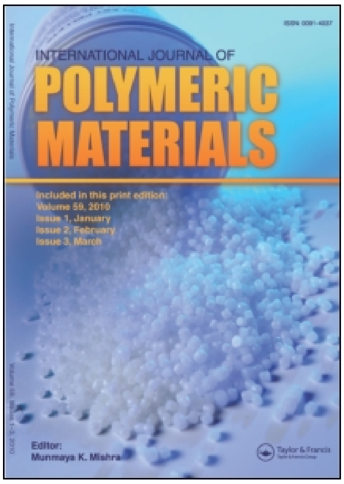

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Photoinitiated Cationic Copolymerization of an Alicyclic Epoxy Compound and a Spiroorthocarbonate

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Photoinitiated Cationic Copolymerization of an Alicyclic Epoxy Compound and a Spiroorthocarbonate†

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This article describes the photoinitiated cationic copolymerization of 1,6,8,13-tetraoxaspiro-(7,7)tridecanes (SOC_7), unconstrictive monomer, and 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexane carboxylate (ERL-4221). The test results show that the adding of a small amount of SOC_7 to ERL-4221 system results in suppression shrinkage without significantly degrading the thermal properties. The proper mol ratio of ERL-4221 to SOC_7 is 4:1. A crosslinked copolymer having Tg 230°C and volume shrinkage below 4.4% on photocopolymerization is given. This paper describes for mechanism of the cationic photocopolymerization of SOC_7 and ERL-4221. That is based on literature and experiments. FT-IR and ^{1}HNMR spectroscopic spectra are used to confirm the reaction mechanism proposed.

KEY WORDS Alicyclic epoxy resin, spiroorthocarbonate, photoinitiation, cationic copolymerization.

1. INTRODUCTION

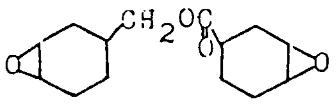
Recently, much attention is being paid to photofunctional polymers and many kinds of them have been developed.[1] SOC_7 and ERL-4221 are reactive monomers toward various sulfonium salt photoinitiated cationic polymerization within our knowledge. Bailey and Endo have shown that the spiroorthocarbonate is one of the useful monomers that suppress shrinkage in volume upon polymerization. It is well known that the presence of thermal mismatch between matrix and fiber is of course a general problem in all kinds of composite. It will be seen from this that the photocopolymer of SOC_7 and ERL-4221 is a fascinating topic.

2. EXPERIMENTAL

Materials

Alicyclic epoxy resin.

ERL-4221



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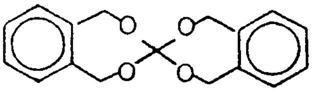
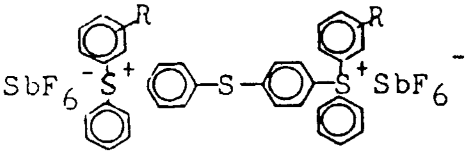
The 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexane carbonate used in this study was from ADEKA OPTOMER CHEMICAL IND. CO, LTD, TOKYO, JAPAN. Unde CHEMICAL IN the trade name ERL-4221. Spiroorthocarbonate monomer.

SOC_7



The 1,6,8,13-tetraoxaspiro[7,7]tridecanes (the monomer is abbreviated to SOC_7) was prepared by myself.
Photoinitiator.

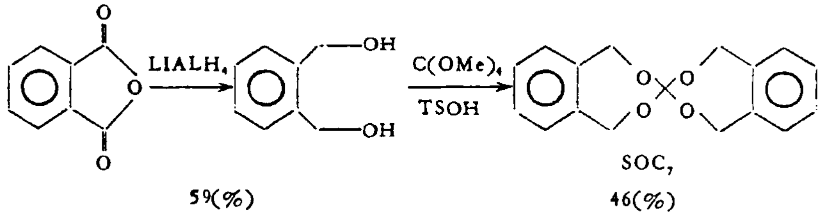
SP-170



The Bis[4-(diphenylsulfonio)alkylphenyl]sulfide-Bishexafluoro antimonate (sp-170) was supplied by ADEKA OPTOMER CHEMICAL IND. CO, LTD, TOKYO, JAPAN.

Synthesis

Synthesis of 1,6,8,13-tetraspiro[7,7]tridecanes (SOC_7) was carried out according to Mr. Toshikazu Tahata and Takeshi Endo reported mothod.[2] The synthetic procedure and analytical data are shown in Scheme I and Table I.



SCHEME I

TABLE I

Analytical data of SOC_7

monomer, mp[a](℃)	FT−IR[b],cm^{-1}	^{1}HMNR. δ[c]
$C_{17}H_{16}O_4$(284)	3067, 3028, 2976, 2932, 2881, 1498, 1446, 1211, 1161, 1141, 1120, 1103, 997, 972, 784	4,93(S. 8H. OCH_2) 7.16(S. 8H. Ar)

[a] Lit 261–263°C. [b] KBr. [c] In dimethyl—d_6 sulfoxide at 80°C; S, singlet. The bulk photocopolymerization of SOC_7 and ERL—4221 containing given amounts of the photoinitiator was carried out in a sealed tube, which is a 50 ml, polymerization pyrextube degassed by repeated cooling and pumping and sealed in the usual manner. The photoirradiation was performed by means of a 400W High Pressure Mercury Lamp or a 300 nm xe—Hg Lamp was used throughout the work. Amounts of photoinitiator and monomer are listed in Table II, which also contains the photocured conditions and analytical data.

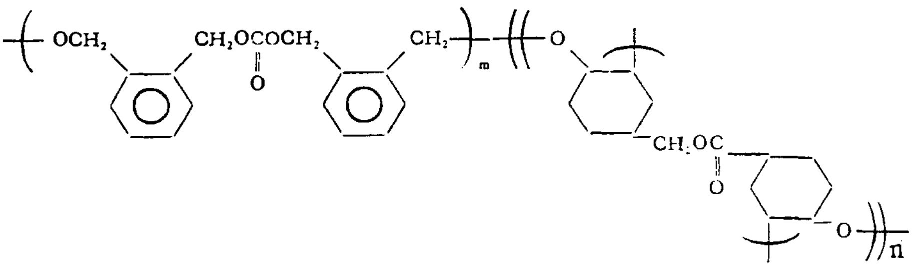
TABLE II

Photopolymerized condition and analytical data of SOC_7 and ERL-4221

run No	m mol ratio			photopolymerization condition	gel content[a] (%)	T_g (℃)	T_d (℃)
	ERL—4221	SOC_7	Photoinitiator				
1	0. 4	0. 1	SP—170(g) 0. 02	High Press Mercury Lamp (400 W, >300nm) irr time (h)			
				4	100	203	326
2	0. 4	0. 2	0. 02	5	100	151	368
3	0. 4	0. 2	0. 02	6	100	156	390
4	0. 4	0. 3	0. 02	5	100	127	280

(a) acetone insol(Wt %) by soxhlet extraction for 8h.

constitutional formula and composition calculated from elemental analysis are as follows.



No. 1 $m = 78, n = 22$; No. 2 $m = 85, n = 15$;
No. 3 $m = 85, n = 15$; No. 4 $m = 90, n = 10$.

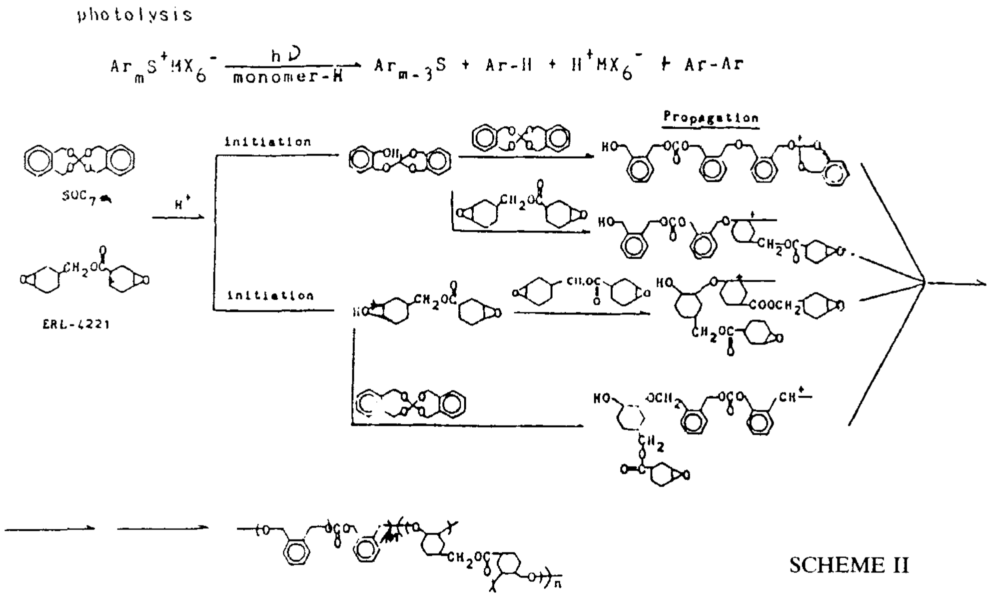
FT-IR spectra were obtained with a JASCO FT/IR-3 at 25°C. ^{1}HNMR spectra were recorded on a JEOL PMX-60 Sispectrometer, using tetramethylsilane (TMS) as internal standard in deuteriochloroform at 27°C, unless otherwise stated. Glass transition temperature (Tg) and decomposition temperature (T_d) were measured by SEIKO DENSHI KOGI0 CO, LTD. DSC-41M.

3. RESULTS AND DISCUSSION

Photocopolymerization Behaviour of SOC_7 and ERL-4221

We would like to propose the mechanism shown in Scheme II for the cationic photocopolymerization of SOC_7 and ERL-4221. That is based on literature[1] and experiments.

FT-IR and ^{1}HNMR spectroscopic technique was used to confirm the reaction mechanism proposed. Figures 1–2 show respectively the IR, and ^{1}HNMR spectra of this system. It can be seen from Figure 1 absorption of 916 cm^{-1}. 1174 cm^{-1} and 1743 cm^{-1} (attributed to epoxy, ester linkage and carbonate $c = 0$ absorption



SCHEME II

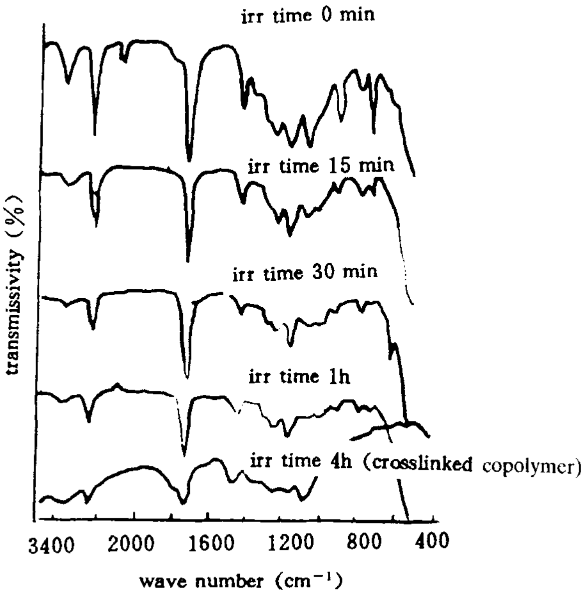


FIGURE 1 IR spectra of ERL-4221/SOC$_7$/SP-170 system before irradiation, and after irradiation for 15 min, 30 min, 1 h and 4 h respectively.

band) were gradually weakened. The results determined by the ^{1}HNMR technique was shown in Figure 2, not to say analogous results were obtained. This variation observed in ^{1}HNMR is sharp contrast to that observed in IR was similar. The structure of the copolymer was confirmed by elemental analysis, IR and ^{1}HNMR. The crosslinked copolymer was obtained as a white solid in high yield by several

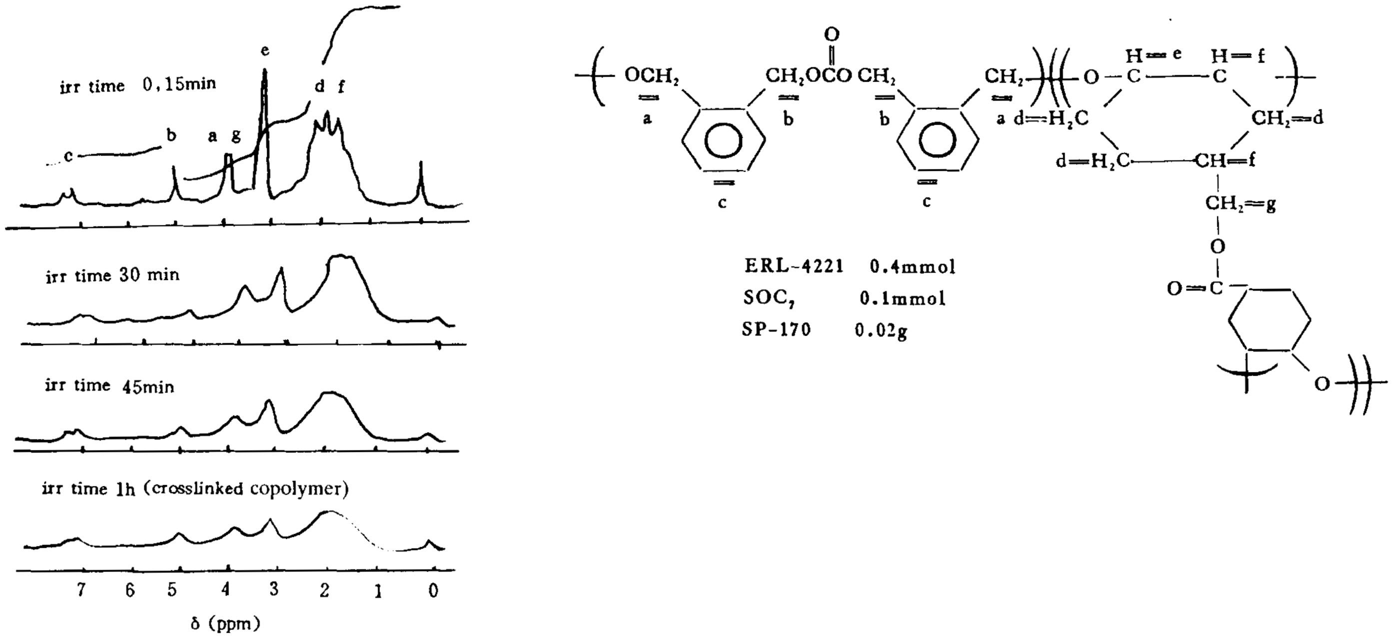


FIGURE 2 ^{1}HNMR study of ERL-4221/SOC$_7$/SP-170 system before irradiation, and after irradiation in CDCL$_3$ with XE-Hg 300 nm.

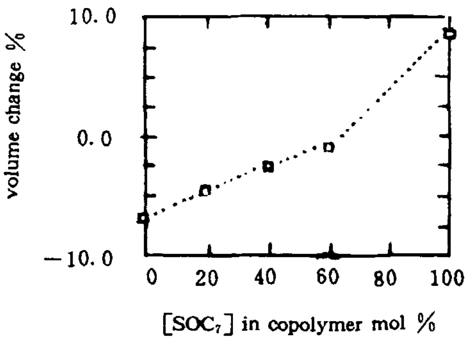


FIGURE 3 Influence of SOC$_7$ on the volume change of photocured crosslinked copolymer. Figure 4 shows the influence of SOC$_7$ on the Tg of copolymer. The results suggests that the Tg very rapidly shifted to lower temperature as the SOC$_7$ is increased. This is probably due to ring opening of SOC$_7$ and the decrease of crosslinking density. This feature indicates that when large amounts of SOC$_7$ (more than 20 mol %) is used, the copolymer shows a lower T_g than 200°C.

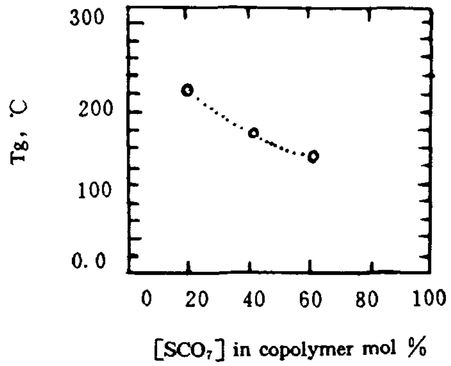


FIGURE 4 Influence of SOC$_7$ on the Tg of crosslinked copolymer. The preceding discussion reveals that the properties of SOC$_7$/ERL-4221/SP-170 system are affected by the concentration of SOC$_7$ directly. We believe that large amounts of SOC$_7$ gives the characteristics of flexibilization to the copolymer, therefore, small amount of SOC$_7$ (less than 20 mol %) should be most effective and is used for further study.

photopolymerization conditions (Table II). Then crosslinked homopolymer of ERL-4221 was colourless and transparent. Consequently, it is enough to prove the copolymerization.

Effect of content of SOC$_7$ on T_g and volume shrinkage of copolymerization

As has been said before, an important problem with polymer matrix composite is that associated with severe internal stresses. Because polymer has high thermal expansivities and expansion coefficients are not truly constants. That is, the polymers expand markedly in a nonlinear way with temperature. Therefore, we are much interested in glass transition temperature and volume shrinkage of the copolymer.

The level of SOC_7 was varied in order to examine what effect is observed on the Tg and volume shrinkage of the copolymerization. Direct observation of volume change[3] on photocopolymerization was carried out by measuring difference of volume of a mixture in a polymerization glass tube (3 mm diameter) before and after photocopolymerization.

As shown in Figure 3, the volume shrinkage decreased with the increase of the SOC_7 content. This experiment again demonstrates the combination of SOC_7 and ERL-4221 may lead to suppression of the volume shrinkage. Thus we think the degree of the volume shrinkage of ERL-4221 is controlled by the amount of added SOC_7.

CONCLUSIONS

The results described above are summarized as follows: 1) The addition of small amounts of SOC_7 to epoxy resin ERL-4221 system results in suppression shrinkage without significantly degrading the thermal properties. In our view, the proper mol ratio of ERL-4221 to SOC_7 is 4 to 1. 2) A photocopolymer having T_g 203°C and volume shrinkage below 4. 4% will have considerable practical application.

References

1. J. V. Criveiio and J. H. W. Lam, *Macromolecules*, **10**, 1307 (1977); idem, *J. Polym. Sci., Polym. Chem.*, **17**, 977 (1979).
2. T. Takate and T. Endo, *Macromolecules*, **21**, 900 (1988).
3. F. Ndkanishi, K. Yamada and H. Nakanishi, *J. Polym. Sci.*, **26**, 330 (1988).
4. T. Takata and T. Endo, *Polymer Preprint JPN.* **37**, 1559 (1988).
5. W. R. Watt, H. T. Hoffman, Jr., H. Poobiner, L. J. Schholmih, L. S. Yang, *J. Polym. Sci., Polym. Chem.*, **22**, 1789 (1984).