

Behavior of Polymers Containing Spiroorthoester or Bicycloorthoester Structure under EB and X-Ray Irradiation Conditions

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Synopsis

Reaction behavior of spiroorthoester and bicycloorthoester to EB and X-ray irradiations has been studied on the basis of infrared spectroscopic analysis. The polymers containing these functional groups showed markedly high sensitivity to EB and X-ray. The formations of C=O and —OH after exposure indicate that these functional groups react through ring opening even in the absence of any cationic catalyst. In the high energy-induced reaction, sensitivity and post-irradiation polymerization effect were found to be greatly influenced by the polymer structure, different from those observed in the cation-induced reaction.

INTRODUCTION

Spiroorthoester and bicycloorthoester groups are sensitive to cations and undergo ring-opening polymerization.¹ However, the behavior of these functional groups under EB and X-ray irradiation conditions has not been reported. The energy transferred to polymers through EB or X-ray irradiation is much higher than that through UV light irradiation. Hence, this high energy can cause organic materials ionization; thus orthoesters such as spiroorthoester and bicycloorthoester would undergo ring-opening polymerization even in the absence of any cationic catalyst. In this report, the radiation-induced reaction behavior of polymers containing spiroorthoester or bicycloorthoester as a functional group is presented, compared with the cation-induced reaction behavior. The reaction mechanism of these functional groups is examined on the basis of IR transition band changes after irradiation, where C=O is produced if the ring-opening reaction takes place.¹ The effects of polymer structure and glass transition temperature on the reaction behavior are also examined, and possible explanations concerning the observed effects are presented from the viewpoint of IR spectroscopic study.

[†] Deceased.

EXPERIMENTAL

Monomer Preparation

1-Ethyl-4-Hydroxymethyl-2,6,7-Trioxabicyclo[2.2.2]octane 1 was prepared by the method involving the transesterification of triethylorthopropionate with pentaerythritol in the presence of *p*-toluenesulfonic acid.²

2-Hydroxymethyl-1,4,6-Trioxaspiro[4.6]undecane 2 was prepared from the condensation of ϵ -caprolactone with glycidol in the presence of boron trifluoride etherate by the same method reported previously.^{1,3}

4-Ethyl-1-Vinyl-2,6,7-Trioxabicyclo[2.2.2]octane 3 was prepared according to the same method described previously, involving the dehydrobromination of 1-(1-bromomethyl)-4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane, which was synthesized from the transesterification of 1,1,1-triethoxy-2-bromopropane with 2-ethyl-2-hydroxymethyl-1,3-propanediol in the presence of *p*-toluenesulfonic acid.⁴

2-Methylene-1,4,6-trioxaspiro[4.6]undecane 4 was prepared from the condensation of epichlorohydrine with ϵ -caprolactone, as described previously.⁵

2-Allyloxymethyl-1,4,6-Trioxaspiro[4.6]undecane 5 was prepared from the condensation of allylglycidylether with ϵ -caprolactone in the presence of boron trifluoride etherate by the same method reported previously.^{1,6}

1-Ethyl-4-Methacryloxymethyl-2,6,7-Trioxabicyclo[2.2.2]octane 6 was prepared by the reaction of **1** with methacrylchloride in the presence of triethylamine.⁷

2-Methacryloxymethyl-1,4,6-Trioxaspiro[4.6]undecane 7 was prepared by the reaction of **2** with methacrylchloride in the presence of triethylamine.³

Polymer Preparation

All the polymers, except 1-ethyl-4-vinylbenzyloxymethyl-2,6,7-trioxabicyclo[2.2.2]octane copolymer with styrene, were prepared using conventional free radical homopolymerization or copolymerization of prepared monomers with acrylonitrile. 1-Ethyl-4-vinylbenzyloxymethyl-2,6,7-trioxabicyclo[2.2.2]octane **8** copolymer with styrene was synthesized by the method involving the condensation of **1** with chloromethylated polystyrene in the presence of sodium hydride.⁸ The chloromethylated polystyrene was prepared by the reaction of polystyrene with chloromethylether using anhydrous $ZnCl_2$. The copolymer composition was altered by varying the monomer ratio, and molecular weight was controlled by catalyst concentration.

Characterization

Molecular weight and molecular weight distribution were determined using gel permeation chromatography. Copolymer composition and general structure were evaluated using infrared spectroscopy, ¹H-NMR and elemental analysis. Softening point was measured using a melting point test apparatus BY-1 (Yazawa Scientific Co., Ltd.).

Sensitivity Evaluation

For sensitivity evaluation, the polymers containing the radiation-active functional groups were dissolved in solvents (allyloxymethyl **5** and methacryloxymethyl **6**, **7** homopolymers in methylcellosolveacetate, **3** and **4** system polymers copolymerized with acrylonitrile in benzonitrile, and **8** system polymers copolymerized with styrene in xylene). After filtration with a 0.5 μm SLSR 025NS filter (Millipore Ltd.), the polymers were cast on silicon wafers by spin coating to a thickness of about 6000 Å and were cured at 80°C for 30 min (allyloxymethyl system polymers were cured at room temperature for 60 min in vacuum due to their low glass transition temperature).

Electron beam exposures were carried out at 20 kV with a JEOL JBX-5A exposure machine. X-ray exposures were performed with the X-ray exposure system described previously (the source containing a water-cooled 1.7 kW stationary A1 target that is columnar in shape⁹). The exposed wafers were soaked in dimethylformamide for 2 min to wash out the sol completely, and were rinsed in isopropanol for 30 s. This developing time was sufficient, because further developing gave no thickness change. The thicknesses of these films were measured with a stylus instrument (Taly step made by Taylor-Habson).

Reaction Mechanism Study

The polymer solutions obtained as described above were deposited on potassium bromide plates and were cured at room temperature for 60 min in vacuum using a vacuum drying oven DPA-30 (Yamato Scientific Co., Ltd.). These samples were subjected to X-ray irradiation using the X-ray exposure system and to deep-UV irradiation using a Canon PLA-521 F aligner with a 250 Cold Mirror.

For the reaction mechanism study to cations and radicals, 4-diazo-*N,N*-diethylaniline tetrafluoroborate (DEAFB) or azobisisobutyronitrile (AIBN) was mixed with polymer solutions to 10% in weight of the polymers. The polymer solutions were cast on potassium bromide plates and were cured at room temperature for 60 min in vacuum. The polymer films mixed with DEAFB, which produces the BF_3 cation with UV light,¹⁰ were subjected to UV irradiation for 10 min using a Kasper Model 2001 exposure machine. The polymer films mixed with AIBN were baked at 90°C for 4 h in vacuum to produce the radical. DEAFB and AIBN do not have the characteristic absorption of C=O and —OH groups which interrupt this study.

The reaction mechanism and the structure dependence of the reaction behavior were studied on the basis of IR spectroscopic analysis. For IR measurements, an A-3 IR Spectrometer (Japan Spectroscopic Co., Ltd.) was used.

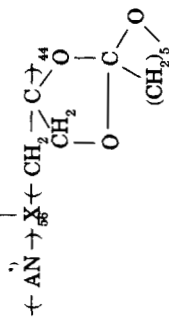
RESULTS AND DISCUSSION

Sensitivity to EB and X-Ray

The polymer films were exposed to electron beams of 10^{-7} – 10^{-3} C/cm². The polymer structures and their sensitivities were listed in Table I. Sen-

TABLE I
Polymer Structures and Characteristics^a

Materials	X	Abbreviations	$1/DgM_w$ ($\text{cm}^2/\text{mol}/\text{Cg}$)	Post-irradiation polymerization effect	Change in C= absorption			
					X-ray	Deep UV	BF_3	AIBN
$\begin{array}{c} \text{CH}_3 \\ \\ \text{---C---} \\ \\ \text{C=O} \\ \\ \text{O} \\ \\ \text{CH}_2 \\ \\ \text{X} \end{array}$	Epoxy	GMA	33.3	Yes	* ^b	*	*	*
$\begin{array}{c} \text{CH}_2 \\ \\ \text{---CH---} \\ \\ \text{X} \end{array}$	Spiro	SMA	4.8	No	† ^c	†	†	†
$\begin{array}{c} \text{CH}_2 \\ \\ \text{---CH---} \\ \\ \text{CH}_2 \\ \\ \text{O} \\ \\ \text{CH}_2 \\ \\ \text{X} \end{array}$	Bicyclo	BMA	4.8	No	†	†	†	†
$\begin{array}{c} \text{CH}_2 \\ \\ \text{---CH---} \\ \\ \text{CH}_2 \\ \\ \text{O} \\ \\ \text{CH}_2 \\ \\ \text{X} \end{array}$	Epoxy	GA	11.2	No	*	*	*	*
$\begin{array}{c} \text{CH}_2 \\ \\ \text{---CH---} \\ \\ \text{CH}_2 \\ \\ \text{O} \\ \\ \text{CH}_2 \\ \\ \text{X} \end{array}$	Spiro	SA	21.7	No	Increase	No change	Increase	No change
$\begin{array}{c} \text{CH}_2 \\ \\ \text{---CH---} \\ \\ \text{CH}_2 \\ \\ \text{O} \\ \\ \text{CH}_2 \\ \\ \text{X} \end{array}$		NTS	1.6	Yes	Increase	No change	Increase	No change



$\begin{array}{c} \text{1)} \\ \leftarrow \text{AN} \rightarrow_{62} \leftarrow \text{CH}_2 - \text{CH} \rightarrow_{38} \\ \\ \text{C} \begin{array}{l} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \\ \text{CH}_2 \text{CH}_2 \\ \text{CH}_2 \text{CH}_2 \\ \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \\ \text{C} - \text{C}_2\text{H}_5 \end{array} \end{array}$	NTB	2.9	Yes	Increase	No change	Increase	No change
$\begin{array}{c} \leftarrow \text{CH}_2 - \text{C} \rightarrow_{80} \\ \\ \text{C}_6\text{H}_5 \\ \\ \leftarrow \text{CH}_2 - \text{CH} \rightarrow_{20} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{CH}_2 - \text{O} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{O} - \text{C} - \text{C}_2\text{H}_5 \\ \quad \quad \quad \quad \quad \quad \\ \text{CH}_2 - \text{O} \quad \quad \quad \text{CH}_2 - \text{O} \end{array}$	BST	2.0	No	No change	No change	Increase	No change

^a AN is acrylonitrile. M_w denotes the weight-average molecular weight and D_g denotes the gel point dose value.

^b Epoxide group does not produce C=O.

^c C=O transition band changes cannot be detected because polymer backbone contains C=O structure.

sitivity is expressed as the reverse of the product of weight-average molecular weight M_w and gel point dose D_g^i . This product was introduced by Ku and Scala to characterize the sensitivity for negative resists.¹¹ Net sensitivity is evaluated from this product; the sensitivity of a polymer with larger $1/D_g^i M_w$ is higher than that of one with smaller product.

Spiroorthoester and bicycloorthoester were found to be markedly highly sensitive to EB, such as epoxide is sensitive to EB.¹² It was also found that the sensitivity of the polymers containing these functional groups was considerably dependent on the polymer backbone structure, not only on the functional groups introduced. For example, in allyloxymethyl type polymers, spiroorthoester-containing polymer SA exhibits higher sensitivity than that of epoxide-containing polymer GA. On the contrary, in methacryloxymethyl type polymers, epoxide-containing polymer GMA exhibits higher sensitivity than that of spiroorthoester-containing polymer SMA. Possible explanations for these observed dependences are presented in the post-irradiation polymerization effect and in the reaction mechanism sections from the viewpoint of infrared spectroscopic analysis and glass transition temperature.

The sensitivities of these polymers to X-ray have been also studied. The polymers containing these functional groups showed high sensitivity to X-ray as well as EB. The relationship between EB and X-ray sensitivities for various resists is shown in Figure 1. In this figure, the values of $1/D_g^i M_w$ under X-ray irradiation are plotted against those under EB irradiation for

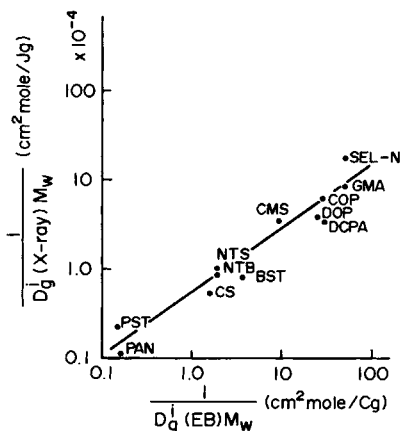


Fig. 1. Relationship between EB and X-ray sensitivities for various resist materials. Abbreviations used in the table are as follows: PAN = polyacrylonitrile ($M_w = 405,000$, $M_w/M_n = 10$), PSt = polystyrene ($M_w = 50,000$, $M_w/M_n = 1.1$); CS = chlorinated polystyrene (chlorination ratio 20%, $M_w = 390,000$, $M_w/M_n = 1.1$); CMS = chloromethylated polystyrene (chloromethylation ratio 50%, $M_w = 15,000$, $M_w/M_n = 1.1$, commercially available as CMS-EEX from Toyo Soda Co., Ltd.); DCPA = poly(2,3-dichloropropyl acrylate) ($M_w = 500,000$); DOP = poly(diallylorthophthalate) ($M_w = 52,000$, $M_w/M_n = 7.6$, commercially available as DAP from Osaka Soda Co., Ltd.); COP = copolymer of glycidyl methacrylate with ethylacrylate ($M_w = 182,000$, $M_w/M_n = 2.2$, commercially available from Mead Associates); PGMA = poly(glycidyl methacrylate) ($M_w = 89,000$, $M_w/M_n = 1.5$, commercially available as OEER-100 from Tokyo Oka); SEL-N ($M_w = 53,000$, $M_w/M_n = 4.0$, available from Somar Manufacturing). Sensitivities were measured at this laboratory.

the same resist materials. It was reported that similar reaction took place in resist materials from the viewpoint of a good correlation as shown in Figure 1.¹³ The polymers studied here, NTB, NTS and BST, also show a good correlation; hence, the reaction induced by X-ray irradiation is presumed to be similar to that induced by EB irradiation, in the polymers containing spiroorthoester or bicycloorthoester as well as in other known resist materials.

On the other hand, all the polymers studied here did not react to deep UV (ca. 250 nm) irradiation. This is because energy transferred through deep UV irradiation is rather less than that through EB irradiation, and cannot ionize these polymers sufficiently.

Post-Irradiation Polymerization Effect

It was reported that polymers containing epoxide, which belong to the cyclic ether group, showed post-irradiation polymerization effect; i.e., after irradiation is terminated, the crosslinking reaction continues.¹⁴ However, polymer structure dependence of this effect has not been reported in its study. Spiroorthoester and bicycloorthoester belong to cyclic ether group; thus they would show the post-irradiation polymerization effect. In this study, polymer structure dependence of the post-irradiation polymerization effect has also been researched, and possible explanations are stated on the basis of IR spectroscopic analysis.

The results shown in Table II indicate that the post-irradiation polymerization effect depends not only on the kind of functional groups but also on the polymer backbone structure. For example, bicycloorthoester-containing polymer NTB showed the post-irradiation polymerization effect; on the contrary, the same group-containing polymer BST did not show this effect. Spiroorthoester-containing polymer NTS showed the post-irradiation polymerization effect; on the contrary, the same group-containing polymer SA did not show this effect. Concerning epoxide-containing polymers GMA and GA, the polymer structure dependence was also observed.

The post-irradiation polymerization effect is basically attributed to the lifetime of active species in polymer films, which bring about the further reaction in polymer films. The lifetime in polymer films is influenced mainly by two factors, i.e., glass transition temperature and stability of active

TABLE II
Polymer Properties

Materials	Softening point Sp (°C)	Weight-average molecular weight $M_w \times 10^{-4}$	Distribution M_w/M_n
GMA	139-144	10.6	5.8
SMA	98-103	5.0	3.7
BMA	97-103	5.2	2.7
GA	< 25	0.2	2.1
SA	< 25	0.3	2.3
NTS	136-142	5.0	2.1
NTB	133-141	7.3	3.3
BST	135-138	13.3	1.3

species. Therefore, the polymer structure dependences observed are interpreted in terms of glass-transition temperature (closely relates to softening point) and stability of active species. Tertiary cations that are rather stable are produced through ring-opening reaction.¹ However, BST does not show the post-irradiation polymerization effect, because bicycloorthoester does not react through ring-opening in the case of BST as shown in the reaction mechanism study section. On the other hand, low glass transition temperature increases the collision of active species to reduce their lifetime.¹⁵ Therefore, the polymers with allyloxymethyl type of backbone structure SA and GA do not show the post-irradiation polymerization effect due to their low glass transition temperature; nevertheless, spiroorthoester undertakes ring opening. The softening points of the polymers are listed in Table II.

Reaction Mechanism

In the case of high energy irradiations: Polymer films deposited on potassium bromide plates were subjected to X-ray irradiation of 7 J/cm². X-ray irradiation was used to elucidate the reaction mechanism, because the wide area needed to measure IR spectra can be easily irradiated. The changes induced in the polymer films have been studied on the basis of IR spectra measured before and after exposures.

Some of the polymers studied here exhibited C=O band (1720 cm⁻¹) and -OH band (3520 cm⁻¹) formations after exposure, as shown in Figures 2(a) and 2(b). From these IR spectrum changes, the crosslinking reaction induced in polymer films by the high energy irradiation is attributed to the ring-opening reaction as shown in Figures 3(a) and 3(b). In Figure 3, the cation A⁺ would be produced by EB and X-ray irradiations, because the energy of secondary electrons responsible for chemical reactions is sufficient to ionize organic compounds. On the other hand, 1-ethyl-4-vinylbenzyloxymethyl-2,6,7-trioxabicyclo[2.2.2]octane copolymer with styrene did not show any observed spectrum change as shown in Figure 2(c). This would be because production efficiency for the cation A⁺ and the acidity of A⁺ are dependent on the polymer structure to a great extent.

In the case of cation and radical initiations: The polymers containing spiroorthoester or bicycloorthoester were also subjected to cation (BF₃) and radical (AIBN) initiations. The results were in agreement with the data reported up to now,¹ i.e., cyclic ethers such as spiroorthoester, bicycloorthoester, epoxide, etc., react through ring opening by cationic initiation as shown in Figure 2(d), but do not react by radical initiation. In Figure 2(d), $\text{—N}^+ \equiv \text{N}$ (2200 cm⁻¹) adsorption and $\text{C—N}^+ \equiv \text{N}$ (1580 cm⁻¹) absorption decreases are attributed to the conversion of DEAFB after UV irradiation. In contrast to the radiation-induced reaction, any backbone structure influence was not observed in all polymers studied here.

As a result, the cyclic ether group-containing polymer reaction to EB and X-ray irradiations are different from the normal reaction to cations. The high energy radiation-induced reaction in cyclic ether group-containing polymers shows markedly larger polymer structure dependences than the cation-induced reaction does.

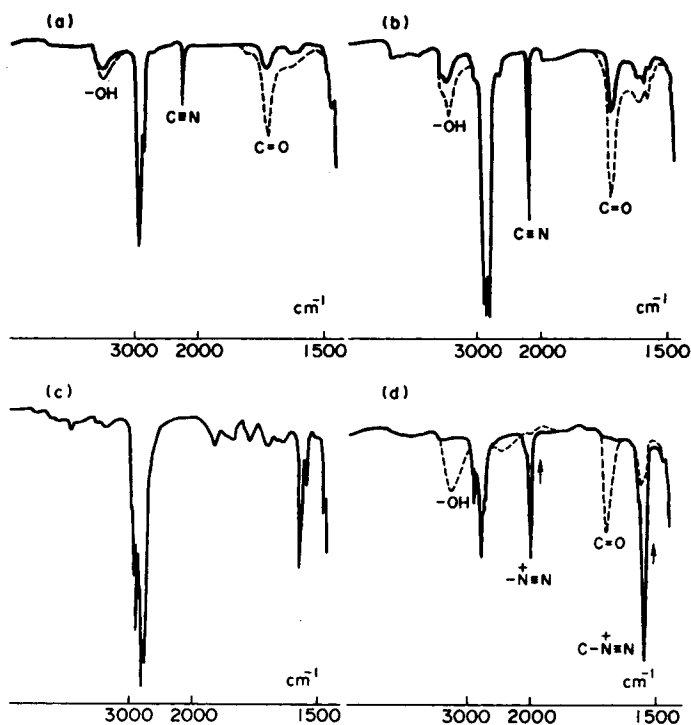


Fig. 2. IR spectra of polymers containing spiroorthoester or bicycloorthoester group: (a) NTS, (—) original and (---) irradiated with X-ray; (b) NTB, (—) original and (---) irradiated with X-ray; (c) BST, (—) original and (---) irradiated with X-ray; (d) BST, (—) before BF_3 production and (---) after BF_3 production.

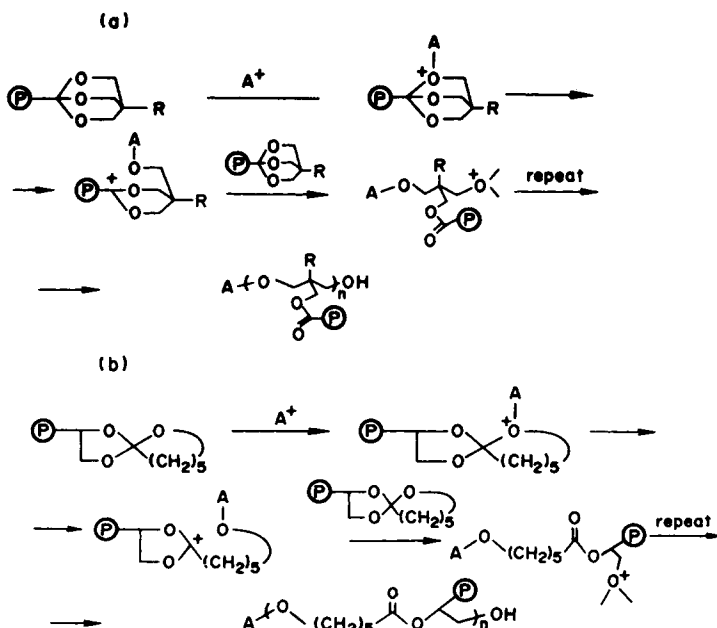


Fig. 3. Reaction mechanism for (a) spiroorthoester- and (b) bicycloorthoester-containing polymers under high energy radiation conditions: A^+ = radiation-induced cation; P = polymer backbone.

CONCLUSION

Polymers containing spiroorthoester or bicycloorthoester structure were found to be markedly highly sensitive to EB and X-ray irradiations. These orthoester groups reacted through ring opening under high energy irradiation conditions even in the absence of any cationic catalyst. It was also found that polymer structure exerted an influence on sensitivity and post-irradiation polymerization effect to a great extent.

The authors thank S. Fujiwara for his discussions, and also thank K. Okada for affording us the chance to use the X-ray exposure system.

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Received May 10, 1984

Accepted August 17, 1984