polymerization R_p is given by Eq. (13).

$$\begin{aligned} R_p &= d[M]_{eff}/dt \\ &= k_i[R\cdot][M] + k_p[M\cdot][M] \\ &= \left(\frac{k_d k_{iso} k_i}{k_{ts} k_{trm}}\right)\left(\frac{k_p + k_{trm}}{k_i + k_{trr}}\right)[M] \end{aligned} \tag{13}$$

On the other hand, the rates of formation of ester and double bond in the polymer are given by Eq. (14).

$$\begin{aligned} d[m]/dt &= d[e]/dt \\ &= k_i[R\cdot][M] \\ &= \{k_d k_{iso} k_i / k_{ts}(k_i + k_{trr})\}[M] \end{aligned} \tag{14}$$

By combination of Eqs. (13) and (14), the ester content and the double bond content in the polymer, we obtain Eq. (15).

$$\begin{aligned} d[m]/d[M]_{eff} &= d[e]/d[M]_{eff} \\ &= k_{trm}/(k_p + k_{trm}) \end{aligned} \tag{15}$$

Moreover, the degree of polymerization $\overline{P}_n$ is given by

$$\begin{aligned} \overline{P}_n &= R_p/R_{trm} \\ &= (k_p + k_{trm})/k_{trm} \end{aligned} \tag{16}$$

Application of Derived Equation

First, Eq. (2), obtained experimentally, satisfied Eq. (13), which was derived theoretically. Secondly, a linear relationship obtained in Fig. 4 showed the completion of Eq. (12). The values of $k_d k_{iso}/k_{ts}$ and $k_d k_{iso} k_i (k_p + k_{trm})/k_{ts} k_{tm} (k_i + k_{trr})$ calculated from the slope of straight lines plotted in Figs. 3 and 4 are summarized in Table 2.

As is clear from Table 1, the ester contents in the polymer were approximately equal to the double bond contents, independent of the monomer concentration. Moreover, the values of degree of polymerization were constant regardless of the monomer concentration. These results support the application of Eqs. (15) and (16) in the initial reaction. The values of $(k_p + k_{trm})/k_{trm}$ estimated from Eq. (15) were very close to those obtained from Eq. (16), as shown in Table 2.

Thus, the values of k_{trr}/k_i and k_{trm}/k_i were calculated to be 0.11

TABLE 2. Polymerization Parameters

Parameter	Value
$k_d k_{iso}/k_{ts} \times 10^8$ (sec^{-1})	4.53
$\left(\frac{k_d k_{iso} k_i}{k_{ts} k_{trm}}\right)\left(\frac{k_p + k_{trm}}{k_i + k_{trr}}\right) \times 10^7$ (sec^{-1})	1.90
$(k_p + k_{trm})/k_{trm}$	
From Eq. (15)	4.61
From Eq. (16)	4.71
Average	4.66

and 0.27, respectively, by combining the parameters in Table 2. This finding shows that on the photopolymerization of VDO, the initiating radical and the propagating radical readily abstract the hydrogen between the two alkoxyl groups in VDO monomer as a radical.

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