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Methacryloyl-Functional Benzoxazine: Photopolymerization and Thermally Activated Polymerization

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ABSTRACT: A novel class of photopolymerizable benzoxazines has been developed. This class has been coined as methacryloyl-functional benzoxazines. It has been synthesized by the reaction of the new benzoxazine monomers: (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methanol and methacryloyl chloride. The structure of the monomer has been confirmed by Fourier transform infrared spectroscopy (FTIR) and ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR). Its photopolymerization has been successfully carried out with and without photoinitiator, while the thermally activated polymerization is compromised by low temperature degradation.

1. Introduction

Benzoxazine resin as a new class of high performance polymers is gaining rapid interest in both academic and industrial fields. This class of materials has many unique properties that allow it to compete and replace traditional polymers in many applications. Benzoxazine monomers can be synthesized from a phenolic derivative, formaldehyde, and a primary amine via Mannich reaction. Benzoxazine monomers are typically polymerized through cationic ring-opening polymerization. Benzoxazine monomers exhibit many attractive properties, including low melt viscosity, no release of volatiles during polymerization, and no need for harsh catalysts to be added. Upon polymerization, a polymer with a phenolic hydroxyl group and a tertiary amine bridge as a repeating unit is produced. In addition, the polymer is characterized by low volumetric shrinkage upon polymerization; low moisture absorption; superb chemical resistance, good flame retardance, excellent electrical properties, high thermal stability and mechanical properties.[1−5] Because of its unique advantages, a number of papers have been published on polybenzoxazines, which can be categorized into two main research areas. The first area is related to the fundamental research aspects for understanding the physical and chemical properties and their relationship with the molecular structure.[6−8] The second area is to further improve the properties to meet specific applications as high performance polybenzoxazines by introducing new functional groups either by blending with monofunctional monomers and difunctional monomers or as part of the monomer structure.[9−18] This has also been extended to even main-chain benzoxazine polymers that show outstanding performance than benzoxazine monomers.[19−21]

Photopolymerization is an elegant method in synthetic polymer chemistry as it congregates a wide range of economic and ecological anticipations.[22] The reactions are more environmentally friendly as they are typically operated without solvents. The reactions can be controlled in both time and space. In contrast to thermally based applications, which usually require elevated temperatures, photopolymerization can also be performed at room temperature and below. When combined with thermally activated benzoxazine polymerization, several additional advantages can be offered. For example, providing photochemically active groups are incorporated into benzoxazine structure, sequential photochemical and thermal activation would lead to the formation of network with higher cross-linked density. This would obviously affect the T_g and consequently mechanical properties of the resultant polymer. Additionally, as the benzoxazine ring structure possesses two hetero atoms and undergoes ring-opening reaction with Lewis acids such as PCl_5,[23] the cationic photoinitiators may also be reactive to induce polymerization.

To date, only a few studies on the photopolymerizable systems containing benzoxazine have been reported. The photoinitiated ring-opening cationic polymerization of neat phenol/aniline benzoxazine monomer (P-a) and its application as hydrogen donors of photoinitiated free radical polymerization for vinyl functionalized compounds have been investigated by Kasapoglu et al.[24,25]

Recently, unsaturated polymerizable groups have been introduced into benzoxazine as a potential photopolymerizable site. A new bifunctional benzoxazine monomer containing coumarin[26] has been reported being capable of undergoing photodimerization and thermal ring-opening polymerization processes for curing applications with highly dense cross-linked networks. The copolymerization of styrene with the maleimide monomer functionalized with benzoxazine and phenylnitrile has been studied. The photoinitiated polymerization has been chosen to obtain linear polymers with pendant thermolabile benzoxazine groups.[27]

Lately, Koz et al.[28] prepared a methacryloyl-functional benzoxazine monomer and did a simple investigation by copolymerizing with styrene through thermally activated free radical polymerization of benzoxazine. However, the incorporation of methacrylate as a photopolymerizable functionality has not been investigated to date. Therefore, to further extend the study, we have developed new methacyloyl−benzoxazine-containing monomer and study its photopolymerization behavior as well as thermal polymerization.

2. Experimental Section

2.1. Materials. Aniline (99%), methacryloyl chloride (97%), benzoyl peroxide (BPO), and dimethoxyphenyl acetophenone (DMPA) (99%) were purchased from Aldrich Chemical Co.. 4-Hydroxybenzyl alcohol was obtained from SAFC Supply Solutions. Triethylamine, ethanol, chloroform, methylene chloride,

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toluene, paraformaldehyde, sodium hydroxide, and sodium sulfate anhydrous (99%) were obtained from Fisher Scientific Co. Benzoyl peroxide was recrystallized from chloroform:ethanol (1:1) mixture. All the other chemicals were used as received.

2.2. Preparation of Vinylester-Functional Benzoxazine Monomers. *2.2.1. Preparation of (3-Phenyl-3,4-dihydro-2H-benzo[e]-[1,3]oxazin-6-yl)methanol (HBA-a).* Into a 50 mL flask were added aniline (1.86 g, 20 mmol), 4-hydroxybenzyl alcohol (HBA) (2.48 g, 20 mmol) and paraformaldehyde (1.2 g, 40 mmol) with a mole ratio of 1:1:2 and toluene (30 mL) were added and stirred at 100 °C for 8 h. The solution was allowed to cool to room temperature. The solid residue was collected by filtration and recrystallized using toluene to afford pale yellow crystals of HBA-a (85%).

^{1}H NMR ($CDCl_3$, ppm, δ): 4.55(s, Ar−CH_2−OH), 4.64 (s, C−CH_2−N−), 5.44 (s, N−CH_2−O−), 6.75−7.27(m, Ar).

^{13}C NMR ($CDCl_3$, ppm, δ): 50.83 (C−CH_2−N-), 65.31 (Ar−CH_2−OH), 79.91 (N−CH_2−O−).

IR (KBr, cm^{-1}): 3092−3625 (−OH stretching), 945 (out-of-plane C−H).

2.2.2. Preparation of (3-Phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)methyl Methacrylate. In a 100 mL flask, HBA-a (2.41 g, 10 mmol) was dissolved in methylene chloride, followed by adding triethylamine (1.52 g, 15 mmol) and methacryloyl chloride (1.57 g, 15 mmol). The solution was stirred for 2 h at room temperature, followed by washing with sodium hydroxide aqueous solution (0.5M, 25 mL × 3) and drying over sodium sulfate anhydrous. Yellowish crystals were obtained after evaporating solvent (90%).

^{1}H NMR ($CDCl_3$, ppm, δ): 1.95 (s, C═C−CH_3), 4.63 (s, C−CH_2−N−), 5.07 (s, Ar−CH_2−OH), 5.36 (s, N−CH_2−O−), 5.56 (s, C═CH_2), 6.11 (s, C═CH_2), 6.78−7.28(m, Ar).

^{13}C NMR ($CDCl_3$, ppm, δ): 18.37 (C−CH_3), 50.48 (C−CH_2−N−), 66.18 (Ar−CH_2−O), 79.45 (N−CH_2−O−), 128.27 (C═C*H_2), 136.22 (CH_3−C*═CH_2), 167.27 (O−C═O).

IR (KBr, cm^{-1}): 1715 (C═O), 1637 (C═C), 945 (out-of-plane C−H).

2.3. Thermally-Activated Polymerization of (3-Phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl Methacrylate. A solution of the monomer in $CHCl_3$ was prepared. Then, the solution was cast over dichlorodimethylsilane-pretreated glass plates. The films as fixed on glass plates were heated stepwise at 100, 140, 180, and 200 °C for 1 h each and then slowly cooled to room temperature. 1% BPO was added to the monomer and the solution was cast as a thin film on a KBr plate. The sample was heated at 70 °C for 1, 2, 4, and 23 h. FTIR spectra were taken at each heating period.

2.4. Photopolymerization of (3-Phenyl-3,4-dihydro-2*H*-benzo-[*e*][1,3]oxazin-6-yl)methyl Methacrylate. (3-Phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl Methacrylate with and without 5% DMPA were dissolved in chloroform and cast as thin films on KBr plates. The film was exposed to UV light for up to 1 min for FTIR investigation. The monomer films were also made on poly(ethylene terephthalate) (PET) film, which was covered by polypropylene (PP) film and underwent up to 5 min UV exposure.

2.4. Measurements. ^{1}H and ^{13}C NMR spectra were acquired in deuterated chloroform on a Varian Oxford AS600 at a proton frequency of 600 MHz and its corresponding carbon frequency of 150.9 MHz. The average number of transients for ^{1}H and ^{13}C is 64 and 1024, respectively. A relaxation time of 10s was used for the integrated intensity determination of ^{1}H NMR spectra. Fourier transform infrared (FTIR) spectra were obtained using a Bomem Michelson MB100 FTIR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. Coaddtion of 32 scans was recorded at a resolution of 4 cm^{-1}. Transmission spectra were obtained by casting a thin film on a KBr plate for partially cured samples.

A differential scanning calorimeter (DSC), TA Instruments DSC model 2920, was used with heating rate of 10 °C/min and a nitrogen flow rate of 60 mL/min for all tests. All samples were crimped in hermetic aluminum pans with lids. The UV source used was 100 W with output from 200 nm to 2.5 μm by Newport.

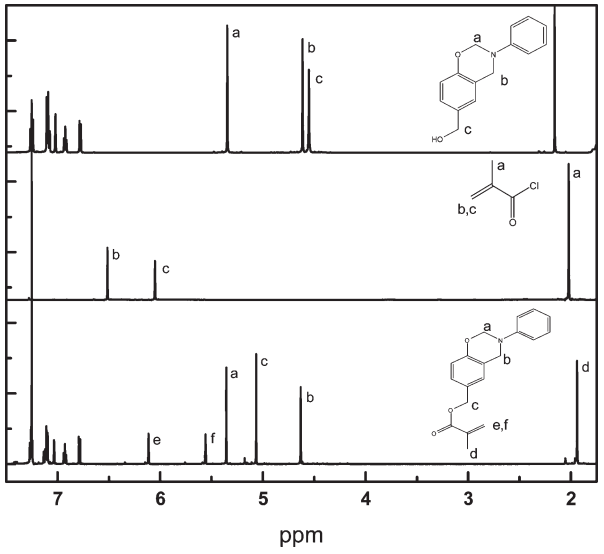
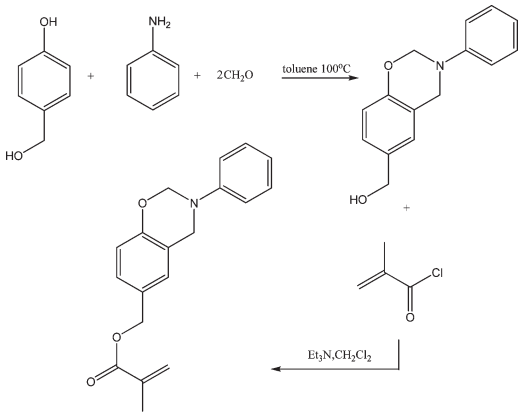


Figure 1. ^{1}H NMR spectra of methacryloyl−benzoxazine monomer (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate and its raw materials.

Scheme 1. Preparation of Methacryloyl−Benzoxazine Monomer (3-Phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl Methacrylate



3. Results and Discussion

3.1. Preparation of (3-Phenyl-3,4-dihydro-2*H*-benzo[e]-[1,3]oxazin-6-yl)methyl Methacrylate. The novel monomer (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate, comprising of both benzoxazine and methacrylate moieties, was prepared by the reaction of HBA and methacroyl chloride, as shown in Scheme 1.

The chemical structure of the monomer was confirmed by ^{1}H NMR, ^{13}C NMR, and FT-IR. Figure 1 shows the ^{1}H NMR spectra of (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)-methyl methacrylate and its original reactants: (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methanol and methacryloyl chloride.

The peak at 1.95 ppm is assigned to the protons of CH_3 of methacrylate group. The characteristic proton resonances of the oxazine ring for the product appear as two singlets with equal integrated intensity at 4.63 and 5.36 ppm, which are assigned to Ar−CH_2*−N− and −O−CH_2*−N−, respectively. The singlet at 5.07 ppm is attributed to −CH_2*−O−C═O, which has a dramatic shift from 4.55 ppm as −CH_2*−OH of (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methanol. The two singlets at 5.56 and 6.11 ppm are assigned to the vinyl protons of CH_3−C═CH_2*, showing a shift from 6.05 and 6.51 ppm from methacryloyl chloride structure. The splitting of vinyl proton

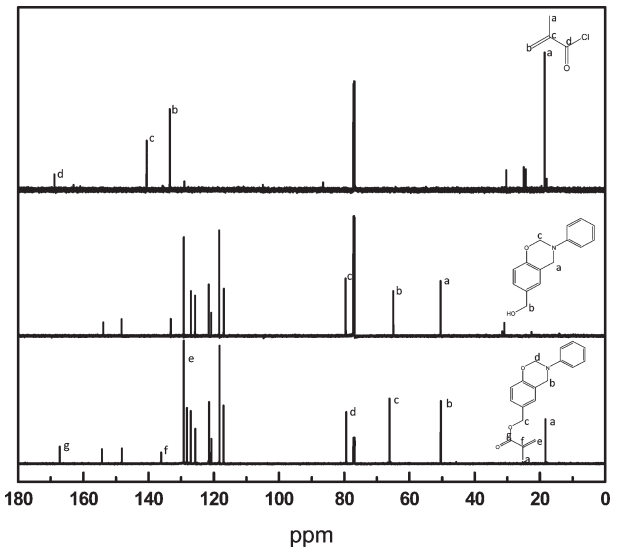


Figure 2. ^{13}C NMR spectra of vinylester benzoxazine monomer (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate and its raw materials. A small amount of impurities present in the original methacryloyl chloride is excluded during the purification procedure of the benzoxazine.

resonance is because the conjugation of carbonyl and vinyl group limits the bond mobility and makes the two protons surrounded by different chemical environments. The multiplet in the range 6.78−7.28 ppm is assigned to the protons of the aromatic ring.

Figure 2 shows the ^{13}C NMR spectra for the monomers. The peak at 18.37 ppm is assigned to the CH_3 carbons in the methacrylate moiety. The characteristic carbon resonances of the oxazine ring appear at 50.48 ppm for C−C*H_2−N− and at 79.45 ppm for N−C*H_2−O−, respectively. The resonance at 66.18 ppm is from Ar−C*H_2−OCO. The peaks at 128.27, 136.22, and 167.27 ppm are attributed to the CH*$_2$=C−C=O, CH_2=C*−C=O and CH_2=C−C*=O, respectively.

The IR spectrum shown at the bottom in Figure 3 is the monomer itself. It exhibits the typical stretching absorption of the carbonyl in the methyl methacrylate structure at 1715 cm^{-1}. It is known that the band from 1650 to 1600 cm^{-1} is assigned to the C=C stretching mode. By comparing the spectrum of methacryloyl-benzoxazine with that of hydroxymethyl-benzoxazine shown in Figure 3, it is concluded that the multiple peaks from 1628 to 1560 cm^{-1} are due to the C=C stretching modes of aromatic rings and the peak at 1637 cm^{-1} is originated from the C=C stretching of the vinyl structure. These assignments are consistent with the literature.[29]

This band at 1637 cm^{-1} is used to follow the polymerization of the vinyl group. For the benzoxazine structure, the characteristic band at 945 cm^{-1} due to the out-of-plane C−H vibration of the benzene ring to which the oxazine ring is attached is observed.

DSC thermogram of the monomer is shown at the bottom in Figure 4.

One exotherm is observed with the onset of the peak around 193 °C. The exothermic maximum is seen at 203 °C with the total heat of polymerization of 315 J/g. It is expected that both benzoxazine ring-openning polymerization and methacrylate free-radical polymerization happen in the range of the exotherm and it will be further explained in the following discussion.

3.2. Polymerization Behavior of (3-Phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl Methacrylate. *3.2.1. Polymerization by Heating*. The polymerization behavior of (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate

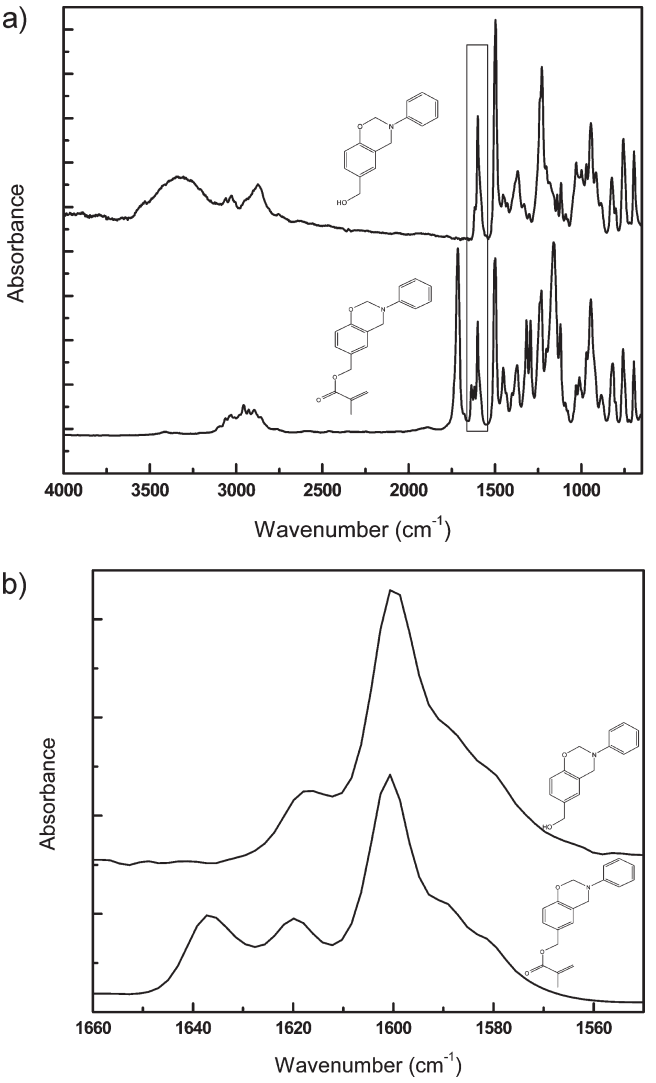


Figure 3. FTIR spectra of methacryloyl−benzoxazine monomer (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate and methylol−benzoxazine (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)-methanol.

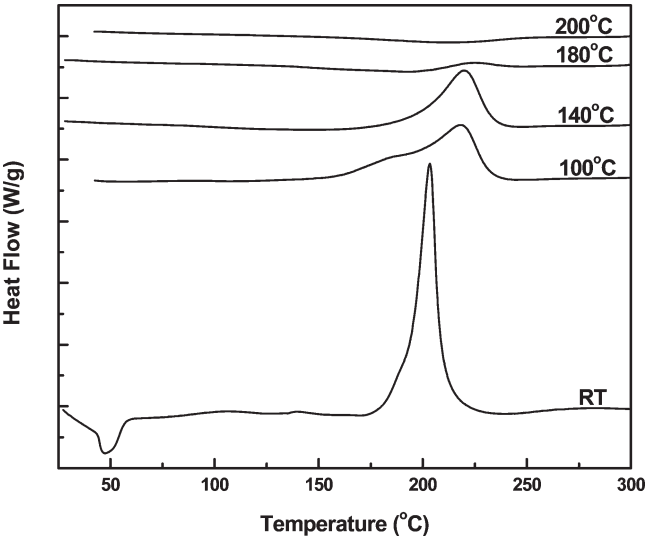


Figure 4. DSC curves of methacryloyl−benzoxazine monomer (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate after each heating stage.

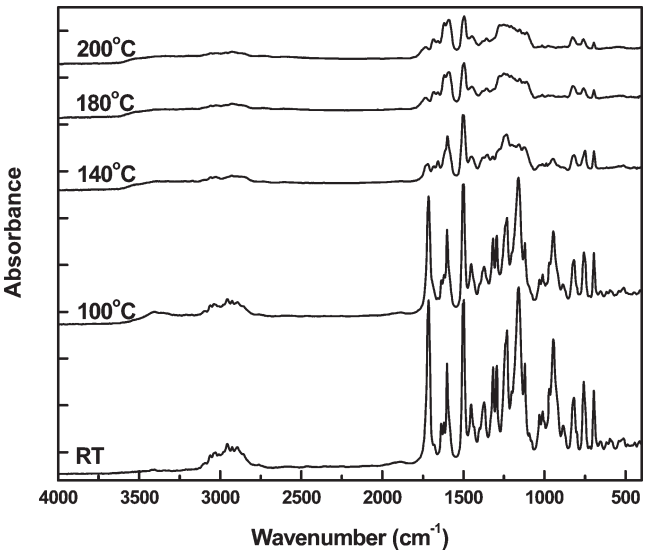


Figure 5. FTIR spectra of vinylester benzoxazine monomer (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate after each heating stage.

was studied by DSC by stepwise heating at 100, 140, 180, and 200 °C for 1 h each. The result is shown in Figure 4. The monomer itself shows one exothermic peak with one shoulder at lower temperature side. The exotherm maximized at 203 °C with the total heat of polymerization of 315 J/g for the unheated sample. With increasing severity of heat treatment, the residual heat of polymerization expectedly decreases to 209, 148, and 14 J/g for 100, 140, and 180 °C treatment, respectively. Meanwhile, the peak moves to higher temperature and two separated peaks are observed for the 100 °C treatment. No exothermic event is seen for the 200 °C treatment, indicating that the polymerization is complete.

The polymerization behavior is also monitored by FTIR after each heat treatment, as shown in Figure 5. A broad peak around 3400 cm^{-1} appears and rest of the peaks decrease after the 100 °C treatment. After the 140 °C stage, the peaks start to show substantial decrease. This phenomenon has not been observed for any other benzoxazine in literature. It is presumed that, by incorporating acrylate chemistry into the benzoxazine, the decompositition at lower temperature has happened.

This is confirmed by the TGA result of the monomer as shown in Figure 6. A sharp peak for derivative weight at 195 °C and about 12% weight loss after the peak is observed. It is believed that $CH_2-O-C=O$ linkage in the monomer structure is a weak portion and, upon heating, the chain breaks, as benzyl ether was used as a good leaving group of protected hydroxyl groups.[30,31] This process produces the benzoxazine with methylol structure, which could undergo the condensation polymerization into phenolic resins, and methacrylic acid as one unstable small molecule, which results in the significant intensity decrease for carbonyl band at 1715 cm^{-1}. The band at 3400 cm^{-1} is attributed to the $-OH$ in the ring-opened polybenzoxazine structure and the $-CH_2OH$ after chain scission. The complicated thermal behavior at this stage explains the shoulder of the exotherm in DSC thermogram. Besides, relatively thermally unstable MMA (methyl methacrylate) segment may contribute to create porosity on the networks prepared from the low molar mass benzoxazines with PMMA−Bz by the controlled thermal degradation. This approach was previously reported in the literature through the basic degradation of polycaprolactone in related benzoxazine systems in order to reduce the dielectric constant of the resultant polymer.[32]

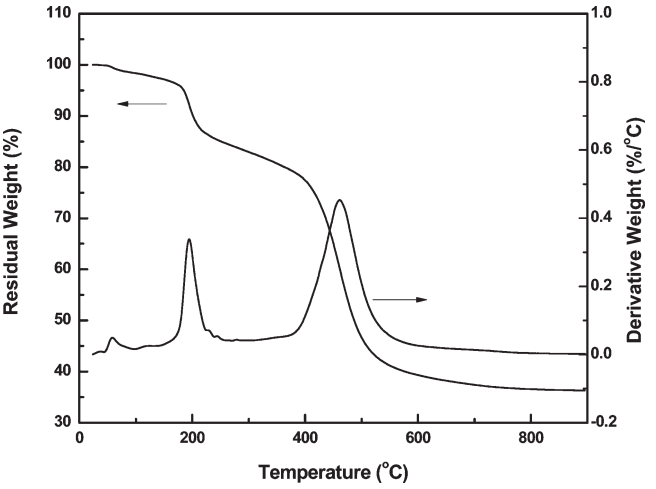


Figure 6. TGA curve of methacryloyl-benzoxazine monomer (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate.

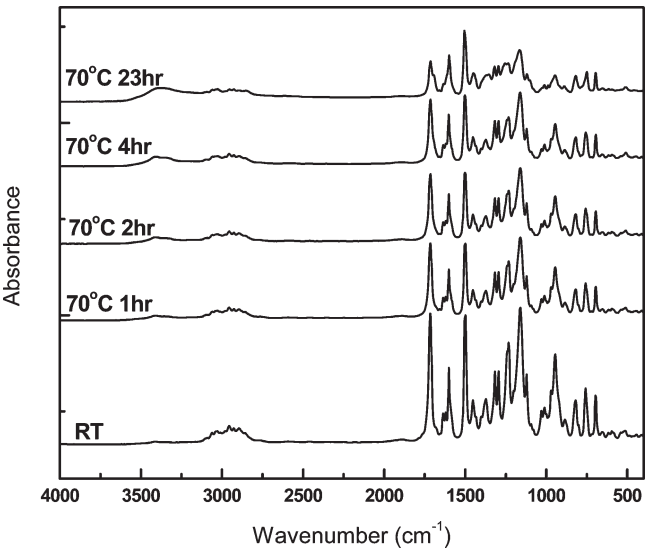


Figure 7. FTIR spectra of methacryloyl−benzoxazine monomer (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate with 1% benzoyl peroxide isothermal at 70 °C.

In order to fully polymerize the monomer, the acrylate portion should be first polymerized to anchor it into the network structure. On the basis of this hypothesis, free radical initiator, benzoyl peroxide (BPO), was added into the monomer at 70 °C to help acrylate polymerize at lower temperature before decomposition. FTIR is used to investigate the change of the molecular structure under the heat treatment, and the result is shown in Figure 7. It can be seen that, even under mild condition at 70 °C, the decomposition is still happening, which is indicated by the significant decrease in intensity of the carbonyl band at 1715 cm^{-1}. Therefore, it appears that the monomer is relatively sensitive to heat, and at least some part of the molecule will undergo decomposition before its polymerization.

3.2.2. Photopolymerization Behavior. Because of the difficulty of polymerizing the monomer by heating, a different approach was taken to polymerize the acrylate portion at room temperature by photoinitiated free-radical polymerization. Photopolymerization of vinylester, vinyl acrylate, and divinyl fumarate has been extensively investigated by researchers.[33,34] On the basis of the previous knowledge, the photopolymerization of (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate was conducted by

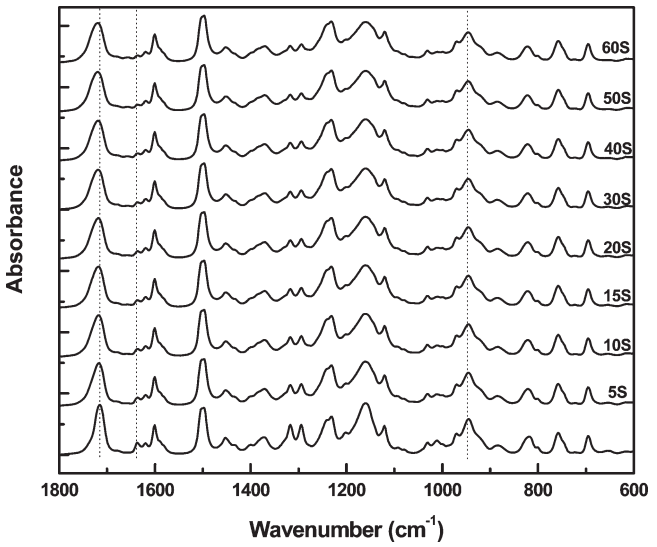


Figure 8. FTIR spectra of methacryloyl-benzoxazine monomer (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate exposed under UV irradiation at room temperature.

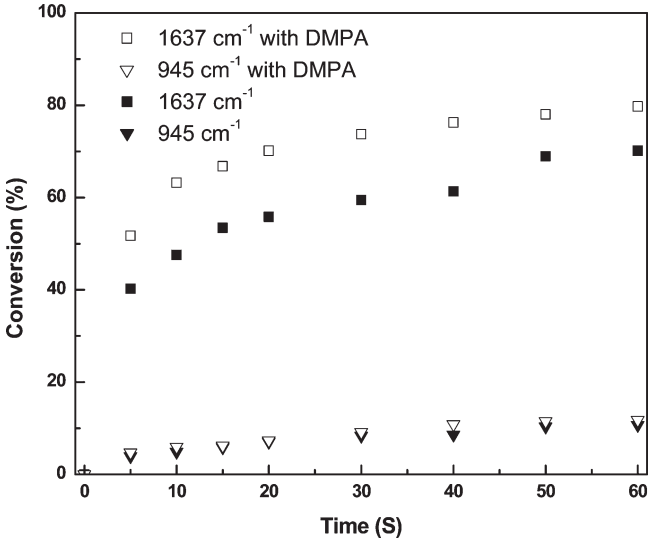


Figure 9. FTIR conversion vs time plots of methacryloyl-benzoxazine monomer (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate or in the presence of 5% DMPA exposed under UV irradiation at room temperature.

exposing the monomer film both with and without a photoinitiator, dimethoxyphenyl acetophenone (DMPA), under the UV light from 5 to 60 s. The corresponding FTIR spectra for the monomer without the initiator as an example are shown in Figure 8.

Instead of dramatic decrease in intensity, the frequency of the carbonyl band gradually shifted from 1715 to 1720 cm^{-1} because of the loss of conjugation by the vinyl polymerization. The intensity change of the peak at 1637 cm^{-1} is used to calculate the photopolymerization conversion of the double bond and the peak at 945 cm^{-1} is used to demonstrate the change of benzoxazine ring during the UV exposure. These are illustrated in Figure 9.

For vinyl polymerization, the monomer with and without the initiator shows a similar trend as a dramatic increase of conversion in 5 s and gradually reaches the asymptotic value in 1 min. The one with the initiator shows an increase of additional 10% conversion compared with the one without

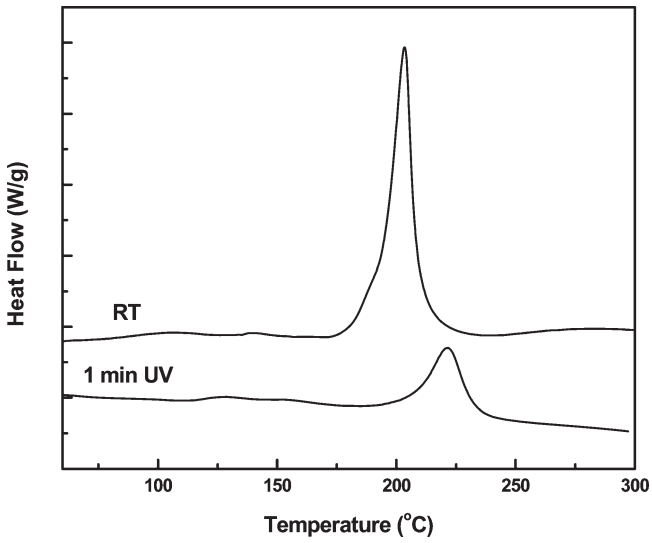


Figure 10. DSC thermograms of methacryloyl−benzoxazine monomer after 1 min UV irradiation.

the initiator during the experimental process. It is known that vinyl acrylate monomer can be used as the photoinitiating monomer,[35] and by adding a photo initiator, a higher extent of the polymerization can be achieved. Ordinary benzoxazines do not polymerize under UV in such small time scale. However, the slight decrease of the benzoxazine-related band at 945 cm^{-1} due to the out-of-plane C−H vibration is observed. Both with and without the initiator monomer show the same trend and achieve about 10% decrease of benzoxazine ring at 1 min. An increase in the band intensity between 3600 and 3300 cm^{-1} is believed to come from hydroxyl group from ring-opening polymerized structure of benzoxazine as there is no indication for loss of carbonyl groups from degradation. This shows that the presence of methacrylate structure expedite the polymerization of benzoxazine under UV exposure.

The DSC thermogram after the photopolymerization for 1 min shown in Figure 10 indicates one exotherm maximized at 222 °C, reflecting the increased rigidity in surrounding environment due to the polymer chain formation and cross-linking. Besides, the heat of the exotherm is much smaller compared with that of room temperature, as the room temperature DSC shows the exotherm for methacrylate polymerization, benzoxazine polymerization and degradation. The cross-linking of benzoxazine could be due to hydrogen abstraction from carbon atom adjacent to the nitrogen atom or from the methyl group in the vinyl. Owing to this H abstraction, new free radical species has been generated that result in two reacting sites in one molecule. This hypothesis explains the insolubility of the photopolymerized monofunctional benzoxazine despite the fact there is only one vinyl group in each molecule.

To further compare the difference among the three polymerization approaches, the difference spectra were generated using one example from each method as shown in Figure 11. In the difference spectra, the band above the baseline means it increases in concentration with the process, while the peak below the baseline indicates the decrease. One characteristic peak is the antisymmetric stretching absorption of the carbonyl group at 1715 cm^{-1}. The peak becomes smaller by the thermal treatment both with and without the free-radical initiator, while it shifts to higher wavenumber without decreasing by the irradiation process. Since the extinction coefficient of the carbonyl group before and after the polymerization is expected to be nearly identical, having nearly equal intensity above and below the baseline of the carbonyl band indicates the structural change by

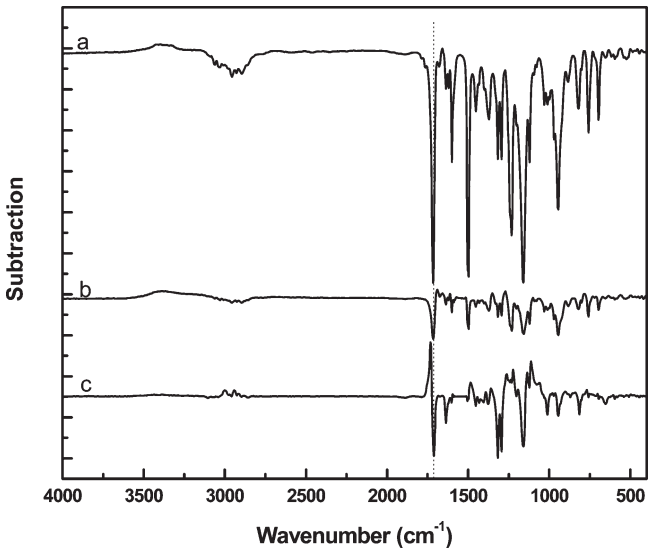


Figure 11. FTIR subtraction spectra of methacryloyl-benzoxazine monomer (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate (a) containing 1%BPO at 70 °C for 1 h and (b) at 100 °C for 1 h, (c) exposed to UV light for 5 s to their original spectra.

the polymerization rather than degradation. Moreover, the intensity increase of the bands between 3000 and 2800 cm^{-1}, which are attributed to the C−H stretching modes from saturated C−H bonds, is observed only in photopolymerization approach. This indicates the success of converting the double bond in acrylate moiety into aliphatic chains. Overall, it is demonstrated that photopolymerization is feasible to anchor the acrylate in the monomer in spite of the difficulty experienced with free radical polymerization with and without an initiator.

4. Conclusion

We have synthesized a novel methacryloyl-functional benzoxazines: (3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl methacrylate by the reaction of (3-phenyl-3,4-dihydro-2*H*-benzo-[*e*][1,3]oxazin-6-yl)methanol and methacryloyl chloride. It has been successfully photopolymerized with and without photoinitiator to extend the application of the material curable at ambient conditions. Its thermally activated polymerization is deteriorated by its degradation at low temperature of 200 °C.

References and Notes

(1) Ning, X.; Ishida, H. *J. Polym. Sci. Polym. Chem. Ed.* **1994**, *32*, 1121–1129.
(2) Shen, S. B.; Ishida, H. *J. Appl. Polym. Sci.* **1996**, *61*, 1595–1605.
(3) Ishida, H.; Sanders, D. P. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 3289–3301.
(4) Allen, D. J.; Ishida, H. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1019–1030.
(5) Low, H. Y.; Ishida, H. *Macromolecules* **1997**, *30*, 1099–1106.
(6) Brunovska, Z.; Liu, J. *Macromol. Chem. Phys.* **1999**, *200*, 1745–1752.
(7) Low, H. Y.; Ishida, H. *Polymer* **1999**, *40*, 4365–4376.
(8) Ishida, H.; Sanders, D. P. *Macromolecules* **2000**, *33*, 8149–8157.
(9) Kim, H. J.; Brunovska, Z.; Ishida, H. *Polymer* **1999**, *40*, 6565–6573.
(10) Agag, T.; Takeichi, T. *Macromolecules* **2003**, *36*, 6010–6017.
(11) Su, Y. C.; Chen, W. C.; Chang, F. C. *J. Appl. Polym. Sci.* **2004**, *94*, 932–940.
(12) Espinosa, M. A.; Cadiz, V.; Galia, M. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 279–289.
(13) Lee, Y. J.; Kuo, S. W.; Su, Y. C.; Chen, J. K.; Tu, C. W.; Chang, F. C. *Polymer* **2004**, *45*, 6321–6331.
(14) Rao, B. S.; Rajavardhana, R. K.; Pathak, S. K.; Pasala, A. R. *Polym. Int.* **2005**, *54*, 1371–1376.
(15) Andreu, R.; Espinosa, M. A.; Galia, M.; Cadiz, V.; Ronda, J. C.; Reinda, J. A. *J. Polym. Sci. Part A: Polym Chem.* **2006**, *44*, 1529–1540.
(16) Santhosh Kumar, K. S.; Reghunadhan Nair, C. P.; Radhakrishnan, T. S.; Ninan, K. N. *Eur. Polym. J.* **2007**, *43*, 2504–2514.
(17) Rimdusit, S.; Mongkhonsi, T.; Kamonchaivanich, P.; Sujirote, K.; Thiptipakorn, S. *Polym. Eng. Sci.* **2008**, *48*, 2238–2246.
(18) Lu, C. H.; Su, Y. C.; Wang, C. F.; Huang, C. F.; Sheen, Y. C.; Chang, F. C. *Polymer* **2008**, *49*, 4852–4860.
(19) Ning, X.; Ishida, H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1121–1129.
(20) Allen, D. J.; Ishida, H. *Polymer* **2007**, *48*, 6763–6772.
(21) Takeichi, T.; Kano, T.; Agag, T. *Polymer* **2005**, *46*, 12172–12180.
(22) Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules*, ASAP, doi: 10.1021/ma1007545
(23) Wang, Y.-X.; Ishida, H. *Polymer* **1999**, *40*, 4563.
(24) Kasapoglu, F.; Cianga, I.; Yagci, Y.; Takeichi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3320–3328.
(25) Tasdelen, M. A.; Kiskan, B.; Yagci, Y. *Macromol. Rapid Commun.* **2006**, *27*, 1539–1544.
(26) Kiskan, B.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1670–1676.
(27) Gacal, B.; Cianga, L.; Agag, T.; Takeichi, T.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2774–2786.
(28) Koz, B.; Kiskan, B.; Yagci, Y. *Polym. Bull.* **2011**, *66*, 165–174.
(29) Lin, Y.; Stansbury, J. W. *Polymer* **2003**, *44*, 4781–4789.
(30) Mandal, P. K.; McMurray, J. S. *J. Org. Chem.* **2007**, *72*, 6556–6561.
(31) Alonso, E.; Ramón, D. J.; Yus, M. *Tetrahedron* **1997**, *53*, 14355–14368.
(32) Su, Y. C.; Chen, W. C.; Ou, K. L.; Chang, F. C. *Polymer* **2005**, *46*, 3758–3766.
(33) Wei, H.; Lee, T. Y.; Miao, W.; Fortenberry, R.; Magers, D. H.; Hait, S.; Guymon, A. C.; Jonsson, S. E.; Hoyle., C. E. *Macromolecules* **2007**, *40*, 6172–6180.
(34) Lee, T. Y.; Kaung, W.; Jonsson, E. S.; Lowery, K.; Guymon, C. A.; Hoyle, C. E. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4424–4436.
(35) Lee, T. Y.; Guymon, C. A.; Jonsson, E. S.; Hait, S.; Hoyle, C. E. *Macromolecules* **2005**, *38*, 7529–7531.