Synthesis and Thermal Self-Crosslinking Reaction of Copolymers from 2,3-Epoxypropyl Methacrylate and *p*-Substituted Phenyl Methacrylates

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Synopsis

Copolymers of 2,3-expoxypropyl (glycidyl) methacrylate (GMA) with various phenyl methacrylates such as 4-nitrophenyl methacrylate (NPMA), 4-chlorophenyl methacrylate (CPMA), or phenyl methacrylate (PMA), and other monomers such as methyl methacrylate (MMA), ethyl acrylate (EA), or styrene (ST) were synthesized by radical copolymerization, and then thermal self-crosslinking reactions of the obtained copolymers were carried out using various catalysts such as quarternary ammonium salts, *tert*-amines, or the crown ether/potassium salt systems at 100–150°C. Although the copolymer of GMA–NPMA–MMA does not produce any gel products without catalyst upon heating at 110°C for 5 h, this copolymer gives gel products in 82% yield using 10 mol% of tetrabutylammonium bromide as a catalyst under the same conditions. The rate of gel production of the copolymer of NPMA is faster than those of copolymers of CPMA and PMA. The rate of the gel production of the copolymer of GMA–NPMA–EA is also faster than those of copolymers of MMA and ST. Furthermore, it was found that the rate of gel production of the copolymer was strongly affected by the kind of catalyst, the catalyst concentration, and the reaction temperature.

INTRODUCTION

Various thermo-crosslinking reactions of polymers and oligomers containing epoxide,[1-5] isocyanate,[1,6,7] cyanate ester,[8,9] carboxylic acid,[1] hydroxyl,[1] methylol groups,[1] iminoethers,[10,11] alkenyl azlactone,[12,13] bicyclo ortho ester,[14-16] or active ester groups[17,18] with the corresponding crosslinking reagents, or the catalysts are known, and some of these reactions are widely used in industry. Thermo- or photocrosslinking reaction of the polymers containing pendant C=C groups such as acrylate, methacrylate, crotonate, vinyl, allyl, propargyl, or cinnamoyl groups in the presence of thermal initiators or photosensitizers has also been reported[1,19,20] so far.

Recently, we reported syntheses and thermal self-crosslinking reactions of polymers with pendant cyclic iminoether moiety and carboxylic acid,[21] or with pendant bicyclo ortho ester and carboxylic acid groups.[22]

This article reports on a synthesis and thermal self-crosslinking reaction of copolymers from 2,3-epoxypropyl (glycidyl) methacrylate (GMA) and phenyl or *p*-substituted phenyl methacrylates, and other monomers.

EXPERIMENTAL

Materials

The solvents were purified by distillation prior to use. 2,2'-Azobisisobutyronitrile (AIBN) was purified by two recrystallization from methanol at 40°C. GMA, methyl methacrylate (MMA), ethyl acrylate (EA), and styrene (ST) were distilled twice under reduced pressure. Reagent grade tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAB), tetrapropylammonium bromide (TPAB), tetrabutylammonium bromide (TBAB), tetrapentylammonium bromide (TPEAB), tetrahexylammonium bromide (THAB), tetramethylammonium chloride (TMAC), tetraethylammonium chloride (TEAC), tetrapropylammonium chloride (TPAC), tetrabutylammonium chloride (TBAC), tetrapentylammonium chloride (TPEAC), tetrabutylammonium iodide (TBAI), tetrabutylammonium hydrogensulfate (TBAH), tetrabutylammonium perchlorate (TBAP), tetrabutylphosphonium bromide (TBPB), benzyltrimethylammonium chloride (BTMAC), benyzltriethylammonium chloride (BTEAC), cetyltrimethylammonium chloride (CTMAC), tributylamine (TBA), dicyclohexyl-18-crown-6 (DCHC), potassium bromide (KBr), potassium iodide (KI), and potassium thiocyanate (KSCN) were generally used without further purification. Potassium phenoxide (KOPh), potassium acetate (KOAc), and potassium benzoate (KOBz) were synthesized from the reactions of potassium hydroxide with corresponding phenols or acids in methanol, respectively, and then they were recrystallized from methanol. 4-Nitrophenyl methacrylate (NPMA) (mp 92.5–93.5°C), 4-chlorophenyl methacrylate (CPMA) (bp 94–96°C at 2 mm Hg) and phenyl methacrylate (PMA) (bp 62–63°C at 1 mm Hg) were synthesized by the reactions of methacryloyl chloride with corresponding phenols using triethylamine as HCl acceptor in THF according to the reported method.[23,24]

Apparatus

The ^{1}H-NMR spectra were performed on the JEOL Models JNM FX-200 (200 MHz) and JNM PS-100 (100 MHz) spectrometer. Infrared (IR) spectra were recorded on JASCO Model A-202 spectrophotometer.

Typical Procedure for Radical Copolymerization

Typical example of the synthesis of the copolymer is as follows. The conditions and results of the syntheses of other copolymers are summarized in Table I.

GMA [4.3 g (30 mmol)], 6.2 g (30 mmol) of NPMA, 4.0 g (40 mmol) of MMA, and 0.14 g (0.85 mmol) of AIBN were dissolved in 140 mL of dioxane, and then the mixture was heated at 60°C for 5 h and 80°C for 3 h under a current of nitrogen. Then, the polymer solution was poured into 1 L of methanol. The resulting polymer (polymer 1) was reprecipitated twice from THF into methanol, filtered, and dried *in vacuo* at 50°C. Yield of the polymer was 11.1 g (76.2%). The amount of GMA and NPMA units in the polymer was 31 and 32%, respectively [calculated from the results of measurement of the epoxide

TABLE I

Syntheses of Copolymers by Radical Copolymerizations of GMA, Phenyl Methacrylates (M_2), and Other Monomers (M_3)[a]

Polymer no.	Amount of GMA (mmol)	Amount of M_2[b] (mmol)	Amount of M_3[b] (mmol)	Amount of AIBN (mmol)	Vol. of dioxane (mL)	Yield (%)	GMA unit in copolymer (mol-%)	M_2 unit in copolymer (mol-%)	M_3 unit in copolymer (mol-%)	copolymer η_{red}[c]
1	30	NPMA(30)	MMA(40)	0.85	140	76.2	31	32	37	0.31
2	20	NPMA(20)	MMA(60)	0.79	120	72.3	19	24	57	0.30
3	15	NPMA(15)	MMA(70)	0.61	100	76.8	15	15	70	0.26
4	10	NPMA(10)	MMA(80)	0.61	100	81.8	11	13	76	0.29
5	10	CPMA(10)	MMA(80)	0.61	100	76.9	12	10	78	0.22
6	10	PMA(10)	MMA(80)	0.61	100	78.4	11	11	78	0.27
7	20	NPMA(20)	EA (60)	0.61	100	76.6	18	20	62	0.24
8	20	NPMA(20)	ST (60)	0.61	100	32.3	18	39	43	0.13
9	30	NPMA(30)	—	0.61	100	72.1	47	53	—	0.15

[a] Copolymerization was carried out at 60°C for 5 h and then 80°C for 3 h under a stream of N_2.

[b] GMA = glycidyl methacrylate, NPMA = 4-nitrophenyl methacrylate, CPMA = 4-chlorophenyl methacrylate, PMA = phenyl methacrylate, MMA-methyl methacrylate, EA = ethyl acrylate, ST = styrene.

[c] Measured at a concentration of 0.5 g/dL in DMF at 30°C.

equivalent[25] (538.5), of elemental analysis of nitrogen and of intensity ratio of ^{1}H-NMR spectrum]. Reduced viscosity was 0.31 (0.5 g/dL in DMF at 30°C). IR (film): 1760 and 1730 (C=O), 1530 and 1350 (—NO$_2$), and 910 cm^{-1} (cyclic C—O—C). ^{1}H-NMR (CDCl$_3$): $\underline{\delta}$ = 1.2 (C—CH$_3$), 2.1 (C—CH$_2$—C), 2.6 and 2.8 (C$\diagdown$—$\diagup$CH$_2$ with O), 3.2 and 3.8 (O—CH$_2$C), 3.6 (O—CH$_3$), 4.4 (C—CH—O), and 7.4 and 8.3 ppm (aromatic protons).

Measurement of Addition Reaction of Pendant Epoxide and Phenyl Ester Groups in the Copolymer

Polymer 1 containing 31 and 32 mol% of pendant GMA and NPMA units [0.25 g (4.63 × 10^{-4} as epoxide)] and 0.015 g (4.63 × 10^{-5}) of TBAB were dissolved in 1 mL of THF. This polymer solution was cast on a KRS (composition: TlCl + TlBr) plate, and then dried *in vacuo* over night. The polymer film on the plate was heated in the test chamber at 130°C for 5 h.

## Typical Procedure for Thermocrosslinking Reaction of the Copolymer

Polymer 1 containing 31 and 32 mol% of GMA and NPMA units [2.50 g (4.63 × 10^{-3} mol as epoxide)] and 0.15 g (4.63 × 10^{-4} mol) of TBAB were dissolved in 10 mL of THF. The polymer solution in the THF was cast on a polytetrafluoroethylene plate and dried. The polymer film was then peeled off the plate, and placed upon a glass plate; then the crosslinking reaction of the polymer film was carried out in the test chamber at suitable temperature. The crosslinked polymer film was stirred in 50 mL of THF at 30°C for 24 h, and then the gel compounds were filtered with a G3-type glass filter, washed with THF several times, and dried *in vacuo* at 50°C.

RESULTS AND DISCUSSION

Various copolymers containing pendant epoxide groups and phenyl ester groups were synthesized by radical copolymerization of GMA, phenyl methacrylates such as NPMA, CPMA, or PMA and other monomers such as MMA, ST, or EA using AIBN as a initiator in dioxane at 60°C for 5 h and then 80°C for 3 h.

As summarized in Table 1, these copolymers did not have any gel fraction, and the yields of these copolymers were relatively high except the copolymer with ST, that is, the rate of copolymerization of ST was slower than that of MMA and EA.

The IR spectrum of the film of polymer 1 with 10 mol% of TBAB showed characteristic absorptions at 1760, 1730, 1530, 1350, and 910 cm^{-1} due to C=O stretching of nitrophenyl ester, C=O stretching of other esters, —NO$_2$ stretching and cyclic C—O—C stretching of epoxide, respectively. On the other hand, the IR spectrum of the polymer film showed the disappearance of absorptions at 1760 (C=O of nitrophenyl ester) and 910 cm^{-1} (epoxide group), and showed no appearance of absorption near 3400 cm^{-1} by heating at 130°C for 5 h. Furthermore, the heated polymer film on the KRS plate became insoluble in THF. This suggests that the addition reaction of the pendant epoxide and phenyl ester groups in polymer 1 occurred with very
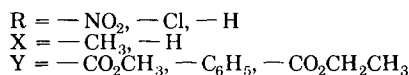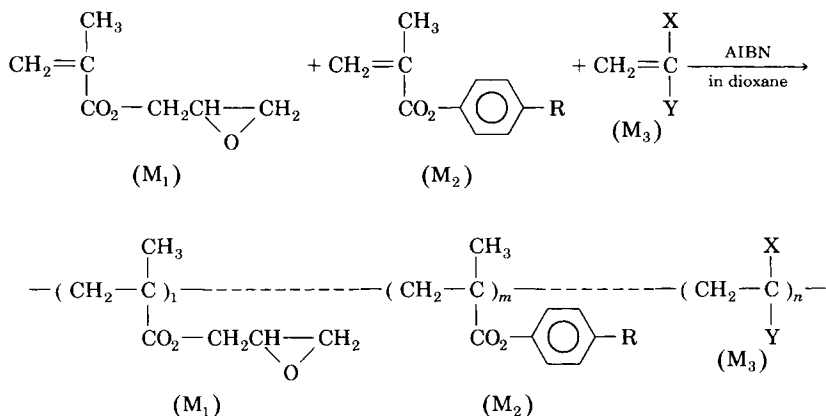
Scheme 1

high conversion in the film state without side reactions such as hydrolysis of ester and epoxide groups to produce gel products.

In addition, we have recently reported regioselective addition reaction of phenyl benzoates with pendant epoxide groups in poly(glycidyl methacrylate),[26] regioselective insertion reaction of phenyl glycidyl ether (PGE) into the ester linkage of poly(4-(4-nitrobenzoyloxy)styrene],[27] and regioselective syntheses of 1-phenoxy-3-thiophenoxy-2-propyl acetate[28,29] by the addition reaction of PGE with *S*-phenyl thioacetate using various quaternary salts as the catalysts. These results indicate that the addition reaction of phenyl ester with epoxide groups proceed regioselectively using quaternary salts, although the addition reaction between the resulting alkyl ester moiety and the epoxide group does not occur under the same conditions.

Accordingly, the thermocrosslinking reaction of copolymers of GMA and phenyl methacrylates can be supposed as Scheme 2.

As shown in Figure 1, polymer 4 did not produce any gel products when the reaction was carried out in the film state without TBAB at 110°C for 5 h. On the other hand, polymers 4, 5, and 6, which were composed of almost the same amounts of GMA, phenyl methacrylates such as NPMA, CPMA, or PMA, and MMA monomer units produced gel products in about 82, 72, and 58% yields, respectively, upon heating at 110°C for 5 h in the presence of 10 mol% of TBAB as a catalyst. This suggests that the rate of gel production is strongly affected by the substituent on the phenyl ester group of the methacrylates as it has already been found for the similar reactions of copolymers of phenyl methacrylates with diepoxy compound[17].

As shown in Figure 2, the rate of gel production of polymers 1, 2, and 3, which have different amounts of GMA, NPMA, and MMA units, was measured with 10 mol% of TBAB at 110°C. Polymer 1 containing 31 mol% of GMA and 32 mol% of NPMA units gives gel products in 100% yield upon heating for 5 h, that is, the rate of gel production of polymer 1 is higher than
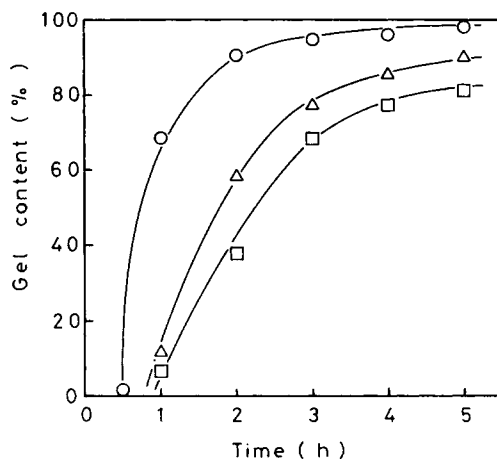
Fig. 1.   The rate of gel production of copolymers of NPMA, CPMA, or PMA with GMA and MMA in the presence of 10 mol% of TBAB as a catalyst or without TBAB at 110°C: (●) polymer 4 without TBAB; (○) polymer 4 with TBAB; (△) polymer 5 with TBAB; (□) polymer 6 with TBAB.

that of polymers 2 and 3. Also the rate of gel production of polymer 3 is lower than that of polymer 2. This means that the rate of gel production is influenced by the amount of reactive units in the copolymer.

The thermocrosslinking reaction of copolymers containing some nonreactive monomer units such as MMA, EA, or ST was carried out in the film state at 110°C using 10 mol% of TBAB (Fig. 3). The rate of gel production of polymer 7 containing EA units is greatly higher than that of polymers 2 and 8 containing MMA and ST units, respectively.

$$R = -NO_2, -Cl, -H$$

Scheme 2

Fig. 2.   The rate of gel production of copolymers of NPMA, GMA, and MMA containing various amounts of NPMA and GMA units in the presence of 10 mol% of TBAB at 110°C: (○) polymer 1; (△) polymer 2; (□) polymer 3.

As shown in Figure 4, the correlation between the degree of conversion of epoxide in some copolymers and the reaction time was also determined by IR spectrometry. The rate of the addition reaction of pendant epoxide group of GMA with NPMA units in polymer 7 is higher than that of the epoxide group of GMA in polymers 5 and 8, when the reaction is carried out in the film state in the presence of 10 mol% of TBAB as a catalyst at 110°C. Also the rate of reaction of polymer 8 is higher than that of polymer 5.

These results suggest that the rate of the addition reaction of pendant epoxide group with phenyl ester groups in the copolymer is also affected[15] by the kind of the nonreactive third monomer unit in the copolymer as well as by the kind of phenyl methacrylate unit, that is, the copolymer composed of soft segments such as EA units has higher rate of gel production than copolymers
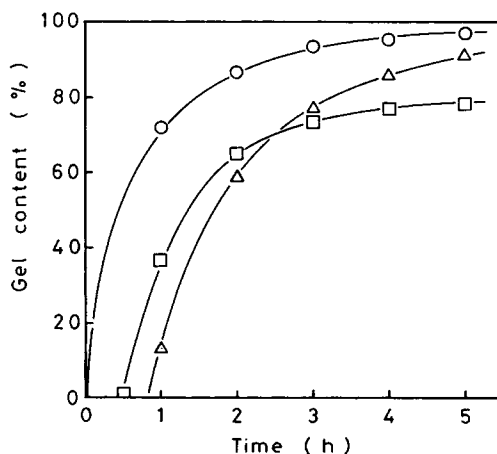

Fig. 3.   The rate of gel production of copolymers of NPMA, GMA with MMA, EA, or ST in the presence of 10 mol% of TBAB at 110°C: (△) polymer 2; (○) polymer 7; (□) polymer 8.
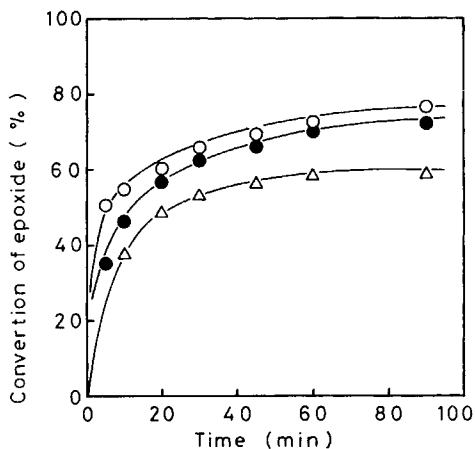
Fig. 4. The rate of disappearance of epoxide group in copolymers of NPMA or CPMA–GMA–MMA, EA, or ST using 10 mol% of TBAB at 110°C: (△) polymer 5; (○) polymer 7; (●) polymer 8.

containing hard segments such as MMA and ST, when these copolymers having almost the same amount of reactive units and the same degree of polymerizations are heated in the film state.

The thermocrosslinking reaction of polymer 4 having 11 mol% of GMA, 13 mol% of NPMA, and 76 mol% of MMA units was carried out in the film state using 10 mol% of TBAB at various temperatures (Fig. 5). This result means that the rate of gel production of the copolymer is also greatly affected by the reaction temperature, that is, the rate of the gel production of the copolymer increased with increasing reaction temperature.

The thermocrosslinking reaction of polymer 9, which is a copolymer of 47 mol% of GMA and 53 mol% of NPMA, was carried out in the film state with various TBAB concentrations at 110°C. As shown in Figure 6, the rate of gel production increases with increasing catalyst concentration, and then the film
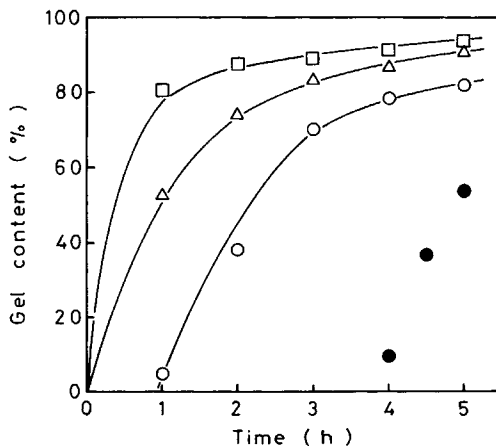

Fig. 5. The rate of gel production of polymer 4 with 10 mol% of TBAB at various temperatures: (●) 100°C; (○) 110°C; (△) 130°C; (□) 150°C.
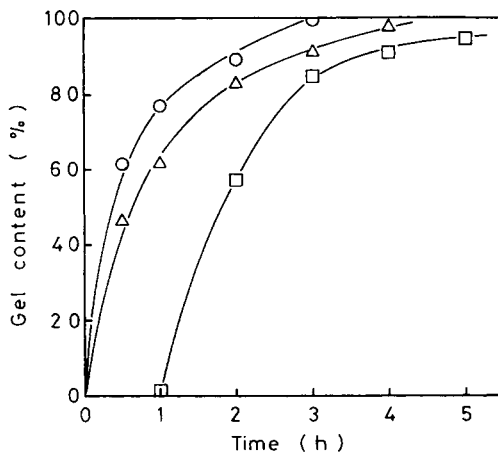
Fig. 6. The rate of gel production of copolymer of 53 mol% of NPMA and 47 mol% of NPMA using various amounts of TBAB at 110°C: (□) 2 mol% of TBAB; (△) 5 mol% of TBAB; (○) 10 mol% of TBAB.

of polymer 9 with 10 mol% of TBAB produced gel products in 100% yield by heating for 3 h.

The catalytic activity in this thermal self-crosslinking reaction was investigated. As shown in Figure 7, when the reaction of polymer 3 was carried out with 10 mol% of symmetric tetraalkylammonium salts having Br^{-1} as a counterion at 110°C for 5 h, TPEAB had the highest activity, and the activity of the other catalysts having Br^{-1} was depressed with either increasing or decreasing carbon number of the alkyl chain of the catalyst. On the other hand, the catalysts having Cl^{-1} as a counterion such as TPAC and TBAC showed almost the same activity as TPEAC, and the activities of these
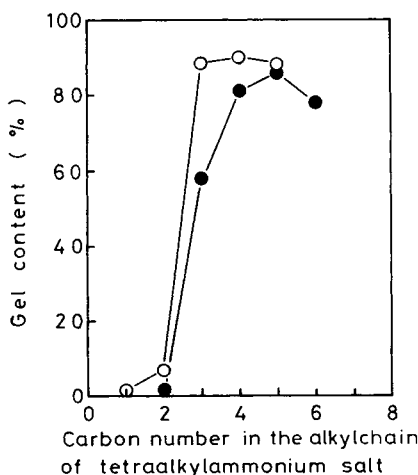

Fig. 7. Correlation between yield of gel products and length of carbon chain in symmetric tetraalkylammonium salts in the reaction of the polymer 3 with 10 mol% of the catalyst at 110°C for 5 h: (●) ammonium salt with Br^-; (○) ammonium salt with Cl^-.

TABLE II
Effect of the Counteranion of Tetrabutylammonium Salts on the Crosslinking Reaction
of Polymer 3[a]

Run no.	Catalyst	Counteranion	Yield of gel products (%)
1	TBAC	Cl^-	90
2	TBAB	Br^-	80
3	TBAI	I^-	0
4	TBAP	ClO_4^-	0
5	TBAH	HSO_4^-	0

[a] Thermocrosslinking reaction was carried out at 110°C for 5 h using 10 mol% of catalyst relative to GMA units in the copolymer.

catalysts were higher than those of TPAB, TBAB, TPEAB, and THAB having Br^- as a counterion. Furthermore, it was found that the catalytic activity of TEAC, TEAB is very low, and TMAC, TMAB and TEAB do not have any activity for the reaction of pendant epoxide groups with the phenyl ester groups.

As summarized Table II, when the reaction of polymer 3 was carried out in the film state with 10 mol% of TBAC and TBAB at 110°C for 5 h, the yields of gel products of these polymer films were about 90 and 80%, respectively. On the other hand, the films of polymer 3 with TBAI, TBAP, or TBAH did not give any gel products under the same conditions.

As summarized in Table III, when the reaction of polymer 3 was carried out in the film state using 10 mol% of BTEAC, TBPB, and TBA at 110°C for 5 h, the yields of gel products were 19, 61, and 60%, respectively. However, the films of polymer 3 with BTMAC and CTMAC did not produce any gel products.

These results indicate that the thermocrosslinking reaction of the copolymer containing both epoxide and phenyl ester groups is strongly affected[16] by the kind of counterion of the quaternary ammonium salt and the length of

TABLE III
Effect of Catalyst on the Crosslinking Reaction of Polymer 3[a]

Run no.	Catalyst	Yield of gel products (%)
6	BTMAC	0
7	BTEAC	19
8	CTMAC	0
9	TBPB	61
10	TBA	60
11	DCHC/KOPh	89
12	DCHC/KOAc	89
13	DCHC/KOBz	88
14	DCHC/KBr	0
15	DCHC/KI	0
16	DCHC/KSCN	92

[a] Thermocrosslinking reaction was carried out at 110°C for 5 h using 10 mol% of catalyst relative to GMA units in the polymer.

alkyl chain of the catalyst. Furthermore, the films of polymer 3 with 10 mol% of crown ether–salt complexes such as DCHC/KOPh, DCHC/KOAc, DCHC/KOBz, and DCHC/KSCN produced gel products in 89, 89, 88, and 92% yield, respectively, that is, the catalytic activity of DCHC/KSCN was the same as or slightly higher than that of TBAC. However, the polymer films with DCHC/KBr or DCHC/KI did not give any gel products in the same conditions.

This result means that the crown ether complexes with potassium salts of organic acids, phenol and thiocyanate, have high catalytic activity in the thermocrosslinking reaction of the polymer containing both epoxide and phenyl ester groups.

From these results, the following conclusions may be drawn: (1) Soluble copolymers having GMA and phenyl methacrylate units are synthesized without any gel fraction by radical copolymerization of GMA, phenyl methacrylates such as NPMA, CPMA, or PMA, and other monomers such as MMA, EA, or ST in dioxane. (2) Thermocrosslinking reactions of the obtained copolymers carried out in the film state either using catalysts or without any crosslinking reagents lead to gel products upon heating at 100–150°C. (3) TPAC, TBAC, TPEAC, TPEAB, DCHC/KSCN, DCHC/KOPh, DCHC/KOAc, and DCHC/KOBz show very high catalytic activity in this reaction system.

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