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SYNTHESIS, CHARACTERIZATION AND COPOLYMERIZATION OF 2-[4-(2-OXAZOLINYL)-PHENOXY]ETHYL METHACRYLATE WITH HEMA AND COPOLYMER CROSSLINKING REACTIONS

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Key Words: 2-Hydroxyethyl Methacrylate, 2-[4-(2-Oxazolinyl)phenoxy]ethyl Methacrylate, Cationic Polymerization, Free Radical Polymerization, Crosslinking Polymers, Differential Scanning Calorimetry [DSC]

ABSTRACT

The bifunctional monomer 2-[4-(2-oxazolinyl)phenoxy]ethyl methacrylate [OPEM] was prepared in good yield using the starting material 4-cyanophenol, via a multi-step synthesis method. Since OPEM is very similar to 2-hydroxyethyl methacrylate [HEMA], OPEM readily copolymerizes with HEMA, using typical free radical initiators. In the presence of proton sources, such as alcohols and acids and using cationic initiators, the oxazoline groups undergo ring-opening polymerization, resulting in crosslinking. The free radical copolymerization and cationic polymerization were investigated by differential scanning calorimetry [DSC].

INTRODUCTION

Through ring-opening polymerizations, 2-substituted oxazoline monomers have important applications in the material design of functional polymers, such as

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the design of improved coatings and adhesives, composites, specialty chemicals for pharmaceuticals, chemicals for the paper and textile industries, polymeric compatabilizers, etc. [1, 2]. As part of a project associated with preparing and evaluating new cyclic imino ether functionalized monomers, we have prepared several new oxazoline monomers [3]. In a previous communication, it was disclosed that the copolymers of the 2-[4-(2-oxazolinyl)phenoxy]ethyl methacrylate [OPEM] monomer had potential applications in water-borne coatings [4]. In this paper, we disclose in detail, the synthesis of the new monomer OPEM.

From one perspective, we might consider the OPEM monomer to be a derivative of 2-hydroxyethyl methacrylate, where the hydroxyl group in HEMA has been substituted by a 2-phenyl oxazoline moiety. Since OPEM and HEMA have the same polymerizable methacrylate group, it is possible to obtain statistical copolymers through free-radical copolymerization. In the latter type copolymers, cationic polymerization of the pendent oxazoline groups may be achieved to produce cross-linking polymeric materials. This result may widen the applications of HEMA. In this paper, we also report the copolymerization behaviors of OPEM and HEMA, using differential scanning calorimetry.

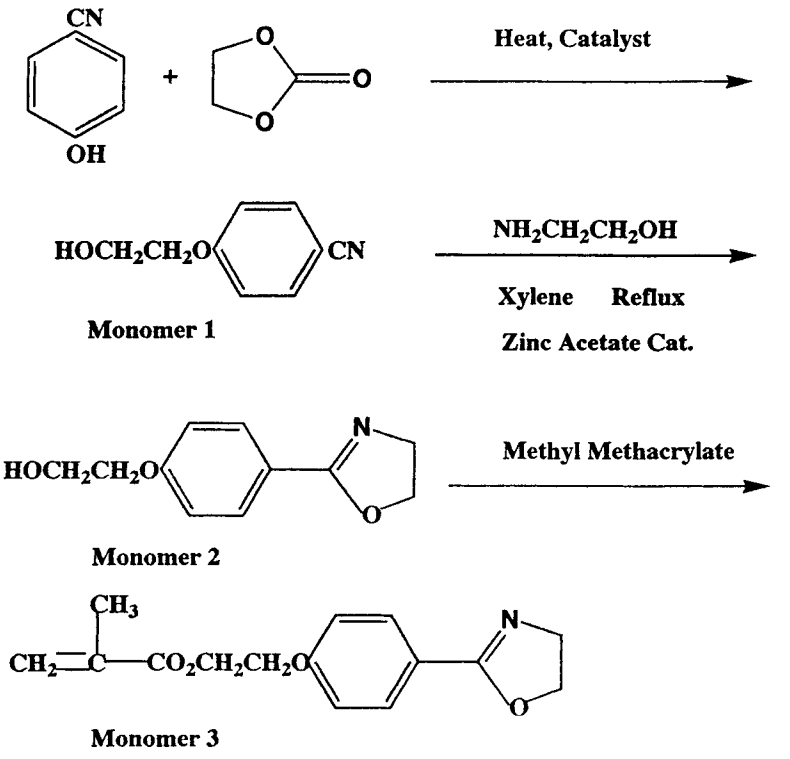
EXPERIMENTAL

Materials

Unless specified, all reagent grade chemicals and solvents were used as received from Aldrich Chemical: 4-cyanophenol, ethylene carbonate (Acros Organics), 2-hydroxyethyl methacrylate (HEMA), ethanolamine (Fisher Scientific), methyl p-toluene sulfonate ($TsOCH_3$), zinc acetate dihydrate, 2,2'-azobisisobutyronitrile (AIBN), methyl methacrylate (MMA), methacrylic acid (MAA), sodium methoxide, 1-methylimidazole, *tert*-butyl acrylate.

Characterization

The ^{1}H-NMR and ^{13}C-NMR spectra were collected on a 300 MHz Bruker AM spectrometer, using deutrated acetone or DMSO as solvent, with TMS as internal standard. FT-IR spectra were obtained on a MIDAC spectrophotometer. Thermal analyses were performed by differential scanning calorimetry (TA Instruments, DSC 910). Melting points, uncorrected, were determined by an Electrothermal Melting Point Apparatus.



Scheme 1. The Synthesis Route of Monomer OPEM

Preparation of Monomers

The route to obtain the OPEM monomer is shown in Scheme 1. The methods to prepare the expected compound and intermediates are described as following.

4-(2-Hydroxyethoxy)-benzonitrile [HEB] Synthesis

A 500 ml, three-necked flask fitted with a condenser, N_2 sparge tube and a thermometer, was charged with 4-cyanophenol 73 g (0.613 mol) and ethylene carbonate 56.2 g (0.625 mol). While the reactants were stirred using a magnetic stirrer, the catalyst 1- methylimidazole 1.29 g (15.7 mmol) was added. The contents of the flask was heated and stirred at 166 ± 2°C for 5 hours under a N_2 blanket. The flask was cooled down to 100°C, and the light, brownish paste was poured into 600 ml of toluene. The light, yellowish raw product 96 g, yield 95%, was collected by filtration. The crude product was washed 3 times using 200 ml of fresh toluene. The

solid was recrystallized from ethyl acetate, obtaining needle-like crystals with a melting point of 86-88°C. FT-IR (KBr, cm^{-1}) showed absorptions of 3600-3200 (-OH), 2938 (CH_2), 2225 (-CN), 1604 (phenyl), 1304, 1261, 1179, 1088 (C-O). ^{1}H-NMR (ppm, solvent: acetone-d_6) showed: δ 3.99 (t, 2H, J = 4.4 Hz), 4.14 (t, 2H, J = 4.6 Hz), 6.98 (d, 2H, J = 8.9 Hz), 7.58 (d, 2H, J = 9.5Hz). ^{13}C - NMR (ppm) showed: δ 60.7, 69.5, 104.1, 115.2, 119.0, 133.9, 162.0.

2-[4-(2-Hydroxyethoxy)phenyl]-oxazoline [HEPO] Synthesis

A 500 ml, three-necked flask, fitted with a mechanical stirrer, thermometer and condenser, was charged with 4-(2-hydroxyethoxy)benzonitrile, 95 g (0.58 mol), ethanolamine, 71.2 g (1.16 mol), 200 ml of xylene solvent, and the catalyst zinc acetate dihydrate, 4.4 g (0.02 mol). The reaction was run at the refluxing temperature of xylenes (137-140°C) with vigorous stirring. FT-IR was used to trace the degree of reaction, following disappearance of the - C≡N band at 2200 cm^{-1}. After cooling to room temperature, the reaction mixture was poured into cold toluene, and left standing overnight. The white crystalline product was collected by filtration. The product was washed with cold water and dried under vacuum at 80-90°C for 24 hours. The white powder was collected in a 99 g (82%) yield. The product was further purified by methanol/ethyl acetate solution, obtaining a crystalline product having a melting point of 149-150°C. FT-IR (KBr, cm^{-1}) showed: 3000-3600 (-OH), 2930, 2870 (CH_2), 1638 (-C=N-), 1610 (phenyl), 1258, 1178, 1085 (-C-O-). ^{1}H-NMR (ppm, solvent: methyl sulfoxide-d_6) showed: δ 3.73 (tetra, 2H, J = 5.1 Hz), 3.91 (t, 2H, J = 9.5 Hz), 4.03 (t, 2H, J = 4.4 Hz), 4.36 (t, 2H, J = 9.4 Hz), 7.00 (d, 2H, J = 8.7 Hz), 7.79 (d, 2H, J = 8.8 Hz). ^{13}C NMR (ppm) showed: δ 54.3, 59.3, 67.1, 69.9, 114.3, 119.8, 129.3, 161.0, 162.6.

2-[4-(2-Oxazolinyl)phenoxy]ethyl Methacrylate [OPEM] Synthesis

This monomer was prepared through the transesterification of HEPO monomer with methyl methacrylate, as follows: a 2000 ml three-necked flask, fitted with a N_2 spurge tube, thermometer, condenser, Dean-Stark trap and a magnetic stirrer, was charged with 2-[4-(2-Hydroxyethoxy)phenyl]-oxazoline, 41.4 g (0.2 mol), methyl methacrylate, 80.0 g (0.8 mol), sodium methoxide catalyst, 1.8 g (33 mmol), phenothiazine inhibitor, 0.4 g (2 mmol) and 1200 ml of tetrahydrofuran solvent. Under a slow N_2 sparge, the solution was heated to the refluxing temperature of THF. The methanol produced during the reaction, co-distilled with THF, was collected in the attached Dean-Stark trap. The reaction was stopped when no more methanol could be detected coming from the reaction. After removal of the THF solvent under reduced pressure, using a rotary evaporator, the crude paste was

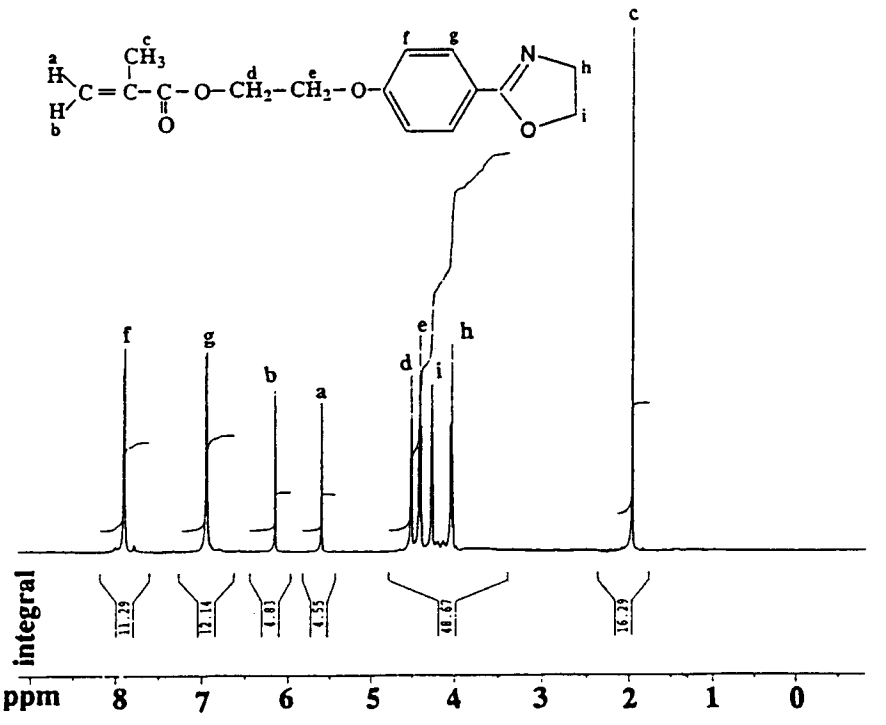


Figure 1. ^{1}H-NMR Spectrum of Monomer OPEM.

dissolved in 300 ml of acetone. After filtration to remove non-soluble impurities, the clear solution was poured into 800 ml of vigorously stirred cold water. The white solid was collected by vacuum filtration, and dried in a vacuum oven at 30-35°C for 24 hours. The final product, collected in a 42.1 g (76 %) yield, had a melting point of 66-68°C. The ^{1}H - NMR, ^{13}C - NMR and FT-IR characterizations are shown in Figures 1-3, respectively. FT-IR (KBr, cm^{-1}): 1717 (-COO-), 1648 (-C=N-), 1639 (shoulder peak, -C=C-), 1608 (phenyl). ^{1}H-NMR (ppm, solvent: acetone-d_6): δ 1.96 (s, 3H), 4.04 (t, 2H, J = 9.4 Hz), 4.26 (t, 2H, J = 4.4 Hz), 4.41 (t, 2H, J = 9.4Hz), 4.51 (t, 2H, J = 4.8 Hz), 5.59 (s, 1H), 6.14 (s, 1H), 6.94 (d, 2H, J = 8.8 Hz), 7.89 (d, 2H, J = 8.8 Hz). ^{13}C - NMR (ppm): δ18.1, 54.8, 62.8, 65.9, 67.4, 114.2, 120.7, 126.0, 129.8, 135.8, 160.9, 164.2, 167.1. While the calculated chemical shifts [5] are (ppm): δ18.2, 55.3, 62.9, 65.8, 67.5, 113.8, 116.6, 125.3, 126.7, 137.4, 161.1, 162.0, 167.2. The results of elemental analysis are: C 65.02%, H 6.34%, N 4.91% and O 23.73%, compatible with the theoretical results C 65.45%, H 6.18%, N 5.09%, and O 23.27%.

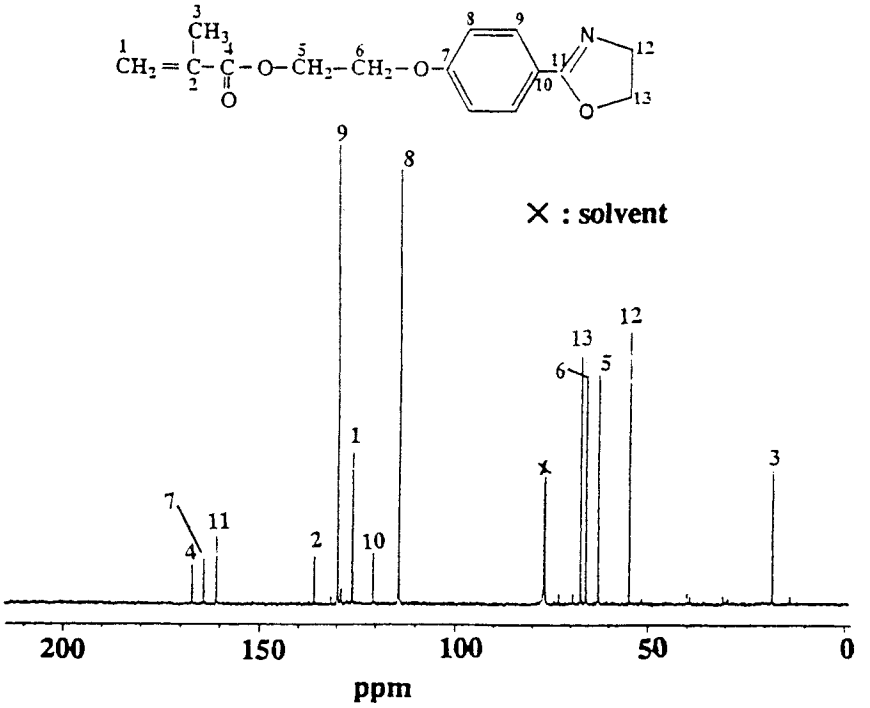


Figure 2. ^{13}C-NMR Spectrum of Monomer OPEM.

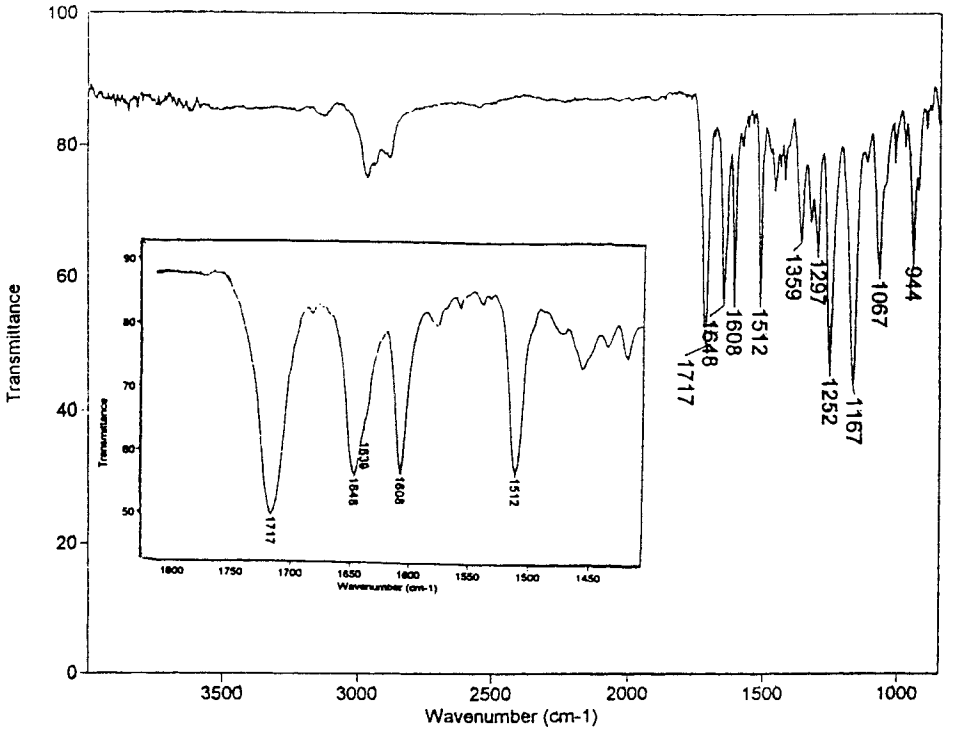


Figure 3. FT-IR Spectrum of Monomer OPEM.

TABLE 1. The Compositions of HEMA and OPEM Copolymerization

Sample No.	HEMA, g (mmol)	OPEM, g (mmol)	AIBN, mg	$TsOCH_3$, mg
HEMA1	0.650 (5)	0.344 (1.25)	5	10
HEMA2	0.650 (5)	0.172 (0.625)	4.2	8.5
HEMA3	0.650 (5)	0.086 (0.3125)	3.6	7.2
HEMA4	0.650 (5)	0	3.2	6.5

Copolymerization of OPEM and HEMA

Feed compositions for the HEMA and OPEM copolymerization are shown in Table 1. In our experiment range, the new monomer OPEM was completely miscible with HEMA. Using AIBN (0.5 wt% of HEMA and OPEM) as free-radical polymerization initiator and $TsOCH_3$ (1 wt% of HEMA and OPEM) as cationic polymerization initiator, the copolymerization behaviors of HEMA and OPEM were examined by DSC. In an aluminum DSC pan, containing 8 mg of the mixture, the polymerization of the sample was monitored by DSC while heating under nitrogen at a rate of 10°C/min from 25°C to 200°C. After keeping isothermal at 200°C for 3 minutes, the sample was cooled to room temperature. A second DSC scan was performed on the polymerized sample at the same heating rate from 25°C to 200°C. All data were treated by the TA thermal analysis 2100 program.

The monomer mixture was also charged in a small glass vial. After sealing under nitrogen, the glass vial was heated at 170 ± 5°C for 12 hours. The optically clear yellowish solid was extracted in a Soxhlet Extractor, using acetone solvent, for 72 hours.

RESULTS AND DISCUSSION

Synthesis and Homopolymerization of Monomer OPEM

As described above, the monomer OPEM can be obtained through our designed procedure (Scheme 1) in high yields, where the starting materials are very common chemicals. The structure was confirmed by FT-IR and NMR spectra. In the FT-IR spectrum, no absorbence peaks could be observed at 3400 cm^{-1}, indicating no hydroxyl groups in the compound. The peak at 1719 cm^{-1} confirmed the existence of the ester group. Because the vibration frequencies of the -C=N-

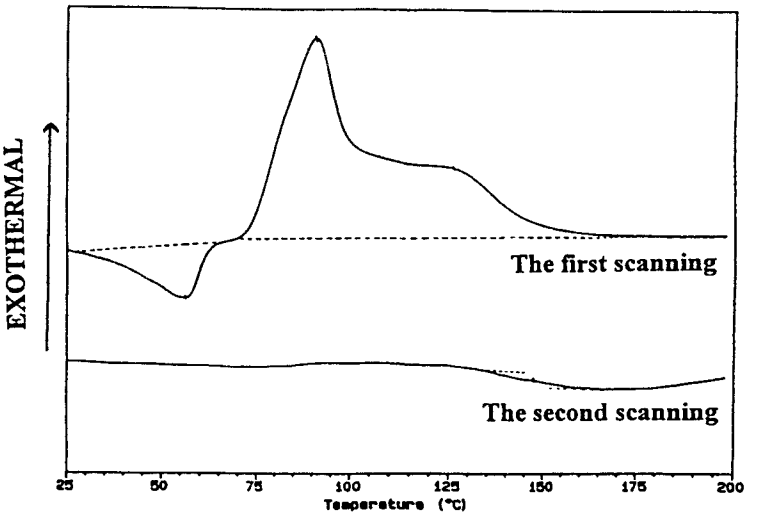


Figure 4. Homopolymerization of the OPEM Monomer.

stretch (at 1649 cm^{-1}) and the -C=C- stretch (at 1639 cm^{-1}) are very close, the peak of the -C=C- stretch can only be observed as a shoulder peak of the -C=N- stretch in the magnified spectrum. In the ^{1}H-NMR spectrum, all chemical shift peaks can be contributed to the hydrogens with different chemical environment. Since the $-CH_2=C$ group has two diastereotopic hydrogens, two single-peaks were shown at 5.59 ppm and 6.14 ppm. Four triplet peaks between 4.0 ppm and 4.5 ppm confirmed the existence of two ethylene groups (ethylene oxide and oxazoline ring) in monomer OPEM. The carbon numbers and chemical shifts shown in the ^{13}C-NMR spectrum are in harmony with the estimated results, which are calculated for our expected chemical structure according to a known computer program [5].

With the $TsOCH_3$ cationic initiator and AIBN free-radical initiator, the homopolymerization of the OPEM monomer was performed by DSC. The homopolymerization behavior is shown in Figure 4. There is a melting peak at 60°C. After the melting peak, an exothermal peak at 90°C was observed, which could be attributed to the free-radical polymerization of methacrylate groups in the OPEM monomer. Also, a wide shoulder peak between 100°C and 165°C was observed. This peak maybe related to the cationic polymerization of oxazolines. After the whole polymerization process, the polymer was not soluble in most common solvents, indicating that the homopolymerization of the OPEM monomer lead to a crosslinked polymer. The second DSC scanning detected the single T_g of the polymer at 147°C.

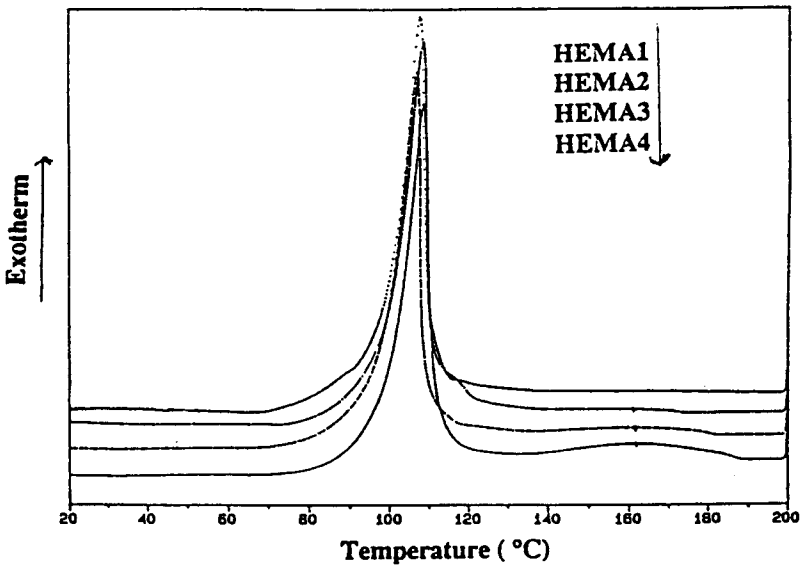


Figure 5. DSC Curves of Monomer HEMA and OPEM Copolymerization.

Copolymerization of Monomers HEMA and OPEM

The monomer OPEM has two polymerizable groups, a -C=C- unsaturation for free-radical polymerization and an oxazoline ring for step-growth or cationic ring-opening polymerizations. Free-radical copolymerization between the HEMA and OPEM monomers should be statistical. The DSC traces of the copolymerization for HEMA and OPEM mixtures are shown in Figure 5. The main exothermic peaks, from 80°C to 120°C, occurred by free-radical polymerizations. There is no significant difference in shapes and temperatures among the polymerization peaks, although the ratios of the monomers are varied. The exothermal peaks at 165°C indicated the cationic polymerization of the oxazoline groups. With the decreasing content of the OPEM monomer in the mixtures, the cationic polymerization peaks became smaller and smaller. The DSC results of the polymerization in the mixtures are listed in Table 2. The increase of the monomer OPEM led to a lower enthalpy (ΔH) value of free-radical polymerization.

Figure 6 shows the glass transition temperatures T_g of the HEMA and OPEM mixtures after polymerization. Only one observed T_g in the DSC trace implies that the copolymer are homogenous. T_g increases as the amount of the OPEM monomer in the mixtures increase. There is a significant enhancement of T_g between the samples containing monomer OPEM and the sample without monomer OPEM. This is because the oxazoline ring-opening polymerization produced

TABLE 2. The DSC Results of the Monomers HEMA and OPEM Polymerization

Mixture	Free Radical Polymerization		Cationic Polymerization		T_g
	Peak Temp. (°C)	ΔH (J/g)	Peak Temp. (°C)	ΔH (J/g)	°C
HEMA1	108	232	164	29	135
HEMA2	107	276	165	14	131
HEMA3	108	301	162	3	125
HEMA4	107	342	----	----	81

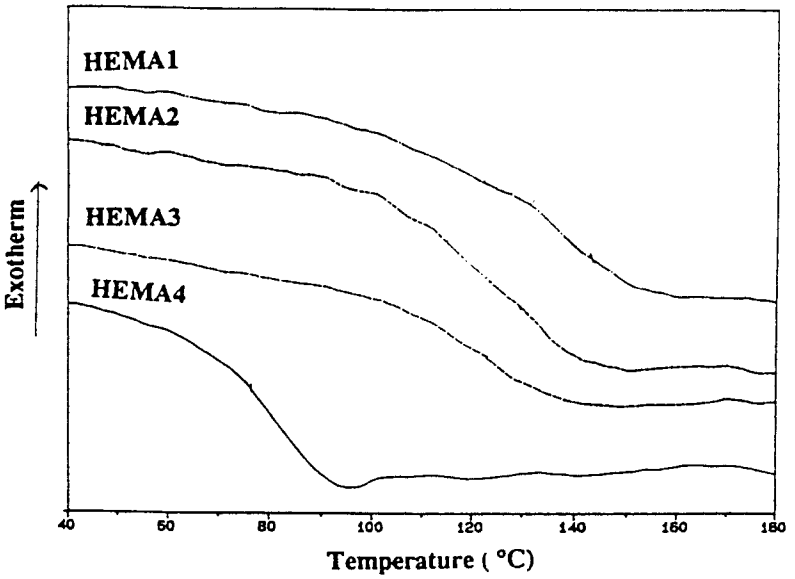


Figure 6. Glass Transition Temperatures of HEMA and OPEM Copolymers.

crosslinked materials. Increasing amounts of OPEM in the mixtures led to a higher crosslink density, giving higher T_g values.

Solvent (acetone) extraction of the OPEM crosslinked HEMA products for 72 hours showed no detectable weight loss. The transparent polymers were non-soluble in most common solvents, such as acetone, methanol, ethyl acetate, diethyl ether, and N,N-dimethylformamide. These results indicated that monomers HEMA

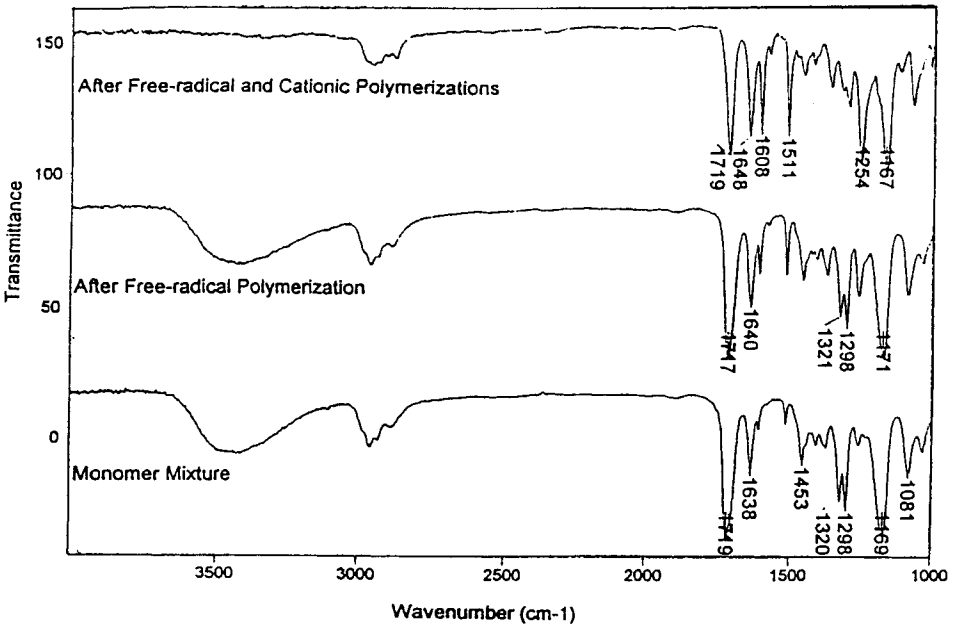
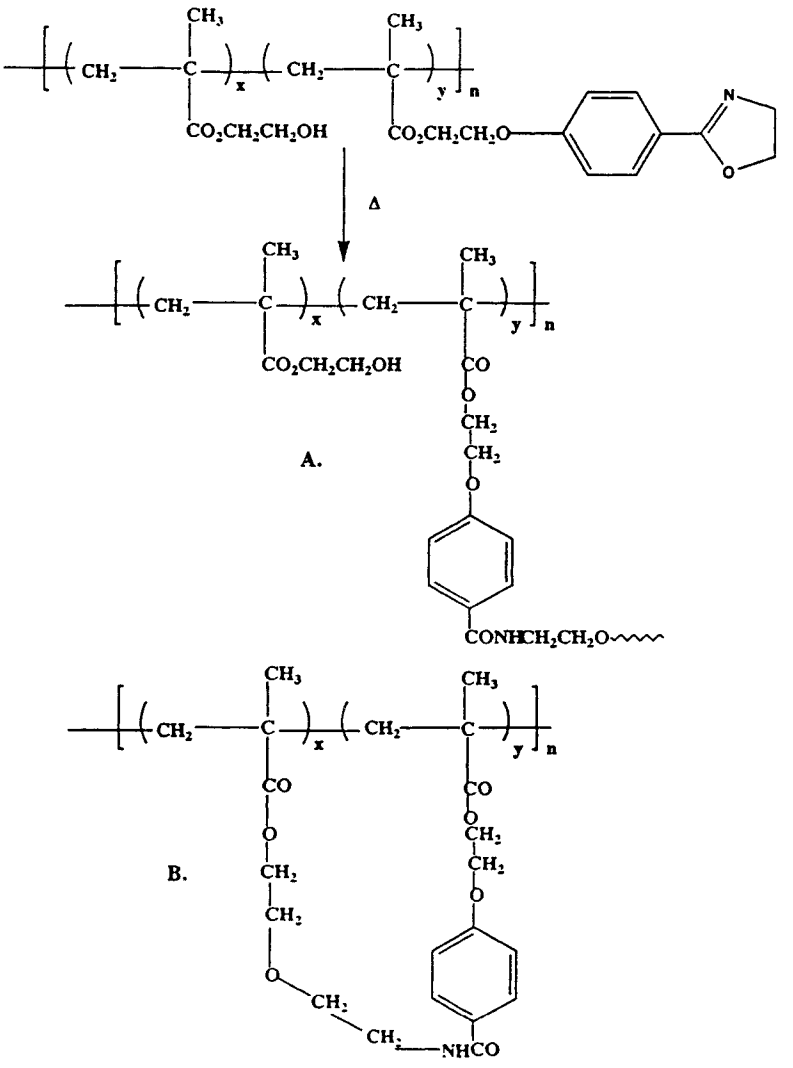


Figure 7. FT-IR Spectra during the polymerization of the Monomers HEMA and OPEM.

and OPEM were copolymerized in the mixtures, while the obtained polymeric materials were crosslinked.

Mechanism of Crosslinking Copolymerizations

As shown in Figure 5, free-radical copolymerization between monomers HEMA and OPEM occurred below 130°C, forming the linear methacrylate copolymer. The cationic ring-opening polymerization of oxazoline groups, crosslinking the linear copolymer, took place at a higher temperature (145°C to 170°C). The FT-IR spectra for the copolymerizations are shown in Figure 7. In the starting monomer mixture, the carbon double bond C=C stretch and C=N stretch in the oxazoline ring show a combination peak at 1638 cm^{-1}. After the free-radical copolymerization, resulting in the disappearance of the C=C double bond, the C=N stretch was observed at 1640 cm^{-1}. As the reaction temperature raised, a new peak at 1648 cm^{-1}, which was attributed to the amide N-C stretch, was observed, indicating the formation of amide group. It is noted that the hydroxyl peak at 3500 cm^{-1} disappeared or significantly reduced after the free-radical and cationic copolymerizations. This



Scheme 2. The Structures of the Monomer HEMA and OPEM Copolymer

result suggests that the hydroxyl groups might be involved in the cationic ring-opening copolymerization.

With the cationic initiator $TsOCH_3$, the structure of the crosslinking copolymers of HEMA and OPEM can be described by Scheme 2A, according to the well-known polymerization mechanisms of 2-oxazolines [6-8]. In our experimental system at higher temperature, the hydroxyl groups can become reactive, providing

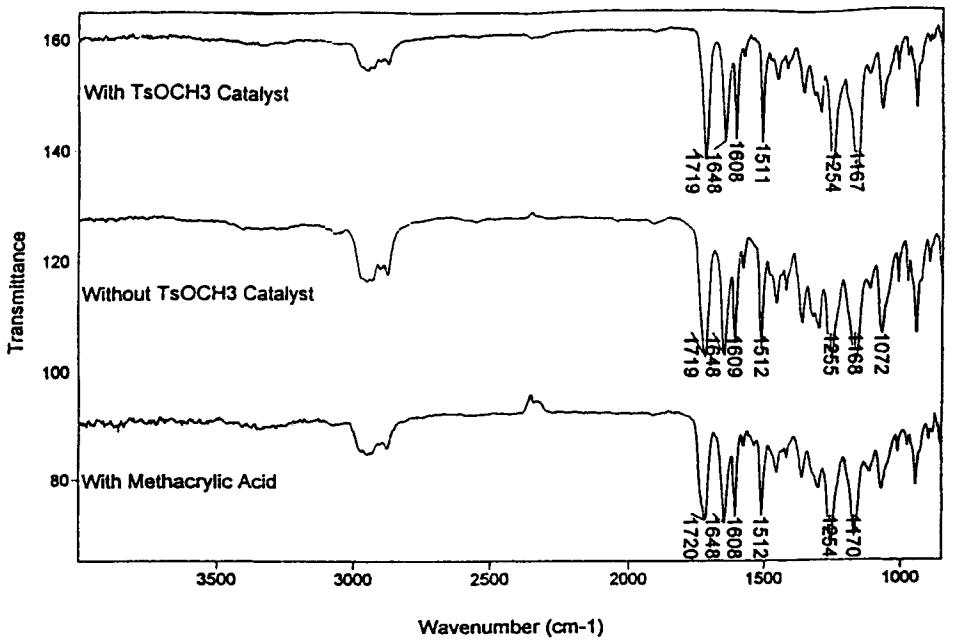
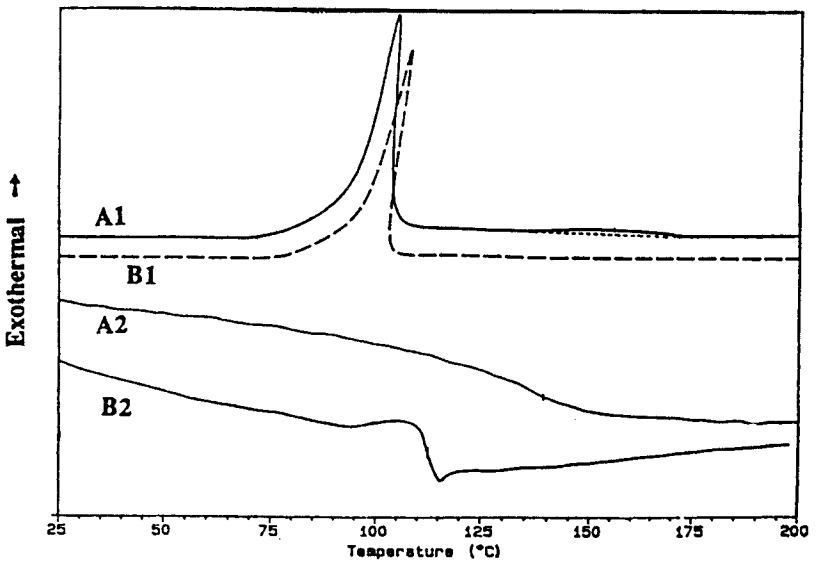


Figure 8. FT-IR Spectra of Crosslinking Polymers with the Monomer OPEM.

the proton source for the ring-opening polymerization of oxazolines. Structure 2A (Scheme 2), generated by an intermolecular reaction, brings about crosslinking in the polymeric materials. The proposed structure is reasonable according to a study on the reaction of alcohols and amines with oxazolines [9]. Structure 2B (Scheme 2), generated by an intramolecular reaction, does not bring about crosslinking. This structure, even through not producing crosslinking, reduces the flexibility of the polymer chain and raise the T_g of the material. This proposed polymerization mechanism, taking the reactive hydroxyl groups as a proton source, was confirmed by the FT-IR spectra in Figure 8. After copolymerization for 30 minutes at 165°C, the FT-IR spectra of the mixtures with and without cationic initiator $TsOCH_3$ showed no significant difference. The copolymer obtained from the HEMA and OPEM mixture without cationic initiator $TsOCH_3$ was non-soluble in most common solvents, indicating it is crosslinked. Figure 9 shows the effect of cationic initiator $TsOCH_3$ on the copolymerization behaviors of the monomer HEMA and OPEM mixtures. There was no detectable exothermal peak of polymerization above 120°C for the mixture without the cationic initiator $TsOCH_3$. The T_g of the HEMA-OPEM copolymers prepared without cationic initiator $TsOCH_3$ was 125°C,

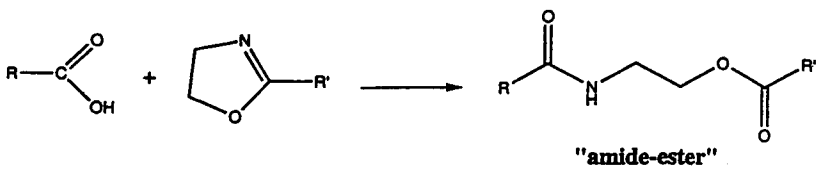


A1: polymerization curve of the monomer HEMA and OPEM mixture with $TsOCH_3$
B1: polymerization curve of the monomer HEMA and OPEM mixture without $TsOCH_3$
A2: glass transition curve after polymerization A1
B2: glass transition curve after polymerization A2

Figure 9. The Copolymerization Behaviors of the Monomer HEMA and OPEM.

compared to a reported [11] T_g of 85°C for the HEMA polymer. The T_g of the HEMA homopolymer prepared in our work was 81°C, also significantly lower than that of the OPEM containing copolymer.

To further investigate the mechanism of the ring-opening polymerization of the monomer OPEM, a mixture of MMA (4 mol), OPEM (1 mol) and MAA (1 mol) was polymerized, using AIBN free-radical initiator. A clear, yellowish cross-linking polymeric material was easily obtained upon heating. The FT-IR spectrum of the material was also shown in Figure 8. This result means that organic acids such as MAA can be used as an effective functionality to open the oxazoline ring on the OPEM monomer. The nucleophilic ring opening reaction of 2-oxazoline with carboxylic acid is illustrated in Scheme 3 [9, 12]. In order to confirm this result, the polymerization of the mixture of MMA (4 mol), OPEM (1 mol) and *tert*-butyl acrylate (1 mol) was performed. First, the mixture was polymerized at 65°C, using AIBN initiator. The polymerized mixture was readily soluble in acetone. A small



Scheme 3. Reaction Between Carboxylic Acid Group and Oxazoline Group

amount of this polymeric material was used for DSC measurement. With a scanning temperature from 25-300°C, the DSC curve showed a single T_g for this materials at 123°C. After isothermal heating at 300°C for 5 minutes under a nitrogen blanket, the sample was cooled to room temperature and weight, exhibiting a quantitative weight loss. Under the same conditions, the sample was reheated in the DSC cell. For this run, a single T_g was observed at 134°C. It is well known that *tert*-butyl esters, such as that found in *tert*-butyl acrylate, are broken apart at elevated temperature, producing an acid and olefin residue [10]. During the first DSC scanning above 180°C, decomposition of the *tert*-butyl acrylate residue eliminated isobutene, leading to the observed weight loss and yielding acid groups on the copolymer backbone. Thus, the acid group participated in a step-growth, ring-opening polymerization of the oxazoline groups on OPEM residue at the higher temperature, giving a crosslinked polymeric material. This yielded a higher T_g, which was found during the second DSC scanning. After the second DSC scanning, the polymeric material was not soluble in acetone. This result indicated that the crosslinking reaction could be controlled through the polymerization temperature, opening up possible applications of the OPEM monomer in the design of thermosetting coatings or adhesives.

CONCLUSION

Using Scheme 1, the new monomer 2-[4-(2-oxazolinyl)phenoxy]ethyl methacrylate [OPEM] was obtained. The structure of the monomer was confirmed by elemental analysis, FT-IR and NMR.

Monomer OPEM and monomer HEMA can be copolymerized with typical free radical initiators. The copolymers are readily crosslinked by cationic, ring-opening polymerization of the oxazoline rings. With increasing amounts of the OPEM monomer used in the copolymerizations, the T_g of the thermoset was significantly enhanced.

Ring-opening polymerization of the OPEM monomer can be initiated by cationic initiators such as $TsOCH_3$. Hydroxyl groups and organic acids react with oxazoline groups, suggesting the potential use of OPEM monomer in design of thermosetting coatings or adhesives at elevated temperature.

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