Cyclic Acetal-Photosensitized Polymerization. XII. Photopolymerizations of Styrene and Methyl Methacrylate in the Presence of Polycyclic Acetals

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ABSTRACT

Styrene (St) and methyl methacrylate (MMA) were photopolymerized in the presence of poly-2-vinyl-1,3-dioxolane (PVDO), poly-2-vinyl-4-hydroxymethyl-1,3-dioxolane (PVHDO), or the terpolymer of vinyl formal/vinyl acetate/vinyl alcohol (PVFAcA) at 30 or 40°C. The ability to accelerate the photopolymerization increased in the order PVFAcA < PVHDO < PVDO; the ability of pendent cyclic acetal was larger than that of cyclic acetals which are not pendent. Moreover, the promoting ability per cyclic acetal increased with the increase in the number of cyclic acetal cyclic acetal group in the molecule.

INTRODUCTION

In previous papers [1, 2], the photopolymerization of styrene (St) in the presence of such mono-or dicyclic acetal compounds as 1,3-dioxolane (DO) or 2,4,8,10-tetraspiro [5,5] undecane(TU), respectively, has been investigated.

It is known that the rate of photopolymerization increased with the increase of the concentration of DO or TU; DO or TU acted as the promoter of photopolymerization of vinyl monomer.

In the preceding paper [3], it was found that poly-2-vinyl-1,3-dioxolane (PVDO) and poly-2-vinyl-4-hydroxymethyl-1,3-dioxolane (PVHDO) were decomposed through a radical mechanism, by means of photoirradiation, and then the terpolymer of vinyl formal/vinyl acetate/vinyl alcohol (PVFAcA) was crosslinked.

Therefore, it was expected that polycyclic acetals could promote the photopolymerization of vinyl monomer.

This paper deals with the photopolymerizations of St and methyl methacrylate (MMA) in the presence of polycyclic acetals; the effects of the number of cyclic acetal groups in the molecule and the difference between pendent and nonpendent cyclic acetal in their effects on the polymerization rate will be discussed on the basis of the kinetic equation derived in a previous paper [1].

EXPERIMENTAL

Materials

PVDO, PVHDO, and PVFAcA used in the preceding paper [3] were applied to the present experiments without purification.

St, MMA, benzene, 1,4-dioxane, and N,N-dimethylformamide (DMF) were purified by conventional methods.

Procedure

The photopolymerization was carried out at 30 or 40°C in the same manner as reported in the previous papers [1, 2], by using a 500- or 300-W high-pressure mercury lamp.

RESULTS AND DISCUSSION

Effect of Polycyclic Acetal on the Conversion of Vinyl Monomer

The results of the photopolymerizations of St and MMA by VPDO, PVHDO, or PVFAcA are shown in Fig. 1 and Table 1, respectively. From these results it was found that the photopolymerizations of St and MMA were accelerated by the addition of polycyclic acetal. From Table 1, it is clear that the promoting effect of polymerization increased with the increase of PVF unit.
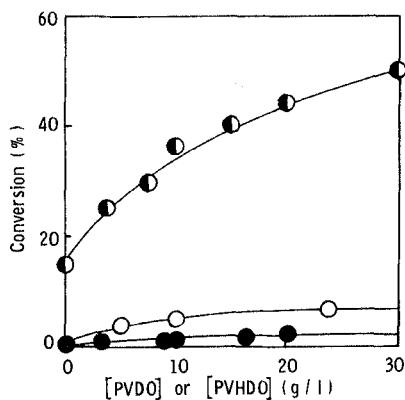
FIG. 1.   Plots of conversion vs. [PVDO] or [PVHDO]: (○) PVDO-St, [St] = 2.62 mole/liter in benzene; (●) PVHDO-St, [St] = 2.62 mole/liter in DMF; (◑) PVHDO-MMA, [MMA] = 2.81 mole/ liter in DMF. With 500-W lamp; 30°C.

TABLE 1.   Photopolymerizations of St and MMA in the Presence of PVFAcA[a]

No.	PVAc (%)	PVA (%)	PVF (%)	n	Conversion (%) St	MMA
1	100	0	0	650	1.48	6.51
2[b]	2	98	0	650	1.41	6.37
3	10.84	5.63	83.53	300	1.98	19.74
4	11.47	5.82	82.71	500	2.25	18.74
5	8.54	8.21	83.25	850	2.00	16.90
6	8.04	9.02	82.94	1160	2.54	18.62
7	49.48	6.09	44.43	855	1.68	16.18
8	51.13	6.13	42.74	382	2.13	17.58
	--	--	--	--	1.45	6.29

[a]PVFAcA, 8.33 g/liter; St, 2.62 mole/liter; MMA, 2.82 mole/liter; in 1,4-dioxane; 300-W lamp; 40°C; 8 hr.
   [b]In H_2O.

TABLE 2. Effects of the Concentration of PVFAcA on the Grafting
Efficiency and the Degree of Polymerization of Poly-MMA[a]

PVFAcA[b] (g/liter)	Conversion (%)	Grafting efficiency GE (%)[c]	$\overline{P}_n$ of homopoly-MMA[d]
2.50	18.07	3.84	2.41×10^4
4.00	18.32	4.53	2.12
5.00	18.81	6.23	1.75
7.50	19.00	7.83	1.23
10.00	20.29	14.38	0.81

[a]Polymerization conditions: MMA, 1.50 mole/liter in 1,4-dioxane;
300-W lamp, 40°C; 8 hr.
[b]No. 5 PVFAcA.
[c]Extracted with benzene in a Soxhlet apparatus for 30 hr. Calcu-
lated by: GE (%) = (weight of unextracted PMMA/total weight of
polymerized MMA) × 100.
[d]$\overline{P}_n$ of homopoly-MMA was calculated by Welch's equation [4],
from the viscosity of measured in benzene at 30°C.

Effects of the Concentration of PVFAcA on the Grafting Efficiency and the Degree of Polymerization of Poly-MMA

The effects of the concentration of PVFAcA on the conversion, graft-
ing efficiency, and the number-average degree of polymerization ($\overline{P}_n$)
of homopoly-MMA obtained are listed in Table 2. It was found that with
increasing concentration of PVFAcA, the efficiency of grafting in-
creased, but $\overline{P}_n$ of the poly-MMA decreased.

Initiation Mechanism

Polycyclic acetals were decomposed or crosslinked by means of
photoirradiation through the radical mechanism described in the pre-
ceding paper [3]. Moreover, the radical polymerizations were re-
confirmed by the composition curves of the copolymerization of St
and MMA, as shown in Fig. 2.
Therefore, it was presumed that the polymerization of vinyl
monomer was initiated by the various radicals generated in the course
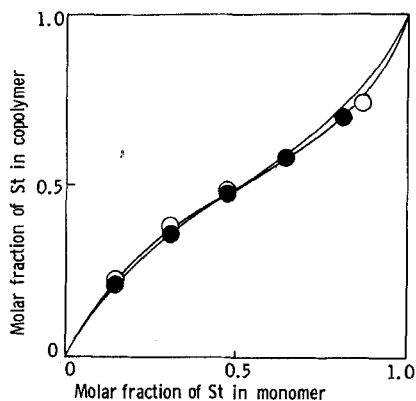of photodecomposition or photocrosslinking of polycyclic acetal.

FIG. 2. Copolymerization of St and MMA: (○) PVFAcA 0.0643 g, total volume 10 ml in 1,4-dioxane, 300 W lamp, 40°C; (●) PVHDO 0.152 g, total volume 10 ml in DMF, 500-W lamp, 30°C. (St + MMA) 5 ml, 8 hr.

Kinetics of Polymerization

The photopolymerizations of St and MMA were carried out in the presence or absence of polycyclic acetal, at 30 or 40°C. The reaction order, as given in Table 3, was obtained for the photopolymerizations of St and MMA in the presence of polycyclic acetals. The polymerization rate in the presence of polycyclic acetals (R_{ppr}) could be generalized as shown in Eqs. (1) and (2). It depends on the concentrations of polycyclic acetal and monomer.

$$R_{ppr} = k_1 [\text{Cyclic Acetal}]^{0-0.5} [\text{St}]^{1.0-1.5} \tag{1}$$

$$R_{ppr} = k_2 [\text{Cyclic Acetal}]^{0-0.5} [\text{MMA}]^{0-1.0} \tag{2}$$

Furthermore, the photopolymerization rate in the absence of polycyclic acetals (R_{pab}) can be expressed by Eqs. (3) and (4):

$$R_{pab} = k_3 [\text{ST}]^{1.5} \tag{3}$$

$$R_{pab} = k_4 [\text{MMA}]^{1.0} \tag{4}$$

Here, k_1, k_2, k_3 and k_4 denote rate constants.

TABLE 3. Reaction Order

Monomer		Cyclic acetal		Solvent	Lamp (Watt)	Temp (°C)	Reaction order[a]	
Type	Concn (mole/liter)	Type	Concn $\times 10^{-2}$ (ca/liter)				m	n
St	2.62	PVDO	2.50-14.6	Benzene	500	30	0.22	-
St	2.62	PVHDO	0.52-3.62	DMF	500	30	0.35	-
St	2.62	PVFAcA	2.08-10.4	1,4-Dioxane	300	40	0.27	-
St	0.873 ~ 2.62	PVFAcA	5.19	1,4-Dioxane	300	40	-	1.4
MMA	2.81	PVHDO	0.53-3.70	DMF	500	30	0.50	-
MMA	0.365 ~ 2.81	PVHDO	2.68	DMF	500	30	-	1.2
MMA	1.50	PVFAcA	1.30-5.19	1,4-Dioxane	300	40	0.16	-
MMA	0.564 ~ 1.88	PVFAcA	2.60	1,4-Dioxane	300	40	-	0.86

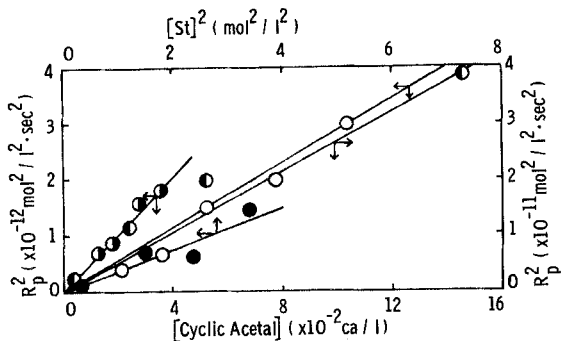[a]$R_{ppr} = \text{const.} [\text{Cyclic Acetal}]^m [\text{Monomer}]^n$.

FIG. 3. Plots of R_p^2 vs. [Cyclic Acetal] or [St]^2: (o) PVFAcA-St, [St] = 2.62 mole/liter; (•) PVFAcA-St, [PVFAcA] = 5.19×10^{-2} ca/liter, in benzene, 300-W lamp, 40°C; (◐) PVDO-St, [St] = 2.62 mole/liter in benzene, 500-W lamp, 30°C; (◑) PVHDO-St, [St] = 2.62 mole/liter in DMF, 500-W lamp, 30°C.
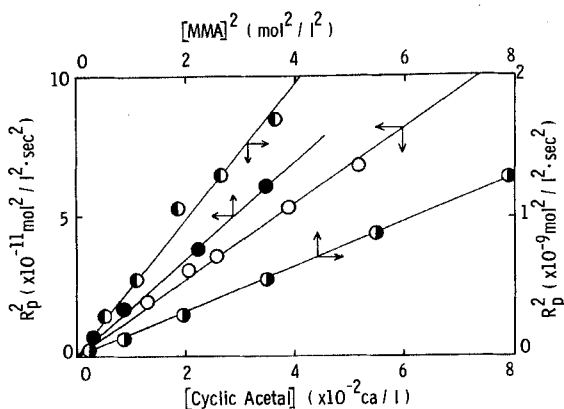

FIG. 4. Plots of R_p^2 vs. [Cyclic Acetal] or [MMA]^2: (o) PVFAcA-MMA, [MMA] = 1.50 mole/liter; (•) PVFAcA-MMA, [PVFAcA] = 2.60×10^{-2} ca/liter, in benzene, 300-W lamp, 40°C; (◐) PVHDO-MMA, [MMA] = 2.81 mole/liter; (◑) PVHDO-MMA, [PVHDO] = 2.68×10^{-2} ca/liter, in DMF, 500-W lamp, 30°C.

TABLE 4. Rate Constant

Cyclic acetal	Monomer	Solvent	Lamp (Watt)	Temp (°C)	$k_d k_p^2 / k_t$ (liter/ mole-sec^2)
DO	St	Benzene	300	40	1.41×10^{-12}
TU	St	Benzene	300	40	1.16×10^{-12}
PVDO	St	Benzene	500	30	4.30×10^{-11}
PVHDO	St	DMF	500	30	7.28×10^{-12}
PVHDO	MMA	DMF	500	30	6.32×10^{-9}
PVFAcA	St	1,4-Dioxane	300	40	3.63×10^{-12}
PVFAcA	MMA	1,4-Dioxane	300	40	6.50×10^{-10}

On the other hand, the rate of photosensitized polymerization (R_p) can be written by Eq. (5), as derived in the previous paper [1].

$$R_p^2 = R_{ppr}^2 - R_{pab}^2$$

$$= (k_d k_p^2 / k_t) [S][M]^2 \qquad (5)$$

Here, k_d, k_p, and k_t are the rate constants of decomposition, propagation, and termination, respectively.

By applying the obtained data to Eq. (5), the relationships among R_p^2, [Cyclic Acetal], [St]^2, or [MMA]^2 plotted in Figs. 3 and 4 were obtained. The fit of experimental data to the linear relationship was good.

The values of $k_d k_p^2 / k_t$ per cyclic acetal calculated from the slopes of these straight lines are summarized in Table 4. Although the solvents, the lamp, and the temperature were different, the abilities to promote the polymerization of vinyl monomers for polycyclic acetals tended to be larger than those for mono- and dicyclic acetal compounds. Moreover, the ability to promote the polymerization of vinyl monomer for pendent cyclic acetals was smaller than that for nonpendent cyclic acetals. The ability of PVDO compounds to promote polymerization was decreased by the hydroxymethyl group at the 2 position.

ACKNOWLEDGMENT

REFERENCES

[1] T. Ouchi, S. Nakamura, M. Hamada, and M. Oiwa, J. Polym. Sci.
     Polym. Chem. Ed., 13, 466 (1975).
[2] T. Ouchi, K. Nagaya, and M. Oiwa, J. Polym. Sci. Polym. Chem.
     Ed., 14, 2835 (1976).
[3] T. Ouchi, C. Sato, and T. Yamamoto, J. Macromol. Sci.–Chem.,
     A14, 265 (1980).
[4] F. J. Welch, J. Polym. Sci., 61, 243 (1962).