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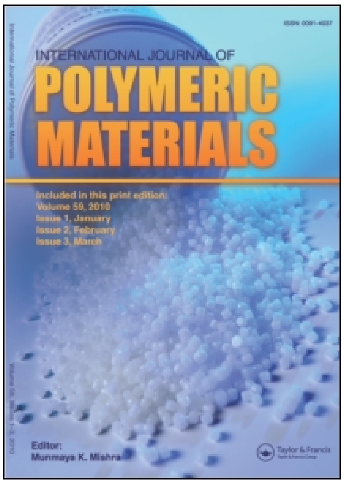

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Effect of Structural Difference of Photoinitiator on Photocopolymerization of an Alicyclic Epoxy Compound and a Spiroorthocarbonate

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Effect of Structural Difference of Photoinitiator on Photocopolymerization of an Alicyclic Epoxy Compound and a Spiroorthocarbonate[†]

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(Received April 20, 1992)

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). With four photoinitiators-Bis[4-(diphenylsulfonio) alkyl phenyl] sulfide-Bishexafluoroantimonate (sp-170), Bis[4-(diphenylsulfonio) alkyl phenyl] Sulfide-Bishexafluorophosphite (sp-150), Benzoloxyphenylbenzylmethyl sulfonium hexafluoroantimonate (BBS) and p-hydroxyphenyl benzyl methyl sulfonium hexafluoroantimonate (PHS). The effect of photoinitiator type on the photocuring rate have been discussed. The test results show the sp-170 is the most efficient photoinitiator. The Tg as might be expected is independent of photoinitiator type, but results indicates that Tg increased with the irradiation time.

KEY WORDS Photoinitiator, photolysis, photoinitiated cationic copolymerization, alicyclic epoxy resin, spiroorthocarbonate.

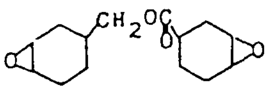
Recently, much attention is being paid to photofunctional polymers and photolysis of photoinitiators.[1-4] Some of the studies concern the photolysis of sulfonium salts.[5,6] It is stated that the site of photoactivity therefore lies in the character of the organic portion of the photoinitiator molecule, whereas the corresponding catalytic activity in photopolymerization still depends on the nature of the anion. To investigate this point, effect of structural difference of photoinitiators, such as sp-170, BBS and PHS, on photocopolymerization of an alicyclic epoxy compound and a spiroorthocarbonate were investigated, to select these photoinitiators is because they are easily prepared and are not quenched by oxygen of other triplet quenchers.[7,8] Our initial experiments have shown that sp-170, BBS and PHS, are of particular interest as photoinitiators of cationic polymerization of SOC_7 and ERL-4221.[9]

[†] This work is supported by National Natural Science Foundation of China.

EXPERIMENTAL

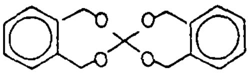
Materials

Alicyclic epoxy resin



ERL-4221

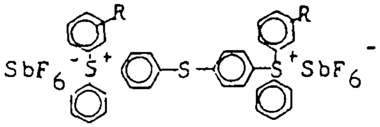
The epoxy resin (3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate) used in this study was from Adeka Optomer Chemical Ind. Co., Ltd., Tokyo, Japan, under the trade name ERL-4221.



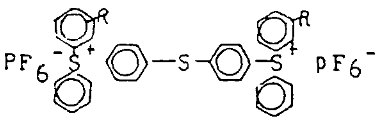
SOC_7

The 1,6,8,13-tetraoxaspiro [7,7] tridecanes (the monomer is abbreviated to SOC_7) was prepared by myself.[10]

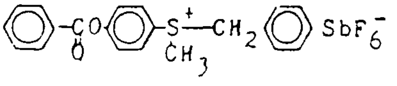
Photoinitiators



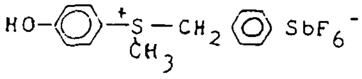
SP-170



SP-150



BBS



PHS

The sp-170 and sp-150 were supplied by Adeka Optomer Chemical Ind. Co., Ltd., Tokyo, Japan. The BBS and PHS were kindly supplied by Mr. Hamats of San-Shin Chemical Ind. Co., Ltd., Tokyo, Japan.

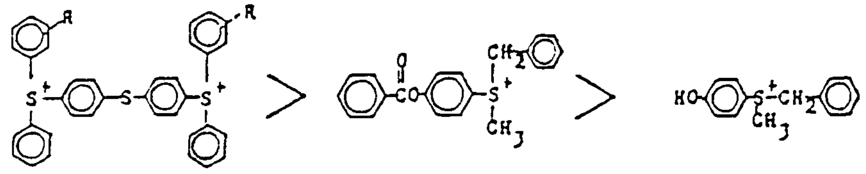
The bulk photocopolymerization of SOC_7 and ERL-4221 containing given amounts of the photoinitiator was carried out in a sealed tube, which is a 50 ml, polymerization pyrex tube degassed by repeated cooling and pumping and sealed in the usual manner. The photoirradiation was performed by means of a 400 W high pressure mercury lamp.

Photolyses of photoinitiator (sp-170) were conducted with a 500 W xenon lamp by irradiating at >300 nm, at 25°C. Each sample consisted of the photoinitiator in cyclohexane in the quartz sample tubes which was repeatedly vacuum freeze-thaw degassed and sealed under argon. The sample cell was placed 5 cm far from the lamp. Glass transition temperature (Tg) and decomposition temperature (T_d) were measured by Seiko Denshi KOG10 Co., Ltd. DSC-41M. UV spectra were obtained with a Shimazu UV-2100 spectrometer.

RESULTS AND DISCUSSION

Effect of Photoinitiator Type

Absorption spectra of SOC_7, ERL-4221, BBS, PHS and SP-170 are shown in Figure 1, respectively. The structure, λ_{max} and ε_{max} of these compounds are shown in Table I. It can be seen from Table I and Figure 1, the order of λ_{max} of these compounds is therefore, PHS > BBS > sp-170 and SOC_7 > ERL-4221, but we have found in the experiments that sp-170 is the most efficient photoinitiator in cationic copolymerization of SOC_7 and ERL-4221.



The effect of photoinitiator type on the photocuring rate was clearly shown in Figure 2. These photoinitiators (i.e., BBS, PHS and SP-150) show substantially lower photocured rate, so that, SP-170 was chosen as a photoinitiator of this system. When SP-170 was used as photoinitiator, crosslinking reaction may be considered

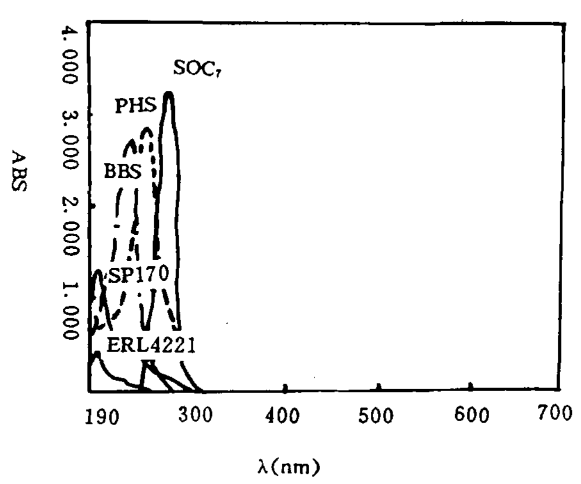


FIGURE 1 Absorption spectra of SOC_7, ERL-4221, BBS, PHS and SP-170.

TABLE I

Determinate and analytical data of Figure 1

SAMPE	solvent	conc (mol/l)	peaak, λ_{max} (nm)	(ABS) value	ε_{max}^{a} (l • mol^{-1} • cm^{-1})
SOC_7	$CHCl_3$	0.8×10^{-4}	270.5	3.261	40762
ERL−4221	$CH_2(CH_4)_4CH_2$	9.6×10^{-4}	198	0.443	461
BBS	CH_3CN	0.7×10^{-4}	238.0	2.739	39128
PHS	CH_3CN	0.4×10^{-4}	248.5	1.418	35450
SP−170	$CH_2(CH_2)_4CH_2$	1.4×10^{-4}	201.0	1.353	9664

[a] Maximum molecular absorptivity is a constant characteristic of particular compound at the maximum wavelength.

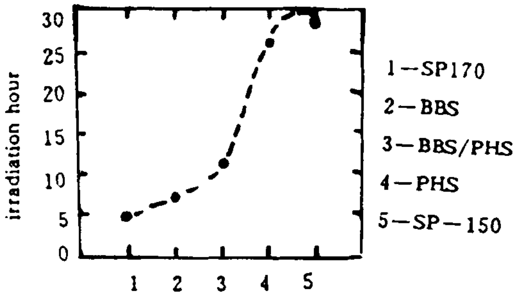


FIGURE 2 Effect of photoinitiator type on photocured time (gel content[a] is reached 100%).

almost complete after irradiation for 4 h at 20°C. Results of Figure 2 show that the order of reactivity of the four photoinitiators having different $ArmS^+$ cations and same SbF_6^- anions in the photopolymerization of SOC_7 and ERL-4221 is therefore then the order of reactivity of the photoinitiators having same $ArmS^+$ but different Mx_n^- anions (SP-170 and SP-150) is therefore $SbF_6 > PF_6$. On the other hand, the larger the negatively charged ion, the more loosely it is bound to the cation and the more active the propagating cationic species in the polymerization.

The relationship between irradiation time and gel formation was shown in Figure 3. It is clear that the reactivity of ERL-4221 is higher than the SOC_7 although the SOC_7 is an functionalized spiroorthocarbonate monomer having photochemically active carbonate, then, the bifunctional epoxy compound ERL-4221, is particularly reactive in cationic photopolymerization because ring opening of epoxy group is easy. From here we see that the photocuring rate is independent of λ_{max} and ε_{max}, that is, depends on the structure of monomer and photoinitiator. This experimental evidence again indicates that oxirane compounds are reactive substrates.

The Tg as might be expected is independent of photoinitiator type as shown in Figure 4, but Figure 5 indicates that Tg increased with the irradiation time. It stands to reason that the degree of crosslinking increased with irradiation time.

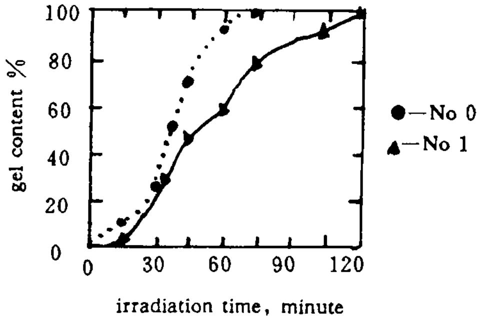


FIGURE 3 Relationship between irradiation time and gel formation

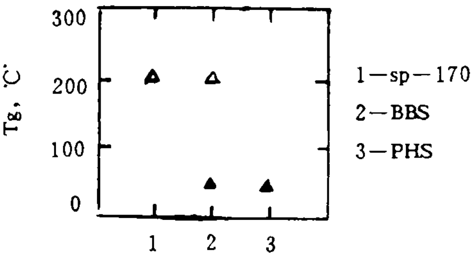


FIGURE 4 Influence of photoinitiator type on the Tg of crosslinked copolymer.

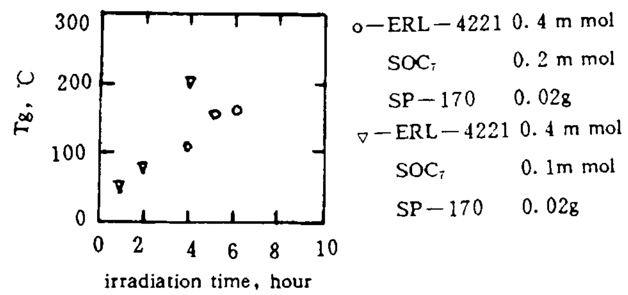
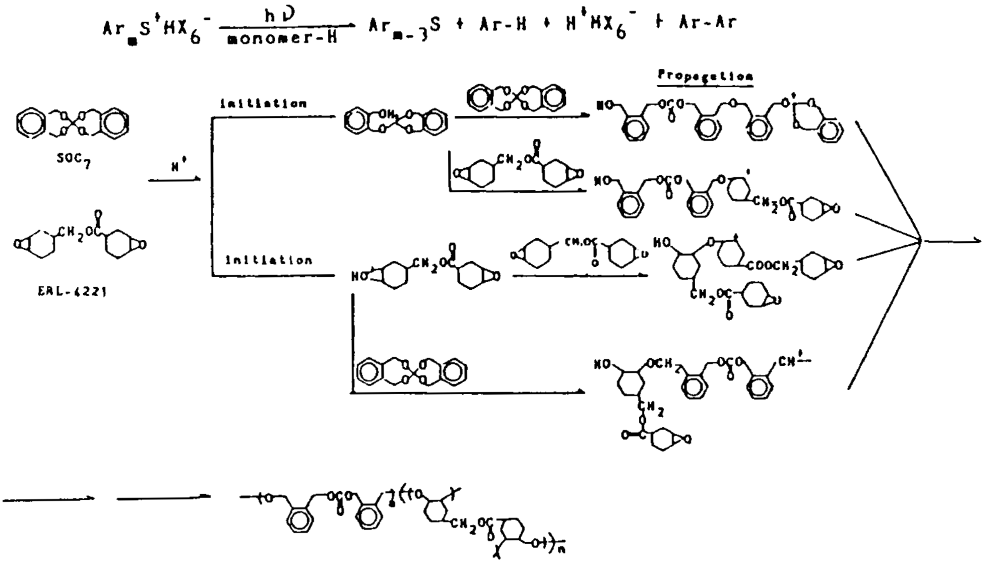


FIGURE 5 Influence of photoirradiation time on Tg of crosslinked copolymer.

Photocopolymerization Behaviour of SOC_7 and ERL-4221

We would like to propose the mechanism shown in Scheme I for the cationic photocopolymerization of SOC_7 and ERL-4221. That is based on literature[1] and experiments. Additional evidence for this mechanism was obtained by an examination of the UV spectra of this system. As a matter of record, we may postulate that the three steps consist of photolysis, initiation and propagation correspond with change in UV spectrum of SOC_7/ERL-4221/SP-170 system during irradiation with 300 nm light. As shown in Figure 6 upon irradiation with light of wavelength 300 nm, the peak having an absorption maximum at 198.5 nm appeared gradually with increasing of irradiation time. The peak at 198.5 nm increased rapidly from the 0 station to the 1 station after 5 min irradiation as a result of the first step consists of the photoinduced generation of the strong protonic acid HMX_6 proceeds



SCHEME I

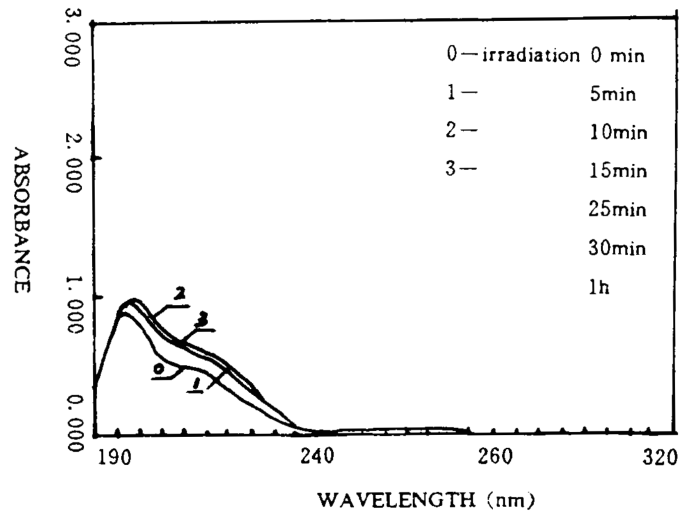


FIGURE 6 Change in UV spectrum of SOC$_7$ (0.1 mmol)/ERL-4221 (0.4 mmol)/SP-170 (0.02$_g$) system during irradiation with 300 nm light, sol: cyclohexane; conc: 4.08 × 10^{-4} mol/l; 300 nm Xe-Hg lamp.

rapidly. Initiation takes place by the addition of the acid to the monomer with formation of a carbonium ion was relatively slow compared with the photolysis, as a consequence, the peak at 198.5 nm increased slowly from the 1 station to the 2 station after 10 min irradiation it stands to reason that the ring-opening of monomer needs an induction period. In the propagation step, the active center propagates by the addition of monomer which results in chain growth. That is, it is dark (nonphotochemical) step, so that the peak at 198.5 nm decreased from the 2 station to the 3 station after 15 min irradiation. It is also conceivable that change of absorbance at 198.5 nm observed during the long irradiation was hardly anything from that time on (i.e. absorption intensity at 198.5 nm did not increase further) indicating that the copolymer was formed at that time.

In addition, our initial experiments have shown that the adding of a small amount of SOC_7 to ERL-4221 system resulted in suppression shrinkage without degrading the thermal properties. The proper mol ratio of ERL-4221 to SOC_7 was 4:1. A crosslinked copolymer having Tg 203°C and volume shrinkage below 4.4% on photocopolymerization was given.[9]

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