

# Syntheses and Properties of Polymers That Undergo No Shrinkage on Cross-Linking by Self-Catalyst

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## SYNOPSIS

The polymers containing spiroorthoester and benzyl sulfonium salt moieties were prepared by the ternary radical polymerization of unsaturated spiroorthoester 2-methylene-1,4,6-trioxaspiro[4.6]undecane (**1**) or 2-methylene-9-methyl-1,4,6-trioxaspiro[4.5]decane (**2**) with vinyl benzyl sulfonium salt ( $\text{VBS}^+\text{SbF}_6^-$ , **3**) and vinyl monomers (acrylonitrile or methyl acrylate). The obtained ternary copolymers such as P<sub>I</sub>, P<sub>II</sub>, P<sub>III</sub>, and P<sub>IV</sub> underwent curing over 75°C by self-catalyst to obtain the corresponding gelled polymers, with expansion or only slight shrinkage on curing.

## INTRODUCTION

Available thermosetting resins such as unsaturated polyester, epoxy, or phenol resins are well known to undergo a considerable shrinkage in volume on curing. Therefore, this phenomenon causes serious problems such as remaining internal distortion or growth of a micro crack in the cured material. To resolve these problems, spiroorthoesters,<sup>1,2</sup> spiroorthocarbonates,<sup>3-5</sup> and bicycloorthoester<sup>6</sup> might be promising monomers because they are polymerized with no shrinkage or only slight expansion in volume on polymerization to obtain the polyester ether or polycarbonate ester. Further, radical ring-opening polymerization of unsaturated spiroorthoesters<sup>7</sup> and spiroorthocarbonates has also been reported.<sup>8</sup>

For the potential use of unsaturated spiroorthoesters in the field of industrial materials, the syntheses of some copolymers containing spiroorthoester<sup>9-11</sup> or bicycloorthoester moiety<sup>12-15</sup> which are cured by cationic additive without volume change, was recently demonstrated.<sup>11,13,14</sup> Amplifying on this phenomenon, we report in this paper the syntheses of ternary copolymers carrying spiroorthoester and thermally latent cationic catalyst

moiety in the same chain.<sup>16</sup> These soluble polymers can be cured by self-catalyst without volume change.

## EXPERIMENTAL

### Materials

Methyl acrylate (MA) and acrylonitrile (AN) were purified by distillation under reduced pressure. Azobisisobutyronitrile (AIBN) was reagent grade. Unsaturated spiroorthoester (SOE), 2-methylene-1,4,6-trioxaspiro[4.6]undecane (**1**) (Ref. 7) and 2-methylene-9-methyl-1,4,6-trioxaspiro[4.5]decane (**2**) (Ref. 11), and vinyl benzyl sulfonium salt ( $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{S}^+\text{SbF}_6^-$ ,  $\text{VBS}^+\text{SbF}_6^-$ ) (Ref. 16) were prepared by the methods reported previously. Acetonitrile was purified by the general method.

### Instrumentation

<sup>1</sup>H-NMR spectra were measured using JEOL PX-100. Infrared (IR) spectra were recorded using JASCO FT/IR-3 or JASCO IRA-2. T.g.-d.t.a. curves were recorded on Rigakudenki CN8076E1 apparatus in N<sub>2</sub> atmosphere.

### Ternary Copolymerization

Ternary copolymerization was carried out at the desired temperature in the presence of AIBN in sealed

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**Table I Ternary Copolymerization of SOE 1, VBS<sup>+</sup>SbF<sub>6</sub><sup>-</sup> 3, and AN<sup>a</sup>**

Run	Monomer (mol %)				Copolymer					
	SOE 1	AN	VBS <sup>+</sup> SbF <sub>6</sub> <sup>-</sup>	AIBN	No.	Yield <sup>b</sup> (%)	Composition (mol %) <sup>c</sup>			
	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	(mol %)			m <sub>1</sub>	m <sub>2</sub>	m <sub>3</sub>	
1	45	45	10	1.8	P <sub>I</sub> -1	75.0 <sup>d</sup>	37	51	12	
2	47	47	6	1.8	P <sub>I</sub> -2	76.2	37	56	7	
3	49	49	2	1.8	P <sub>I</sub> -3	77.7	44	54	2	
4	40	50	10	1.8	P <sub>I</sub> -4	79.8	35	54	11	
5	30	60	10	1.8	P <sub>I</sub> -5	85.4	26	64	10	
6	20	70	10	1.8	P <sub>I</sub> -6	89.7	23	68	9	

<sup>a</sup> Monomers/MeCN = 1 g/1 g, at 60°C for 24 h.<sup>b</sup> Insoluble polymer in MeOH.<sup>c</sup> Estimated by elemental analysis.<sup>d</sup>  $[\eta] = 0.06$  (in 0.1M/NaSbF<sub>6</sub>-MeCN soln. at 30°C).

tubes using acetonitrile as solvent. The copolymers were isolated by pouring the reaction mixture into methanol or hexane. These results are summarized in Tables I-III. The data of the typical IR spectra of ternary copolymers are shown in Table IV.

### Self-catalyzed Cross-linking Reaction

Cross-linking reaction was performed in sealed tubes using acetonitrile as solvent. The obtained gelled polymers were washed repeatedly by acetonitrile.

### Measurement of Polymer Density

Polymer densities were measured with a density-gradient tube at 25°C. The samples of the polymers

before cross-linking were obtained by casting chloroform solution containing the corresponding polymers.

## RESULTS AND DISCUSSION

### Preparation of Monomers

Unsaturated spiroorthoester (SOE), 2-methylene-1,4,6-trioxaspiro[4.6]undecane (**1**) (Ref. 7), and 2-methylene-9-methyl-1,4,6-trioxaspiro[4.5]decane (**2**) (Ref. 11) were prepared by the reaction of epichlorohydrin and corresponding lactone followed by dehydrochlorination with a base:

**Table II Ternary Copolymerization of SOE 1, VBS<sup>+</sup>SbF<sub>6</sub><sup>-</sup> 3, and MA<sup>a</sup>**

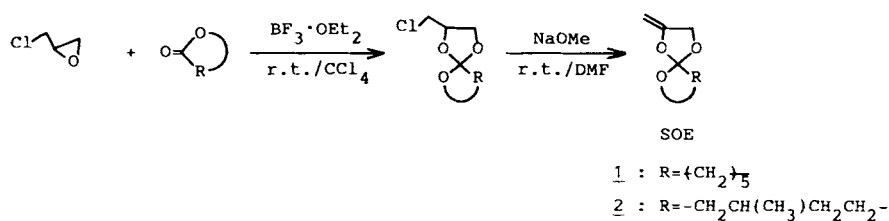
Run	Monomer (mol %)				Copolymer						
	SOE 1	MA	VBS <sup>+</sup> SbF <sub>6</sub> <sup>-</sup>	AIBN	No.	Yield (%)			Composition (mol %) <sup>b</sup>		
	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	(mol %)		MeOH Insoluble	Hexane Insoluble	Total	m <sub>1</sub>	m <sub>2</sub>	m <sub>3</sub>
1	45	45	10	1.9	P <sub>II</sub> -1	45.5 <sup>c</sup>	44.4	99.9	11	79	10
2	47	47	6	1.8	P <sub>II</sub> -2	56.0	28.5	84.5	18	77	5
3	49	49	2	1.6	P <sub>II</sub> -3	61.1	23.9	85.0	33.7	66	0.3
4	40	50	10	1.9	P <sub>II</sub> -4	57.4	31.2	88.6	10	84	6
5	30	60	10	1.8	P <sub>II</sub> -5	62.6	32.9	95.5	21	70	9
6	20	70	10	1.7	P <sub>II</sub> -6	56.4	35.5	91.9	2	91	7

<sup>a</sup> Monomers/MeCN = 1 g/1 g, at 80°C for 24 h.<sup>b</sup> Estimated by elemental analysis.<sup>c</sup>  $[\eta] = 0.13$  (in 0.1M/NaSbF<sub>6</sub>-MeCN soln. at 30°C).

**Table III Ternary Copolymerization of SOE 2, VBS<sup>+</sup>SbF<sub>6</sub><sup>-</sup> 3, and Vinyl Monomers<sup>a</sup>**

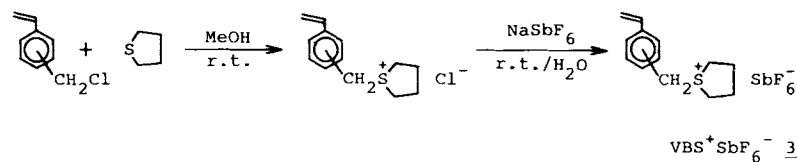
Run	Monomer (mol %)					Temp (°C)	No.	Copolymer			Composition (mol %) <sup>b</sup>		
	SOE 2 M <sub>1</sub>	Vinyl Monomer		VBS <sup>+</sup> SbF <sub>6</sub> <sup>-</sup> M <sub>3</sub>	AIBN (mol %)			Yield (%)					
		M <sub>2</sub>	M <sub>3</sub>					MeOH Insoluble	Hexane Insoluble	Total	m <sub>1</sub>	m <sub>2</sub>	m <sub>3</sub>
1	45	AN 45	10	1.8	60	P <sub>III</sub>	70.4	—	70.4	39	50	11	
2	45	MA 45	10	1.9	80	P <sub>IV</sub>	33.8	49.8	83.6	19	77	6	

<sup>a</sup> Monomers/MeCN = 1 g/1 g, for 24 h.

<sup>b</sup> Estimated by elemental analysis.


The synthesis of vinyl benzyl sulfonium salt (VBS<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, 3), which could initiate cationic po-

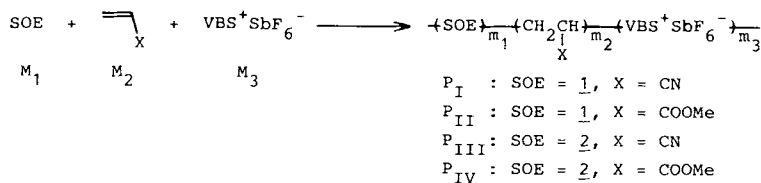
lymerization at a elevated temperature, was carried out according to the previous paper.<sup>16</sup>


**Table IV IR Spectra of Ternary Copolymers**

Copolymer No.	Wave Number of Absorption Band (cm <sup>-1</sup> )							
	C—O—							SbF <sub>6</sub> <sup>-</sup>
P <sub>I</sub> -1	2241 (C≡N)	1450	1178	1134	1065 (s)	1039	960	659
P <sub>II</sub> -1	1738 (C=O)	1452	1199	1168 (s)	1070 (s)	1039	960	659
P <sub>III</sub>	2241 (C≡N)	1456	1226	1192	1167	1064 (br)	979	659
P <sub>IV</sub>	1736 (C=O)	1452	1228	1192 (br)	1167	1066 (br)	979	659

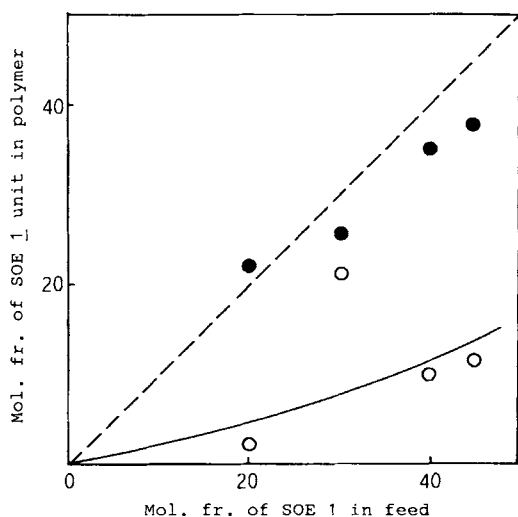
Ternary Copolymerization of SOE 1,  $\text{VBS}^+\text{SbF}_6^-$ , and Vinyl Monomers

The preparation of ternary copolymers was carried out at 60 or 80°C in a sealed tube with azobisisobutyronitrile (AIBN) in acetonitrile:



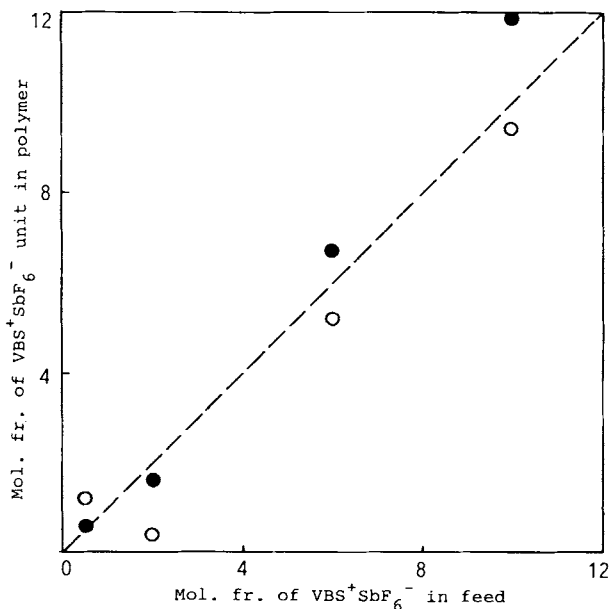
The ternary copolymerization of SOE 1,  $\text{VBS}^+\text{SbF}_6^-$ , and AN was carried out various monomer ratios in feed to obtain copolymers  $P_{\text{I}}$  as pale yellow powders in good yield, as summarized in Table I. They are soluble in aprotic polar solvents such as acetonitrile, dimethylformamide, and dimethyl sulfoxide. These obtained copolymers  $P_{\text{I}}$  were confirmed by IR and  $^1\text{H}$  NMR spectra. The IR spectra showed the absorption bands  $2241\text{ cm}^{-1}$  (C=N) and  $1200\text{--}950\text{ cm}^{-1}$  (spiroorthoester structure). The characteristic absorption based on  $\text{SbF}_6^-$  was observed at  $659\text{ cm}^{-1}$ .  $^1\text{H}$ -NMR showed the chemical shifts in  $\delta$  value 7.4 ppm (aromatic protons), 4.3 ppm ( $\text{Ph}-\text{CH}_2-\text{S}$ ), 4.1–3.0 ppm ( $-\text{CH}_2-\text{O}$  and  $-\text{CH}_2-\text{S}$ ), and 2.5–1.2 ppm ( $-\text{CH}_2-$  and  $\text{>CH-}$ ). These spectral data suggested that the spiroorthoester structure was introduced into the co-

polymers without the ring-opening isomeric reaction. Figure 1 shows the relationship between feed molar ratio of SOE 1 and the molar fraction of that in copolymer  $P_{\text{I}}$  when the feed molar ratio of  $\text{VBS}^+\text{SbF}_6^-$  is constant. Further, Figure 2 shows the relationship between feed molar ratio of  $\text{VBS}^+\text{SbF}_6^-$  and molar fraction of that in copolymer  $P_{\text{I}}$  when the feed ratio of SOE 1 and AN is constant. The molar fraction of SOE 1 and  $\text{VBS}^+\text{SbF}_6^-$  in copolymer was directly proportional to the feed ratio of those, respectively. These results indicate that the random copolymerization proceeds under these conditions.



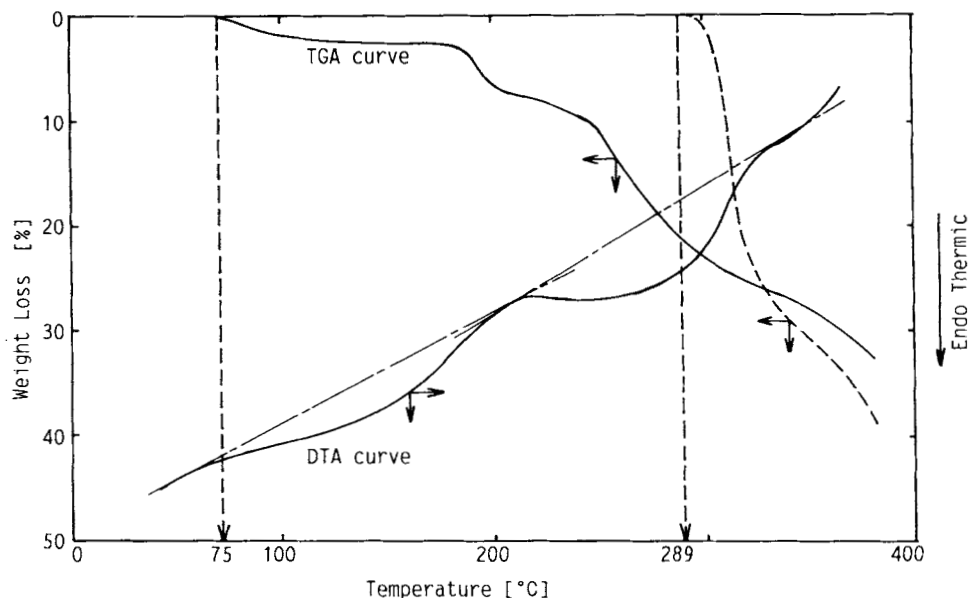
**Figure 1** Relationship of feed molar ratio of SOE 1 and copolymer composition:

(●)  $\left\{ \text{SOE } 1 \right\}_{m_1} \left\{ \text{AN} \right\}_{m_2} \left\{ \text{VBS}^+\text{SbF}_6^- \right\}_{m_3}$   
 (○)  $\left\{ \text{SOE } 1 \right\}_{m_1} \left\{ \text{MA} \right\}_{m_2} \left\{ \text{VBS}^+\text{SbF}_6^- \right\}_{m_3}$  (Mol fraction of  $\text{VBS}^+\text{SbF}_6^- = 10\text{ mol } \%$  in feed.)



**Figure 2** Relationship of feed molar ratio of  $\text{VBS}^+\text{SbF}_6^-$  and copolymer composition:

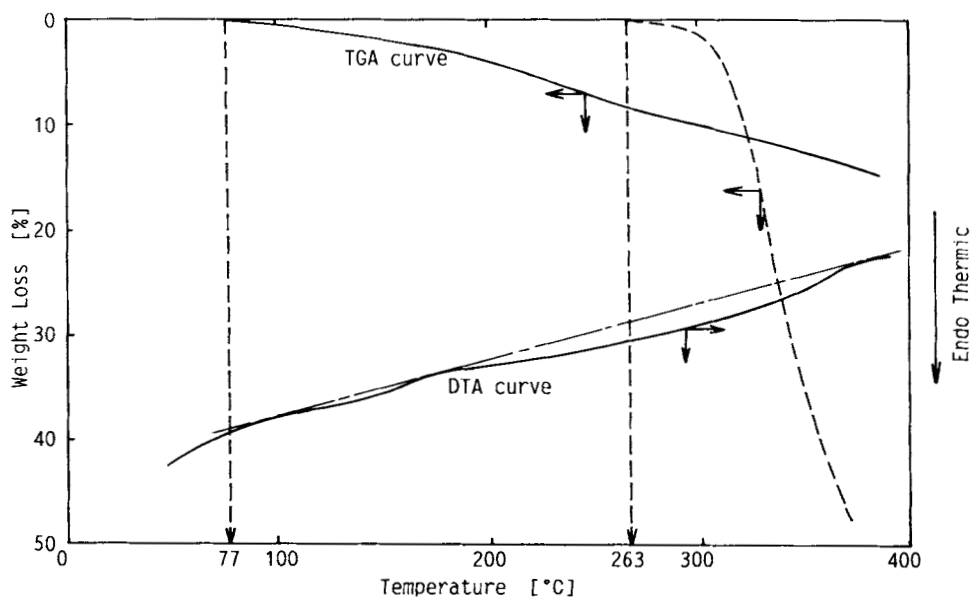
(●)  $\left\{ \text{SOE } 1 \right\}_{m_1} \left\{ \text{AN} \right\}_{m_2} \left\{ \text{VBS}^+\text{SbF}_6^- \right\}_{m_3}$ ;  
 (○)  $\left\{ \text{SOE } 1 \right\}_{m_1} \left\{ \text{MA} \right\}_{m_2} \left\{ \text{VBS}^+\text{SbF}_6^- \right\}_{m_3}$ . (SOE 1/AN or MA = 1 mol/1 mol in feed.)



**Figure 3** T.g.-d.t.a. curve of P<sub>I</sub>-1 (heating rate 10°C/min, in N<sub>2</sub>):  
 (—) (SOE 1)<sub>37</sub>(AN)<sub>51</sub>(VBS<sup>+</sup>SbF<sub>6</sub><sup>-</sup>)<sub>12</sub> (---) (SOE 1)<sub>42</sub>(AN)<sub>58</sub>.

In addition, the yellow powdery copolymers P<sub>II</sub> were obtained by the ternary copolymerization of SOE 1, VBS<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, and methyl acrylate (MA). The results are summarized in Table II. The IR spectra of P<sub>II</sub> showed the absorption bands 1738 cm<sup>-1</sup> (ester group), 1200–950 cm<sup>-1</sup> (spiroorthoester structure),

and 659 cm<sup>-1</sup> (SbF<sub>6</sub><sup>-</sup>), respectively, and <sup>1</sup>H-NMR showed the chemical shifts in  $\delta$  value 3.6 ppm (methoxy protons) and 7.3 ppm (aromatic protons). The relationship between feed ratio of SOE 1 and the molar fraction of that in obtained copolymer P<sub>II</sub> is shown in Figure 1. Further, the relationship be-



**Figure 4** T.g.-d.t.a. curve of P<sub>II</sub>-1 (heating rate 10°C/min, in N<sub>2</sub>):  
 (—) (SOE 1)<sub>11</sub>(MA)<sub>79</sub>(VBS<sup>+</sup>SbF<sub>6</sub><sup>-</sup>)<sub>10</sub>; (---) (SOE 1)<sub>39</sub>(MA)<sub>61</sub>.

tween feed molar ratio of  $\text{VBS}^+\text{SbF}_6^-$  and the molar fraction of that in the copolymer  $\text{P}_{\text{II}}$  is also shown in Figure 2. These results indicate that the random copolymerization will proceed, but that the SOE 1 is less copolymerizable in polymer when MA was used as comonomer in comparison with copolymer  $\text{P}_{\text{I}}$ .

Yellow powdery polymers  $\text{P}_{\text{III}}$  and  $\text{P}_{\text{IV}}$  were also obtained in good yield by the ternary copolymerization of SOE 2,  $\text{VBS}^+\text{SbF}_6^-$ , and vinyl monomers (AN or MA), as summarized in Table III.

### Thermal Properties of $\text{P}_{\text{I}}$ and $\text{P}_{\text{II}}$

The T.g.-d.t.a. curve of  $\text{P}_{\text{I-1}}$  and the copolymer of SOE 1, and AN (shown by the dotted line) as reference are shown in Figure 3. The reference copolymer that has no  $\text{VBS}^+\text{SbF}_6^-$  fraction was more stable than was the copolymer  $\text{P}_{\text{I-1}}$  because the weight decrement started at 289°C. The endothermic weight decrement of  $\text{P}_{\text{I-1}}$  starting at 75°C was caused by the loss of tetrahydrothiophene produced by the reaction of  $\text{VBS}^+\text{SbF}_6^-$  with the spiroorthoester moiety. Therefore, the copolymer  $\text{P}_{\text{I-1}}$  was stable at ambient temperature, and the cationic cross-linking reaction of that started at 75°C. At more elevated temperature (over 200°C), thermal degradation of

the polymer chain caused the vigorous weight decrement.

The result of thermal analysis of  $\text{P}_{\text{II-1}}$  is shown in Figure 4. The reference copolymer of SOE 1 and MA (shown by the dotted line) was stable until 263°C, but the weight of ternary copolymer  $\text{P}_{\text{II-1}}$  gently started to decrease at 77°C; the cationic cross-linking reaction may occur above 77°C.

### Cross-linking of $\text{P}_{\text{I}}$ , $\text{P}_{\text{II}}$ , $\text{P}_{\text{III}}$ , and $\text{P}_{\text{IV}}$

Self-catalyzed cross-linking reactions of  $\text{P}_{\text{I}}$ ,  $\text{P}_{\text{II}}$ ,  $\text{P}_{\text{III}}$ , and  $\text{P}_{\text{IV}}$  were carried out at 120°C in a sealed tube using MeCN as solvent. As shown in Table V, those copolymers were cross-linked successfully without any cross-linking agents to obtain hard amber gels. The IR spectra of the cured polymers showed the absorption band at 1736–1738  $\text{cm}^{-1}$  (ester group) resulting from the cationically ring-opening transfer reaction of spiroorthoester moiety, and the absorption bands between 1200 and 950  $\text{cm}^{-1}$  due to the spiroorthoester structure disappeared completely. But in the case of cured polymers obtained from  $\text{P}_{\text{II}}$  and  $\text{P}_{\text{IV}}$ , the new absorption band based on C=O was overlapped with the ester group of MA.

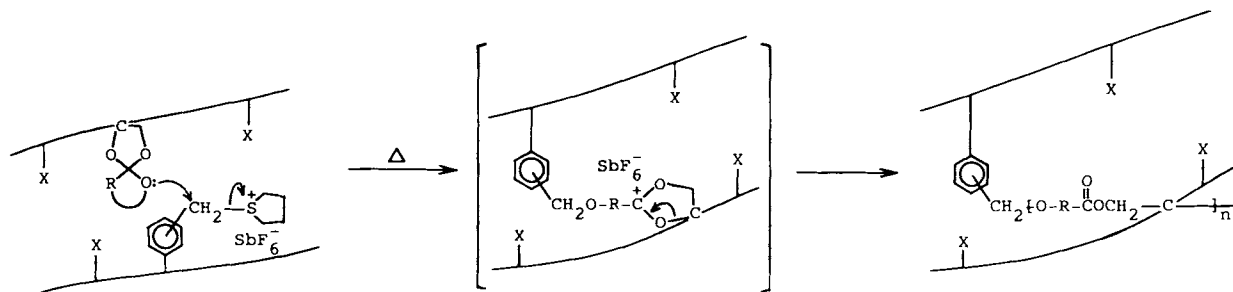
The self-catalyzed cross-linking of  $\text{P}_{\text{I}}$ ,  $\text{P}_{\text{II}}$ ,  $\text{P}_{\text{III}}$ , and  $\text{P}_{\text{IV}}$  would proceed presumably as follows:

Table V Cross-Linking of Ternary Copolymers<sup>a</sup>

Copolymer No.	Gel <sup>b</sup> Yield (%)	Polymer Density		Volume Change (%)
		Before Cross-Linking $d_{25}^4$ (g/cm <sup>3</sup> )	After Cross-Linking $d_{25}^4$ (g/cm <sup>3</sup> )	
$\text{P}_{\text{I-1}}$	71.6	1.343	1.331	0.89
$\text{P}_{\text{I-2}}$	82.3	1.257	1.283	-2.07
$\text{P}_{\text{I-3}}$	60.3	1.180	1.212	-2.71
$\text{P}_{\text{I-4}}$	81.0	1.350	1.314	2.67
$\text{P}_{\text{I-5}}$	80.6	1.340	1.330	0.75
$\text{P}_{\text{I-6}}$	80.4	1.338	1.295	3.21
$\text{P}_{\text{II-1}}$	86.1	1.380	1.415	-2.54
$\text{P}_{\text{II-2}}$	80.4	1.292	1.285	0.54
$\text{P}_{\text{II-3}}$	79.8	1.231	1.260	-2.36
$\text{P}_{\text{II-4}}$	84.6	1.350	1.341	0.67
$\text{P}_{\text{II-5}}$	86.8	1.362	1.371	-0.66
$\text{P}_{\text{II-6}}$	84.5	1.384	1.393	-0.65
$\text{P}_{\text{III}}$	88.0	1.323	1.350	-2.04
$\text{P}_{\text{IV}}$	73.9	1.358	1.411	-3.90

<sup>a</sup> Copolymer/MeCN = 1 g/1 g, at 120°C for 24 h.

<sup>b</sup> Washed sufficiently by MeCN.



### Volume Change of Copolymers on Cross-linking

The volume change of the obtained copolymers on the cross-linking reaction was estimated by the measurement of the polymer density of before and after cross-linking using a density-gradient tube at 25°C. These results are also summarized in Table V. In all cases, the copolymers underwent expansion or only slight shrinkage on cross-linking.

These self-catalyzed curable polymers might offer a class of useful resins to reduce internal distortion and growth of micro cracks observed in commercially available thermosetting resins.

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