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Cyclic Acetal-Photosensitized Polymerization. XI. Photoirradiations onto Polycyclic Acetals

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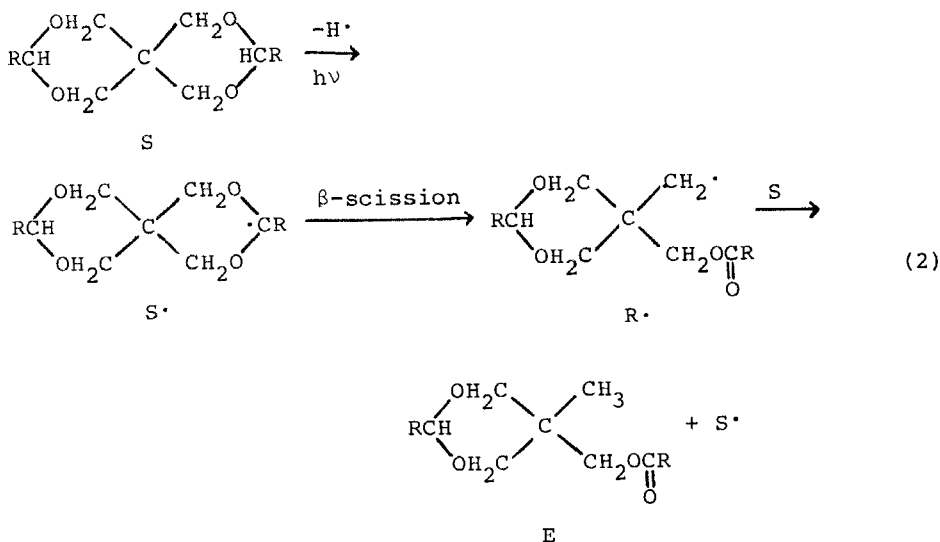
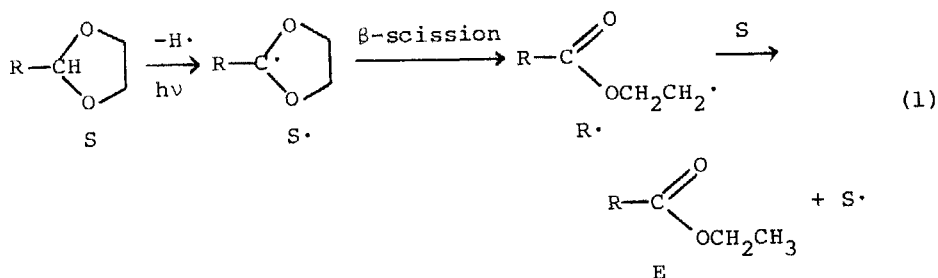
ABSTRACT

Photoirradiations onto polycyclic acetals, i. e., polymers containing cyclic acetal groups in the molecule, were carried out at 30 or 40°C. The terpolymer of vinyl formal/vinyl acetate/vinyl alcohol (PVFAcA) was decomposed by means of irradiation, while poly-2-vinyl-1,3-dioxolane (PVDO) and poly-2-vinyl-4-hydroxymethyl-1,3-dioxolane (PVHDO) were crosslinked. These results indicate the possibility of control of the decomposition or the crosslinking of polymer.

INTRODUCTION

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

It was found that the monoester radicals generated by photoirradiation on DO and TU could initiate the polymerization of St. We then reported that DO and TU containing one and two cyclic acetal groups in a molecule, respectively, are radically rearranged to the corresponding monoester compounds by photoirradiation, as shown in Eqs. (1) and (2).



Therefore, it was predicted that such polycyclic acetals as vinyl formal/vinyl acetate/vinyl alcohol (PVFAcA), poly-2-vinyl-1,3-dioxolane (PVDO), and poly-2-vinyl-4-hydroxymethyl-1,3-dioxolane (PVHDO) also generated ester radicals on photoirradiation and then were decomposed or crosslinked.

In this paper, the decomposition and the crosslinking of polymer having polycyclic acetal groups in the molecule by photoirradiation are discussed from the standpoint of the difference between polymers with nonpendent and pendent acetals.

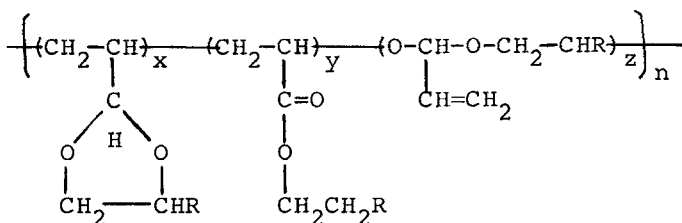
EXPERIMENTAL

Materials

PVDO and PVHDO. 2-Vinyl-1,3-dioxolane (VDO) and 2-vinyl-4-hydroxymethyl-1,3-dioxolane (VHDO) were prepared by the

dehydration condensations of ethylene glycol and glycerol with acrolein according to the method of Fischer et al. [3].

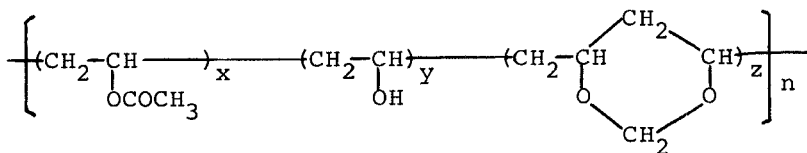
VDO and VHDO were polymerized in the presence of 2,2-azobisisobutyronitrile (AIBN) in bulk at 65°C in the dark, as described by Maeshima et al. [4]. The polymers obtained were then reprecipitated from benzene and DMF solution with methanol, respectively. From the IR spectra, the saponification and bromination values, and elemental analysis, it was confirmed that these polymers were composed of the following three unit structures:



I, II

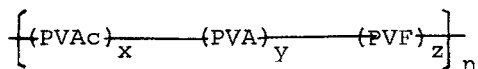
For PVDO (R=H): $x = 66.4$ mole %, $y = 5.3$ mole %, $z = 28.3$ mole %
 $n =$ about 10; for PVHDO (R=CH₂OH): $x = 23.1$ mole %, $y = 23.7$ mole %,
 $z = 53.2$ mole %, $n =$ about 4.

PVFAcA. PVFAcA polymers having various compositions and degrees of polymerization n as shown in Table 1, provided by Chisso Co., were purified by reprecipitation from 1,4-dioxane solution with *n*-butanol.



PVFAcA

or



Solvents were purified by conventional methods.

TABLE 1. PVFACa Samples

| No. | Structure III | | | n |
|-----|---------------|---------------|---------------|------|
| | x (mole %) | y (mole %) | z (mole %) | |
| 1 | 100 | 0 | 0 | 650 |
| 2 | 2 | 98 | 0 | 650 |
| 3 | 10.84 | 5.63 | 83.53 | 300 |
| 4 | 11.47 | 5.82 | 82.71 | 500 |
| 5 | 8.54 | 8.21 | 83.25 | 850 |
| 6 | 8.04 | 9.02 | 82.94 | 1160 |
| 7 | 49.48 | 6.09 | 44.43 | 855 |
| 8 | 51.13 | 6.13 | 42.74 | 382 |

Procedures

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

Characterization of Polycyclic Acetals

The characterizations of polycyclic acetals after photoirradiation were done by measurements of IR, viscosity, molecular weight, and gel-permeation chromatography (GPC). The intrinsic viscosity $[\eta]$ of PVFACa was measured in 1,4-dioxane at 40°C. The number-average molecular weight \bar{P}_n of PVDO and PVHDO were determined by vapor-pressure osmometry at 37°C in methanol.

RESULTS AND DISCUSSION

Photoirradiation of PVFACa

The variation of intrinsic viscosities of PVFACa samples 3, 5, 6, 7 photoirradiated in 1,4-dioxane at 40°C for 15 hr is shown in Table 2. With the increase of polyvinylformal (PVF) units and the decrease of degree of polymerization (n) of PVFACa, the rate of decrease for $[\eta]$ increased; the main chain was presumed to be cleaved easily.

TABLE 2. Photoirradiation of Various Kinds of PVFACa^a

| No. | $[\eta]_0$ (dl/g) ^b | $[\eta]_t$ (dl/g) ^b | $1 - [\eta]_t/[\eta]_0$ |
|-----|--------------------------------|--------------------------------|-------------------------|
| 3 | 0.916 | 0.621 | 0.322 |
| 5 | 0.967 | 0.698 | 0.278 |
| 6 | 1.479 | 1.417 | 0.042 |
| 7 | 0.727 | 0.654 | 0.100 |

^aPVFACa 5.00 g/liter in 1,4-dioxane; 300-W lamp; 40°C; 15 hr.

^bMeasured in 1,4-dioxane at 40°C.

Moreover, the viscosities of PVFACa sample 5 photoirradiated at various concentrations are shown in Table 3. With the decrease of the concentration of PVFACa, the value of $[\eta]$ after irradiation tended to decrease. The addition of AIBN did not affect $[\eta]$. The decrease of $[\eta]$ by photoirradiation in air suggests that the decomposition of PVFACa was accelerated by autoxidation.

On the other hand, the IR spectrum of PVFACa after photoirradiation compared with that before photoirradiation is shown in Fig. 1. On photoirradiation, the four peaks of cyclic acetal at 1200-1040 cm^{-1} become smaller, the absorption of C=O at 1735 cm^{-1} becomes larger,

TABLE 3. Photoirradiation of PVFACa^a

| [PVFACa] ^b (g/liter) ^b | [AIBN] (g/liter) | $[\eta]$ (dl/g) ^c |
|---|---------------------|---------------------------------|
| Before irradiation | — | 0.967 |
| 3.00 | 0 | 0.598 |
| 5.00 | 0 | 0.698 |
| 5.00 | 1.00 | 0.662 |
| 5.00 | 2.00 | 0.637 |
| 8.00 | 0 | 0.768 |
| 10.00 | 0 | 0.940 |
| 5.00 ^d | 0 | 0.491 |

^aIn 1,4-dioxane; 300-W lamp; 40°C; 15 hr.

^bPVFACa No. 5.

^cMeasured in 1,4-dioxane at 40°C.

^dIn air.

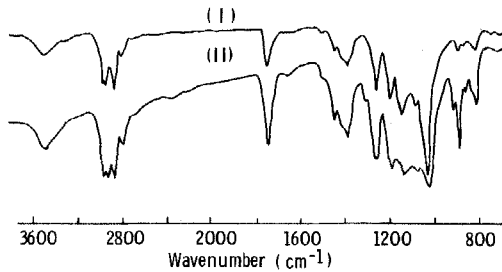


FIG. 1. IR spectra of PVFACa (No. 5): (I) before irradiation and (II) after irradiation. Spectra measured by KBr method.

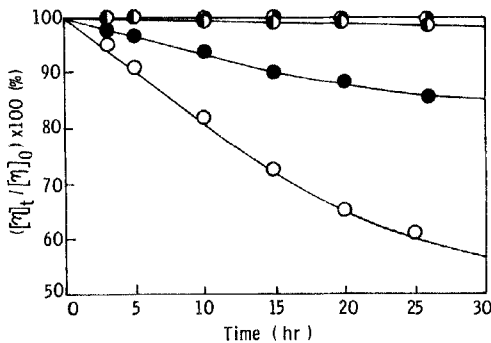


FIG. 2. $[\eta]_t / [\eta]_0$ vs. time: (●) No. 1; (○) No. 2; (○) No. 5; (●) No. 7. Irradiation: No. 5 PVFACa 5.00 g/liter in 1,4-dioxane; 300-W lamp; at 40°C. Viscosities were measured at 30°C. Solvent: 1,4-dioxane (No. 1, 5, 7) or H₂O (No. 2).

and peaks attributable to the double bond at 1635 and 860 cm⁻¹ appear. The double bond peaks do not appear on irradiation of mono- or di-cyclic acetals [1, 2].

Rate of Decomposition. PVFACa of PVAc (No. 1), PVA (No. 2), and Nos. 5 and 7 were irradiated and their viscosities were measured. The results are shown in Fig. 2 as the relationship between the degree of decomposition ($[\eta]_t / [\eta]_0$) vs. time. PVAc photo-decomposed slightly but PVA did not. Furthermore, the rate of decomposition of PVFACa No. 5 was larger than that of No. 7. Therefore, the PVF unit was concluded to be decomposed by photo-irradiation.

It is known that Eq. (3) is generally valid when the main chain of polymer is cleaved:

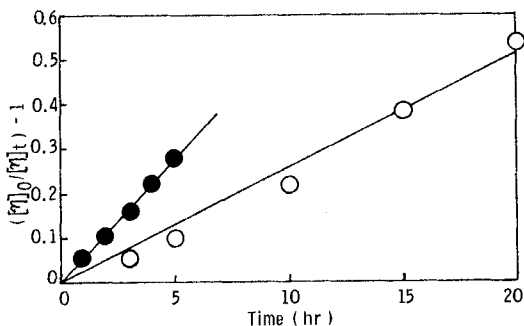


FIG. 3. $([\eta]_0/[\eta]_t) - 1$ vs. time: (\circ) under vacuum; (\bullet) in air. Irradiation: No. 5 PVFACa 5.00 g/liter, in 1,4-dioxane; 300-W lamp; at 40°C . Viscosities were measured in 1,4-dioxane at 30°C .

$$\overline{M}_{no}/\overline{M}_{nt} - 1 = kt \quad (3)$$

We next tried to plot the relationship between $([\eta]_0/[\eta]_t) - 1$ and the irradiation time and found (Fig. 3) that there is a good linear relationship. These results show that PVFACa is cleaved randomly by photoirradiation, and the value of α in $[\eta] = K[M]^\alpha$ is about 1.0, regardless of the presence or absence of oxygen. Here, the acceleration of decomposition rate by oxygen was presumed to be due to the peroxide formed by photooxidation.

Results of GPC. The GPC curves of PVFACa for No. 5 before and after photoirradiation are shown in Fig. 4. This figure shows that PVFACa is cleaved randomly on irradiation.

Mechanism of Photodecomposition. When the ESR spectrum of PVFACa after irradiation was measured, the absorbance of a stable radical was recognized in the neighborhood of 2.00 g. As shown in the following paper [5], the radical composition curve was obtained on the copolymerization of styrene (St) and methyl methacrylate initiated with PVFACa. Accordingly, the photoreaction of PVFACa was presumed to proceed through a radical mechanism.

From the above results, the photodecomposition of PVFACa was able to be explained by assuming the reactions PVF unit shown in Eqs. (4) and (5).

Photoirradiations of PVDO and PVHDO

The photoirradiations of PVDO and PVHDO were carried out in 1,4-dioxane for 30 hr. The results obtained are shown in Table 4.

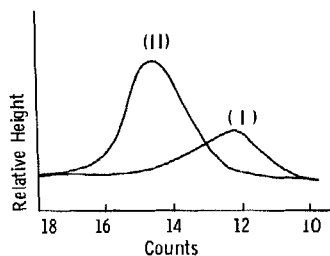
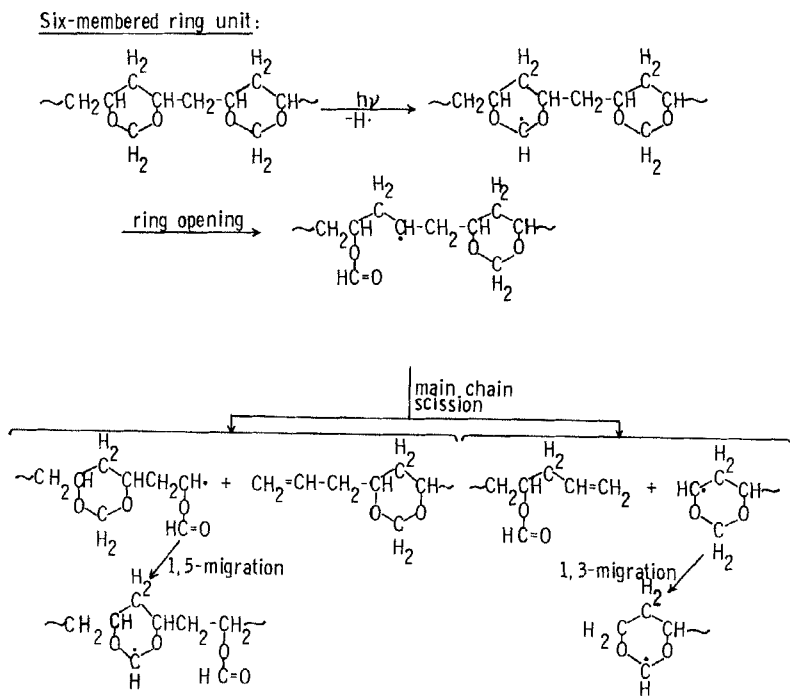
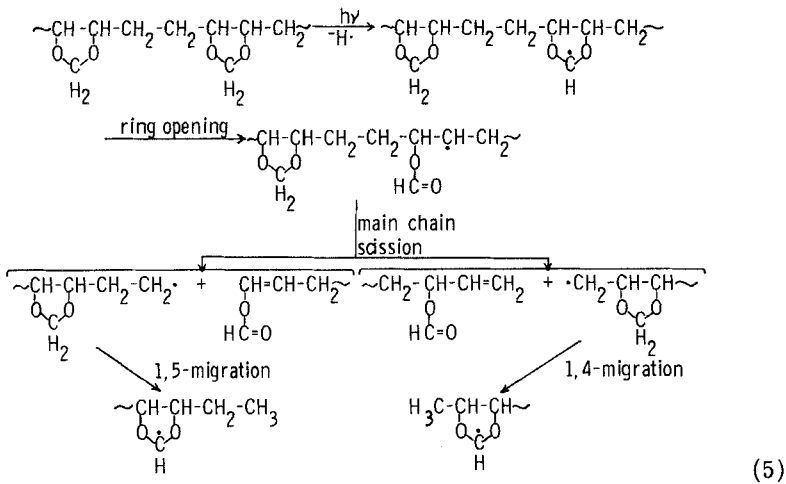


FIG. 4. GPC curves of PVFACa (No. 5): (I) before irradiation and (II) after irradiation. GPC measured in THF at 31°C by using $10^4 \cdot 10^3 \cdot 10^2$ Å columns. Irradiation: No. 5 PVFACa 5.00 g/liter, in 1,4-dioxane; 300-W lamp; at 40°C; for 24 hr.



(4)

Five-membered ring unit:

TABLE 4. Photoirradiations of PVDO and PVHDO^a

| 1,3-DO polymer (g) | AIBN (g) | Conditions | Insoluble portion (%) | \bar{M}_n^b |
|--------------------|----------|----------------|-----------------------|---------------|
| PVDO | 0 | Vacuum | 5.5 | 3820 |
| PVDO | 0.01 | Vacuum | 8.8 | 3020 |
| PVHDO | 0 | Vacuum | 4.9 | 7510 |
| PVHDO | 0.01 | Vacuum | 6.8 | 4560 |
| PVHDO | 0 | O ₂ | 7.0 | 7730 |
| PVHDO | 0.01 | O ₂ | 8.4 | 5600 |

^a1,3-DO polymer 0.300 g, 1,4-dioxane 3 ml; 500-W lamp; 30°C; 30 hr.

^bMeasured by means of VPO method in MeOH at 37°C; \bar{M}_n of PVDO before irradiation, 1110; \bar{M}_n of PVHDO before irradiation, 2490.

With the irradiation, the number-average molecular weight of the soluble portion and the yield of the insoluble portion were increased.

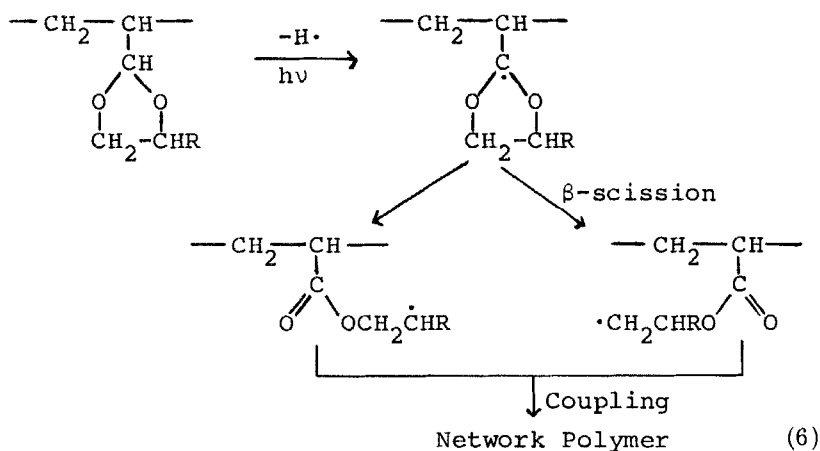
Furthermore, on photoirradiation of the copolymer of PVHDO and St, an insoluble portion formed as shown in Table 5. The above results mean that the copolymer containing pendent cyclic acetal units can be hardened at room temperature by means of photoirradiation.

TABLE 5. Photoirradiation of copolymer of VHDO and St^a

| Molar fraction of VHDO in copolymer | AIBN (g) | Insoluble portion (%) |
|-------------------------------------|----------|-----------------------|
| 0.115 | 0 | 1.7 |
| 0.115 | 0.01 | 3.4 |

^aCopolymer 0.300 g; 1,4-dioxane 3 ml; 500-W lamp; 30°C, 7 hr.

Moreover, the absorption of C=O at 1720 cm⁻¹ in the IR spectrum of PVDO became more pronounced on photoirradiation. Therefore, a photocrosslinking mechanism of PVDO or PVHDO was presumed to operate, as shown in Eq. (6).



Accordingly, it is expected that the photodecomposition or the photocrosslinking of polymer can be controlled by introducing cyclic acetal groups into the main chain or by adding pendent cyclic acetal groups to main chain, respectively.

ACKNOWLEDGMENT

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REFERENCES

- [1] T. Ouchi, S. Nakamura, M. Hamada, and M. Oiwa, J. Polym. Sci. Polym. Chem. Ed., 13, 455 (1975).
- [2] T. Ouchi, K. Nagaya, and M. Oiwa, J. Polym. Sci. Polym. Chem. Ed., 14, 2835 (1976).
- [3] R. F. Fisher and C. W. Smith, J. Org. Chem., 25, 319 (1960).
- [4] N. Yamashita, S. Kunitani, S. Komiyama, M. Toshihara, and T. Maeshima, J. Polym. Sci. Polym. Letters Ed., 10, 675 (1972).
- [5] T. Ouchi, N. So, and Y. Komatsu, J. Macromol. Sci.-Chem., A14, 277 (1980).

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