Synthesis of Polybenzoxazine Precursors Using Thiols: Simultaneous Thiol–Ene and Ring-Opening Reactions

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Received 10 April 2012; accepted 29 May 2012; published online
DOI: 10.1002/pola.26202

ABSTRACT: A new class of polybenzoxazine precursors of combined molecular structure of benzoxazine in the open and ring form has been developed. Thermally curable benzoxazine networks were obtained by simultaneous photoinduced thiol-ene and Catalytic Opening of the Lateral Benzoxazine Rings by Thiols (COLBERT). The thiol-ene reactions were initiated by photolysis of a free radical photoinitiator, 2, 2-dimethoxy-2-phenyl acetophenone (DMPA), and the competing COLBERT reaction was triggered by thiol compound, 1,2-ethanedithiol, present in the reaction mixture. The extent of reactions was evaluated by conducting experiments both under UV irradiation and in dark using model benzoxazines. The precursor soft films (pre-P(B-ala-DTE)) were prepared by irradiating solutions of diallyl functional benzoxazine (B-ala), 1,2-ethanedithiol and DMPA. The obtained pre-P(B-ala-DTE) films were then cured through thermally activated ring opening reaction of remaining benzoxazine groups yielding a more rigid and tough film. Thermal and mechanical properties of the films were investigated by DSC, DMA and TGA and compared with a typical polybenzoxazine, P(B-ala). © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

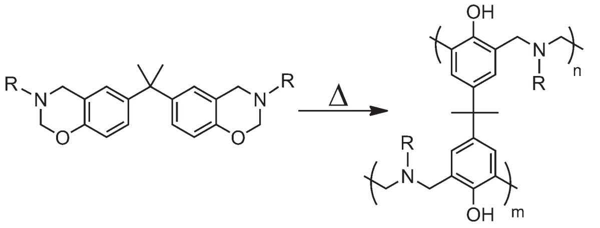
KEYWORDS: benzoxazine; polybenzoxazine; crosslinking; ring-opening polymerization; thiol-ene; thermosets; phenolic resin

INTRODUCTION Benzoxazine-based phenolic thermosets have gained an increasing interest in the field of polymer research owing to the superior properties that overcome several shortcomings of conventional novolac and resole-type phenolic resins. These materials offer low water absorption, high char yield, resistance against flame, high modulus, high strength, high glass transition temperatures, chemical resistance, long shelf life, they have very limited volumetric change upon curing and strong acid catalysts are not required for curing.[1] Moreover, the molecular design flexibility of benzoxazines is enormous. Basically, the synthesis of a monomer is carried out by the reaction of any suitable phenols, formaldehyde, and primary amines (aliphatic or aromatic).[2–15] Synthesis of polybenzoxazine network is a thermally induced ring-opening polymerization of precursor 1,3-benzoxazines which can be accomplished without any initiator or curing agent (Scheme 1).[16–19]

Despite their various attractive properties, polybenzoxazines have drawbacks and limitations related to their processability, brittleness, high curing temperatures (~200°C or more), and low degree of polymerization for mono-functional monomers.[20,21]

To overcome these problems, various modification strategies have been proposed. To improve the performance of polybenzoxazines, additional sites such as allyl-,[7,22] acetylenyl-,[23–26] nitrile-,[27] and propargyl[25,28] groups have been introduced into benzoxazine monomers. These groups take part in further crosslinking reactions, yielding three-dimensional networks that exhibit high thermal and mechanical stability, and high solvent and moisture resistance. Similarly, incorporating some functional groups such as carboxylic and phenolic groups allows lowering curing temperature. The side-, main-, and end-chain polymeric benzoxazine precursors or blending benzoxazines with a high-performance polymer, filler, and fiber have been successfully used to reduce brittleness and improve thoughness.[29–45]

Thiol–ene reactions, originally developed for UV-curing application, are versatile techniques for the synthesis of numerous polymeric structures and considered to represent some characteristic related to the click reactions.[46] Relative to the other click reactions, thiol–ene chemistry provides improved tolerance to oxygen and water, rapid reaction, and significant versatility in ene functional groups.[47,48] Moreover, these reactions can be conducted thermally and photochemically at room temperature without any catalyst. Typical applications of thiol–ene reactions include modification of polymers and surfaces, preparation of bioconjugated polymers, synthesis of star polymers, dendrimers, dental materials, etc.[49–56]

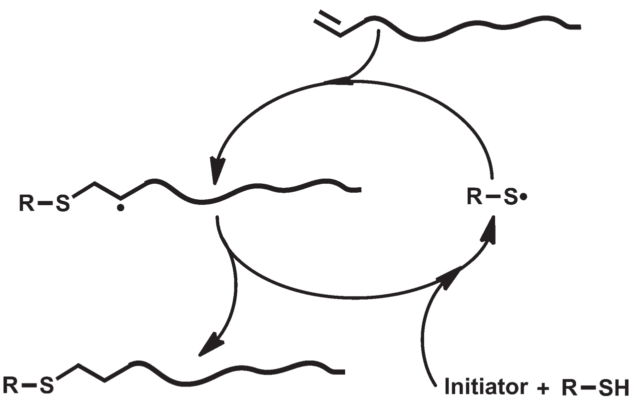


SCHEME 1 Thermally activated ring-opening polymerization of bisbenzoxazines.

Thiol–ene reactions are fundamentally based on free radical reactions, but proceed through a step-growth process. As presented on the example of polymer functionalization in Scheme 2, the thiol–ene reaction is established by the radical formation, hydrogen abstraction, and thiyl radical addition to the olefinic bond. The primary radical addition and coupling reactions reduces the efficiency of the overall process.

In a recent publication, benzoxazines were reported to undergo catalytic ring-opening reaction at ambient conditions by thiols. The process is known as "Catalytic Opening of the Lateral Ben-zoxazine Rings by Thiols" (COLBERT) which proceeds via a two-step acid catalyzed nucleophilic addition.[57] In the first step, the benzoxazine amine is protonated by thiol to form an ionic intermediate. Then, immediate attack by sulfide on the methylene carbon results in the ring opening of the benzoxazine (Scheme 3).

However, when the benzoxazine moiety is equipped with the allyl functionalities, these investigations do not answer the question whether the added thiol groups react directly with benzoxazine according to COLBERT reaction and whether thiol–ene reactions are dominant process upon photolysis in the presence of a photoinitiator. Also, both and other reactions may prevail. Therefore, detailed polymerization and model studies by using appropriately functionalized molecules were performed to provide information that would be useful in confirming the validity of the both mechanisms. In this connection, it is worth to mention the work of Agag et al. who demonstrated that two independent reactions of benzoxazines may proceed simultaneously when benzoxazines are equipped with suitable functionalities.[58] In this study, a bisbenzoxazine-based ene-monomer, namely diallyl benzoxazine (B-ala), and a difunctional thiol compound, 1,2-ethanedithiol, were utilized in photoinduced thiol–ene and COLBERT reactions. As will be discussed below, these competing reactions essentially yield thermally curable benzoxazine networks as precursor films. Subsequently, the precursor films were subjected to thermal treatment for the conventional ring-opening reaction of benzoxazine units. The films were thermally and mechanically characterized before and after thermal process.



SCHEME 2 Polymer functionalization by thiol–ene reactions.

SCHEME 3 Proposed mechanism for the ring opening of benzoxazine by thiols.

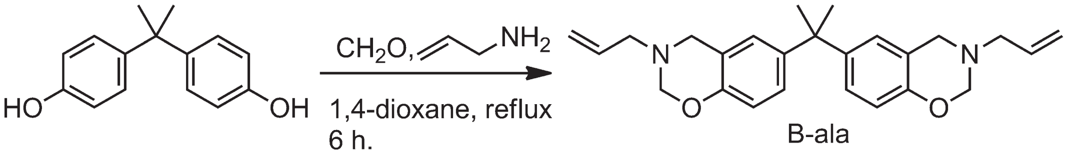
EXPERIMENTAL

Materials

The reagents and solvents including 4,4′-isopropylidenediphenol (Aldrich, 97%), paraformaldehyde (Acros, 96%), allyl amine (Aldrich, 98%), sodium hydroxide (Acros, >97%), sodium sulfate (Acros, 99%), 1,4-dioxane (Aldrich, 99%), toluene (Aldrich, 99%), methanol (MeOH, Aldrich, 99%), diethylether (Carlo Erba, 99.8%), *N, N*-dimethyl formamide (DMF, Merck, 99.8%), and chloroform (Acros, >99%) were used as received for the synthesis of the benzoxazine derivative (B-ala). Difunctional thiol compound, 1,2-ethanedithiol (Merck, 99%), and free radical photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba), were also used as received.

Characterization

^{1}H NMR spectrum of B-ala was recorded in CDCl3 with Si(CH3)4 as an internal standard, using a Bruker AC250 (250.133 MHz) instrument. Fourier transform infrared (FTIR) spectra of the precursor and cured films were obtained with Perkin-Elmer FTIR Spectrum One spectrometer. Curing of the films was monitored on a Perkin Elmer Diamond differential scanning calorimetry (DSC) with a heating rate of 10°C·min^{-1} under nitrogen flow. Thermal gravimetric analysis (TGA) was performed on Perkin-Elmer Diamond TA/TGA with a heating rate of 10°C·min^{-1} under nitrogen flow. Dynamic viscoelastic measurements were conducted on Perkin Elmer dynamic mechanical analyzer model DMS6100 at 1 Hz at a heating rate of 5°C·min^{-1}. Molecular weight of oligomeric linear polymer was determined by gel permeation chromatography (GPC) instrument, Viscotek GPCmax Autosampler system, consisting of a pump, three ViscoGEL GPC columns (G2000H$_{HR,}$ G3000H$_{HR,}$ and G4000H$_{HR}$), a Viscotek UV detector, and a Viscotek differential refractive index detector with a tetrahydrofuron at a flow rate of 1.0 mL min^{-1} at 30°C. Both detectors were calibrated with PS standards,



SCHEME 4 Synthesis of B-ala monomer.

having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software.

Synthesis of 6,6′-(Propane-2,2-diyl)bis(3-allyl-3,4-dihydro-2*H*-benzo[*e*][1,3] oxazine) (B-ala)

In a 250-mL flask, allyamine (30.8 g, 0.54 mol) was dissolved in 200 mL of 1,4-dioxane at room temperature. The solution was cooled in an ice bath, followed by portion-wise addition of paraformaldehyde (32.5 g, 1.08 mol) during 10 min of stirring in an ice bath. Then, bisphenol-A (61.6 g, 0.27 mol) was added to the cooled solution. The temperature was raised and refluxed for 24 h. After the removal of 1,4-dioxane under vacuum, the resulted crude product was purified by dissolving in 200 mL of diethyl ether and washing various times with 0.1 N sodium hydroxide, and finally two times with distilled water. Pale yellowish oily product was obtained after drying with $NaSO_4$, filtering and evaporating diethyl ether. The oily viscous product was dissolved in 20 mL of MeOH; water was added to this solution until it became turbid, and then the mixture was refrigerated. The precipitated sticky mass was obtained after decantation and subsequently washing with water. The mass was dried under vacuum at 60°C for 24 h to afford solid (Yield, 62%). The ^1H NMR spectrum of B-ala is as follows: δ (CDCl3) 6.94 (dd, $J =$ 8.3 and 2.1 Hz, 2H, ArH); 6.79 (dd, $J = 2.0$ Hz, 2H, ArH); 6.67 (dd, $J = 8.3$ Hz, 2H, ArH); 5.89 (multiplet, 2H, $CH_2 = CH$—); 5.23 (dd, $J = 12.2$ and 1.5 Hz, 2H, $CH{=}CH_2$); 5.17 (dd, $J = 5.3$ and 1.3 Hz, 2H, $CH{=}CH_2$); 4.82 (s, 4H, $N{-}CH_2{-}O$); 3.93 (s, 4H, $Ar{-}CH_2{-}$); 3.37 (d, 4H, $CH_2{=}CH{-}CH_2{-}$); 1.58 (s, 6H, $-CH_3$).

Preparation of Precursor Films [pre-P(B-ala-DTE)] by Photolysis

Typical procedure for the preparation of the precursor films is as follows: B-ala (1.0 g, 2.6×10^{-3} mol), 1,2-ethanedithiol (214 μL, 2.6×10^{-3} mol), and photoinitiator DMPA (6.7 mg, 2.6×10^{-5} mol, 1 % equiv of thiol reagent) were dissolved in a minimal amount of the solvent, chloroform, required to dissolve the photoinitiator. For the preparation of flexible films, the mixture was placed equally into Teflon® plates and exposed to light continuously at room temperature for 6 h in a Rayonet merry-go-round photo reactor in which the sample was surrounded by a circle of 16 lamps emitting light nominally at 350 nm. The light intensity at the location of the sample was measured by a Delta Ohm model HD-9021 radiometer ($I = 3.0$ mW·cm^{-2}).

Thermal Curing of B-ala and pre-P(B-ala-DTE) Films

Films of bisallyl benzoxazine were prepared by solvent casting of B-ala (50% w/v in DMF) over Teflon® plates. Curing of both B-ala and pre-P(B-ala-DTE) films was performed stepwise at 80°C for 5 h and 110°C for 3 h, and then at 160, 180, and 200°C for 2 h each in an air oven. The films then were postcured at 240°C for 1 h resulted in transparent brown films.

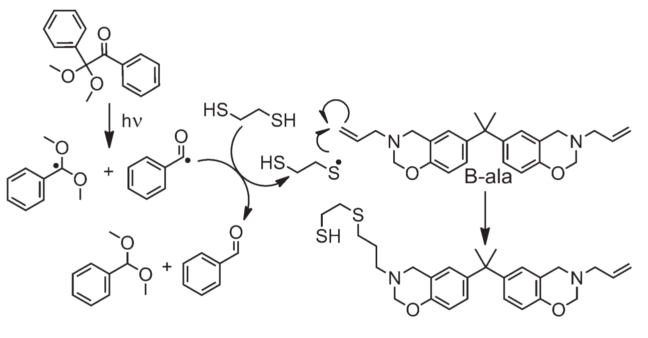
RESULTS AND DISCUSSION

To use in the proposed reactions, first, allyl functional benzoxazine (B-ala) was synthesized through the Mannich and respective ring closure reactions between 4,4′-isopropylidenediphenol (bisphenol-A) and allylamine in the presence of formaldehyde in one pot (Scheme 4).

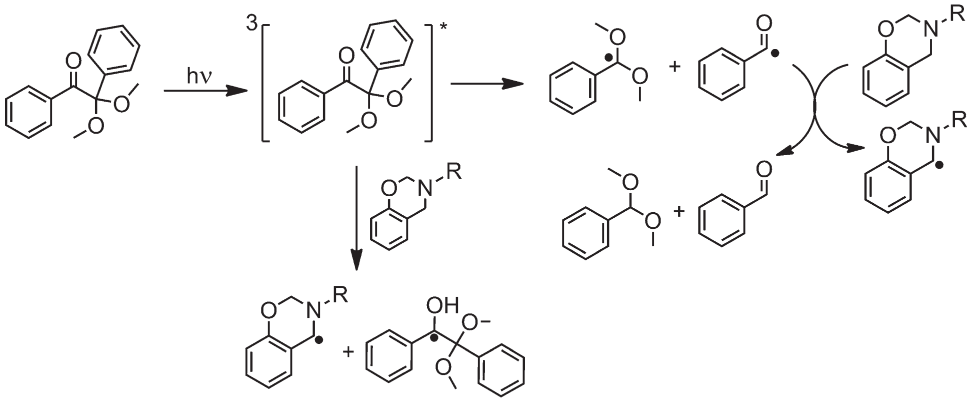
We started our investigation by studying the photolysis of B-ala (ene-monomer) and 1,2-ethanedithiol in the presence of a typical free radical photoinitiator DMPA. It should be pointed out that photochemically, benzoxazines can be polymerized only by a cationic route. As stated in the **INTRODUCTION** section, it is expected that thiols could participate in thiol–ene reactions with the allylic groups present in the structure. DMPA generates alkoxybenzyl and benzoyl radicals by α-cleavage under UV irradiation. Both radicals can abstract labile hydrogens of the thiol compound, leading to the formation of thiyl radicals (Scheme 5). Subsequently, the thiyl radicals readily react and couple with allylic group. As both components are difunctional, such step-growth reactions are expected to form linear polymeric structures.

Hydrogen abstraction reactions of either triplet excited state or photochemically generated radicals from benzoxazine methylene bridge should also be considered.[59] Both pathways would give rise to additional reactions with thiol and oxazine groups (Scheme 6).

In contrast to the expected linear polymer formation, upon photolysis soft but mostly crosslinked polymeric materials were obtained, indicating, in addition to thiol–ene reactions, participation of simultaneous ring-opening reactions. Some of the benzoxazine groups may interact from the ring side



SCHEME 5 Photoinduced thiol–ene reaction of B-ala.



SCHEME 6 Possible photoinduced side reactions of benzoxazines in the presence of DMPA.

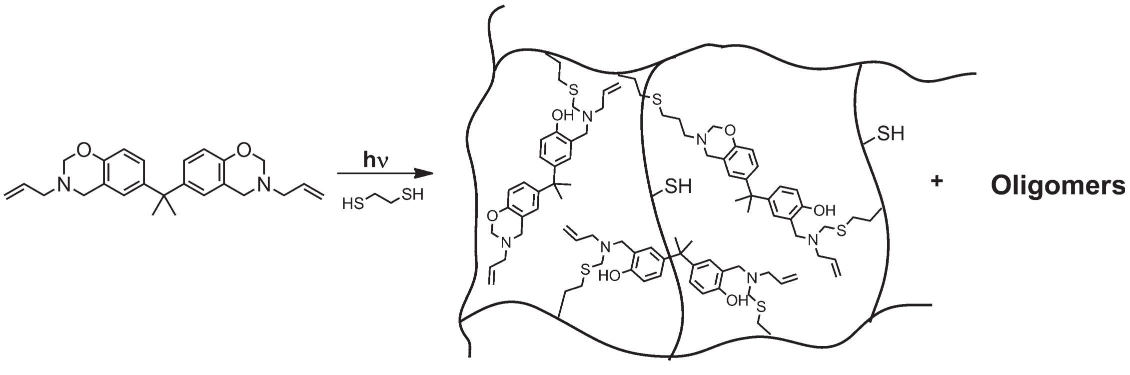
with thiols and undergo ring-opening reaction as shown in Scheme 3. Either or both reactions would essentially yield branched and networked polymers, possessing both ring and open benzoxazine structures (Scheme 7).

In this process, besides insoluble crosslinked structures, hardly soluble oligomeric products were also formed. The molecular weights of these oligomers were found to be $M_n = 1000–2000$. The relatively low molecular weights observed with the linear polymers are probably owing to the chain transfer reactions favored by oxygen. Indeed, the experiments conducted under oxygen-free conditions yielded insoluble polymers.

The occurrence of simultaneous thiol–ene and COLBERT ring-opening reactions was confirmed by FTIR spectral analysis. Figure 1 shows FTIR spectra of the starting compound B-ala, the film [pre-P(B-ala-DTE)] (Precursor Poly(B-ala-Dithiol-ethane) obtained by the photolysis in the presence of 1,2-ethanedithiol and photoinitiator DMPA and thermally post-cured film [P(B-ala-DTE)]. The pure monomer B-ala exhibits characteristic absorption bands of the allyl groups emerging at 3084 cm^{-1} (stretching of =C—H) and 1644 cm^{-1} (stretching of C=C) (Fig. 1). Moreover, spectrum also reveals asymmetric stretching of C—O—C at 1225cm^{-1} and tri-substituted benzene ring modes at 925 and 1495 cm^{-1} belonging to the absorptions of benzoxazines. The absorption of =C—H stretching of allyl group at 3084 cm^{-1} slightly decreases after the reaction of B-ala and thiol compound. The presence of the bands at 1495, 925, and 1225 cm^{-1} clearly confirms that there is remaining unopened oxazine rings. Notably, after the thermal treatment of [pre-P(B-ala-DTE)], while the absorption band at 1495 cm^{-1} shifts to 1474 cm^{-1}, the bands at 1225 and 925 cm^{-1} disappear completely (Fig. 1).

To get more insight to the polymerization mechanism and evaluate the structure of the final network, we conducted some model experiments using benzoxazine compounds with and without allyl groups, P-ala and P-a, respectively. These compounds were separately irradiated 350 nm for 24 h in the presence of monofunctional thiol compound, propane-1-thiol and photoinitiator, DMPA under the same experimental conditions to that applied for obtaining [pre-P(B-ala-DTE)]. Depending on the presence of ally functionality, possible reactions involving both COLBERT and/or thiol–ene reactions are shown in Scheme 8.

Experimentally, samples were taken from reaction mixtures at different intervals and analyzed by NMR spectroscopy. Figures 2 and 3 show ^{1}H NMR spectra of solutions prior to irradiation and after 24 h of irradiation. In both experiments, oxazine ring opening was observed which was particularly intense for P-ala monomer (Fig. 3). However, the thiol–ene reaction also took place although most of the thiols reacted



SCHEME 7 Photoinduced curing of B-ala in the presence of DMPA and 1,2-ethanedihiol forming pre-P(B-ala-DTE).

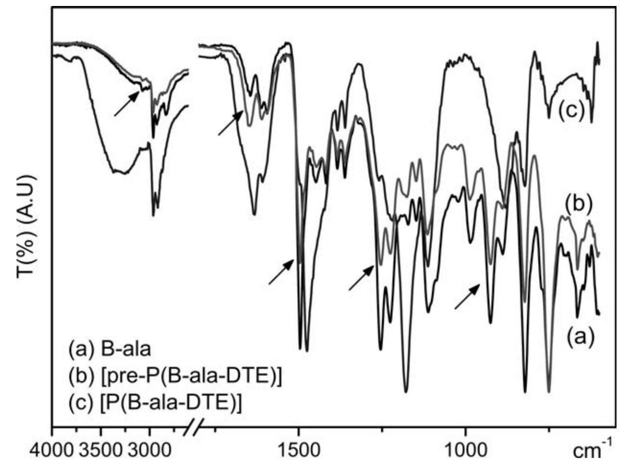
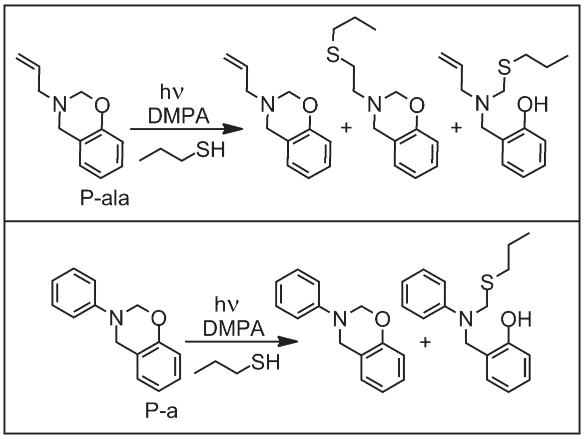


FIGURE 1 FTIR spectra of (a) B-ala, (b) pre-P(B-ala-DTE), and (c) [P(B-ala-DTE)].

with oxazine rings that is proved by the shift of the peak belonging N—C$\boldsymbol{H_2}$—C=CH at 3.37–2.70 ppm. Using the integrated area ratios of the peaks at 2.70 and 3.37 ppm, it is calculated that 14% of the allyl groups reacted with thiol compound after 24 h. Based on the results of the model experiments, it is evident that COLBERT reaction is predominant for P-ala monomer. In contrast, the corresponding reaction with P-a monomer occurred in a much less extend. The same model reactions were also performed in dark. NMR analysis of the reaction products gave strong evidence for the occurrence of the ring-opening reaction between thiol compound and oxazine ring. These observations are in agreement with the previous report which confirms in dark, indicating the independency of COLBERT reaction from light. This result is in agreement with the previous reports about COLBERT reaction.[57]

It should be noted that after thiol treatment some of the benzoxazine rings preserved and unreacted thiol functionalities were also determined. Upon heating, the soft film became more rigid and tough owing to the ring-opening polymerization of the remaining benzoxazines (Scheme 9).



SCHEME 8 Photoinduced reactions of benzoxazine monomers with propan-1-thiol in the presence of DMPA.

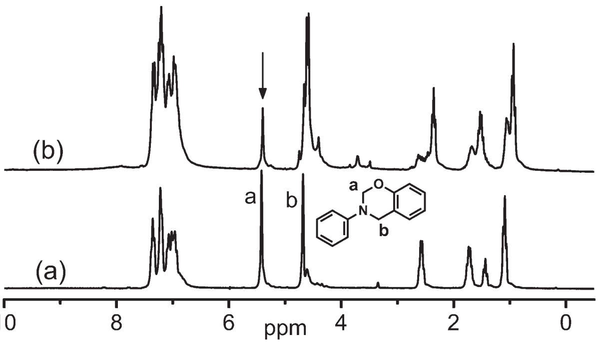


FIGURE 2 ^{1}H NMR spectrum of model reaction for P-a.

Thermal postcurings of both the pure B-ala film and the film obtained by the thiol–ene reaction were monitored by DSC. A typical unsymmetrical broad exotherm with a shoulder was observed during the curing of pure B-ala film. The ring-opening exotherm of the oxazines was observed around 230°C as a shoulder, whereas the exotherm centered around 278°C was attributed to thermal cure of the allyl groups [Fig. 4(a)]. On the other hand, two exotherms were observed on thermogram of pre-P(B-ala-DTE) around 175 and 260°C [Fig. 4(b)]. The first exotherm with onset temperature at 140°C and exotherm maximum at 175°C was attributed to exothermic thiol–ene reaction between unreacted allyl functionality of benzoxazines and unreacted thiol groups, whereas the second exotherm with onset at 225°C and peak at 260°C was resulted from thermal curing of the benzoxazine and residual allylic double bonds.

Dynamic mechanical analysis (DMA) of pre-P(B-ala-DTE) and P(B-ala-DTE) was examined, and compared with polybenzoxazine P(B-ala). Figures 5–7 show the temperature dependence of the storage modulus (E'), loss modulus (E'') and tan δ for pre-P(B-ala-DTE), P(B-ala-DTE), and P(B-ala), respectively. The T_g values as defined by the E'' and tan δ peaks are summarized in Table 1. For the precursor polymer, pre-P(B-ala-DTE), two T_gs were observed at 12 and 123°C from the maximum of loss modulus and at 30 and 151°C from the maximum of tan δ. The storage modulus decreased sharply

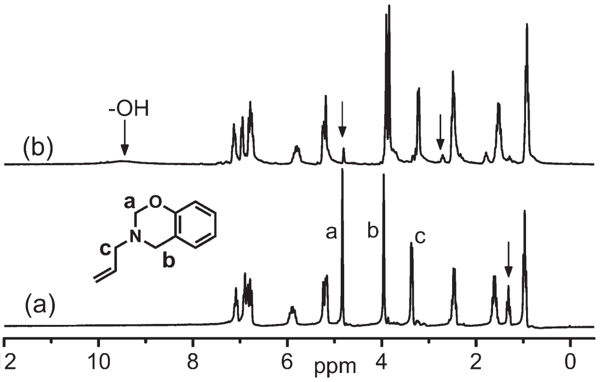
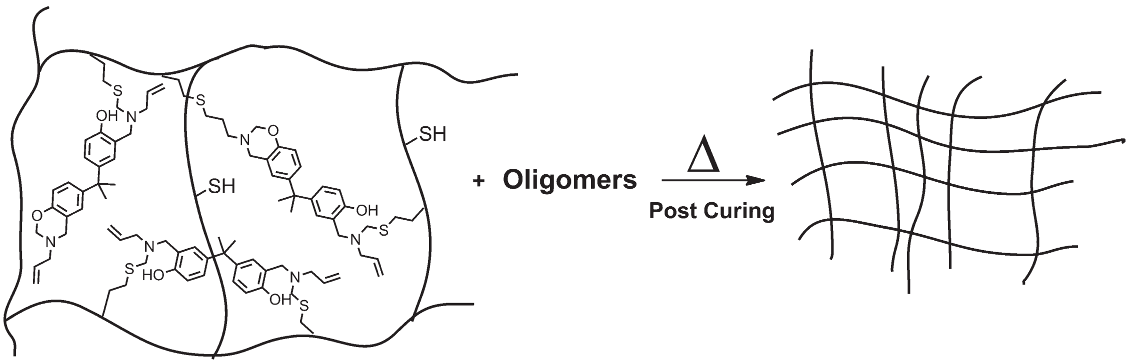


FIGURE 3 ^{1}H NMR spectrum of model reaction for P-ala.



SCHEME 9 Thermally activated post curing of pre-P(B-ala-DTE).

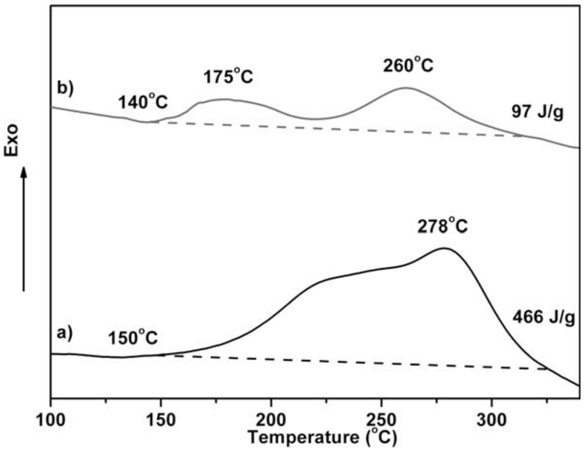


FIGURE 4 DSC profiles of (b) pure B-ala film and (a) pre-P(B-ala-DTE) during their postcuring.

at *ca*. 2 and 115°C. According to these results, it could be assumed that the polymer obtained by thiol reactions, pre-P(B-ala-DTE), was not completely crosslinked and still contained some oligomeric parts. The presence of these oligomeric structures was proved by GPC analysis of the soluble part. Thermal treatment of pre-P(B-ala-DTE) resulted in ring-opening polymerization of the benzoxazine moieties and augmented rigidity of the polymer because of increased crosslinking density in certain domains. It is quite likely that the network contains two different macromolecular chains: polymers rich in thiol and polybenzoxazine. This statement was evidenced by the observation of microphase separation in DMA investigations of the cured films since two T_gs were detected for P(B-ala-DTE) at 150 and 255°C from the maximum of loss modulus and at 170 and 245°C from the maximum of tan δ. In contrast, the typical polybenzoxazine, P(B-ala), exhibited only one T_g at relatively higher temperature,

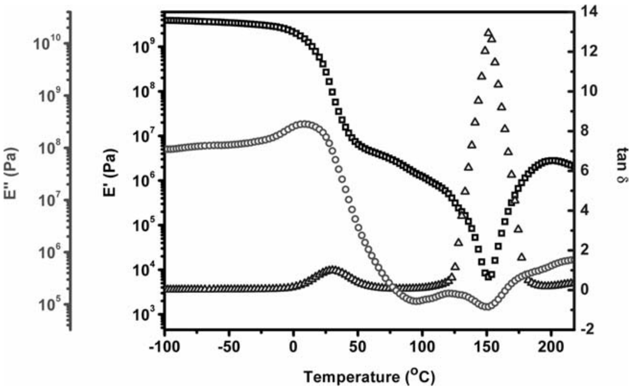


FIGURE 5 Dynamic mechanical analysis of pre-P(B-ala-DTE) polymerized under $\lambda > 350$ nm light for 6 h in air: (□) *E*′, (○) *E*″, and (△) tan δ.

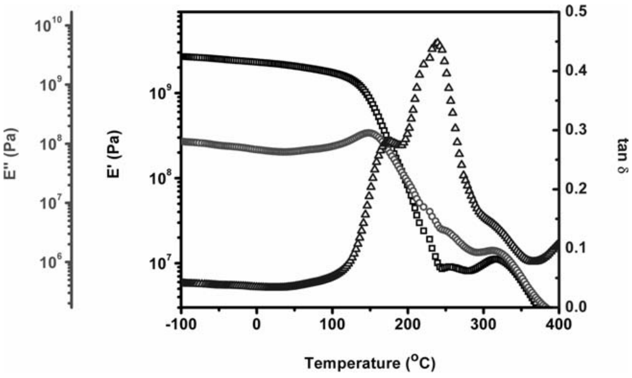


FIGURE 6 Dynamic mechanical analysis of P(B-ala-DTE) polymerized at 240°C for 1 h in air: (□) *E*′, (○) *E*″, and (△) tan δ.

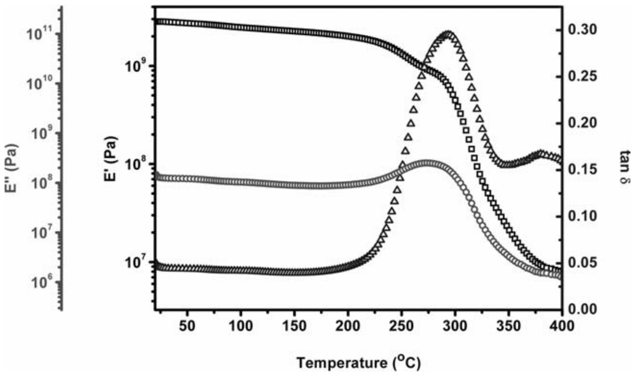


FIGURE 7 Dynamic mechanical analysis of P(B-ala) polymerized at 240°C for 1 h in air: (□) *E*′, (○) *E*″, and (△) tan δ.

TABLE 1 Thermal Properties of Benzoxazine Polymers

	T_g (°C)		Weight-Loss Temperature (°C)		
Polymer	E''	Tan δ	$T_{5\%}$	$T_{10\%}$	Char Yield (%)
Pre-P(B-ala-DTE)	12 and 123	30 and 151	–	–	–
P(B-ala-DTE)	150 and 255	170 and 245	255	300	17
P(B-ala)	276	298	334	363	25

276°C from the maximum of loss modulus and 298°C from the maximum of tan *δ*. The storage modulus started to decrease at *ca*. 280°C. The lower T_g for P(B-ala-DTE) compared to P(B-ala) may be attributed to the presence of crosslinked parts of pre-P(B-ala-DTE), leading to a lower crosslinking density.

Thermal stabilities of the films were investigated by TGA under nitrogen atmosphere. The comparative TGA thermograms of P(B-ala-DTE) and P(B-ala) are shown in Figure 8. The results are also summarized in Table 1. The 5 and 10% weight loss temperatures ($T_{5\%}$ and $T_{10\%}$) for P(B-ala) are at 334 and 363°C, respectively. Incorporation of linear alkyl groups into the polybenzoxazines decreases aromatic content of the materials and consequently their thermal stabilities.[30] Therefore, the $T_{5\%}$ and $T_{10\%}$ for P(B-ala-DTE) were around 255 and 300°C, respectively. Moreover, the similar fashion was observed for char yields of P(B-ala) (25%) and P(B-ala-DTE) (17%) at 800°C.

CONCLUSIONS

In conclusion, we have demonstrated that crosslinked but additionally curable soft benzoxazine films can be prepared by simultaneous photoinduced thiol–ene and COLBERT reactions using difunctional thiol and diallyl benzoxazine. As a consequence of the competing nature of the reactions, the obtained polybenzoxazine precursors still contained benzoxazine and allyl groups readily available for the subsequent curing. In the subsequent heat treatment, both the ring-opening polymerization of oxazine ring and the crosslinking reaction of thiol groups took place. The double-cured polymers by successive photochemical and thermal means exhibited comparable thermal stability to classical polybenzoxazines owing to the higher crosslinked density.

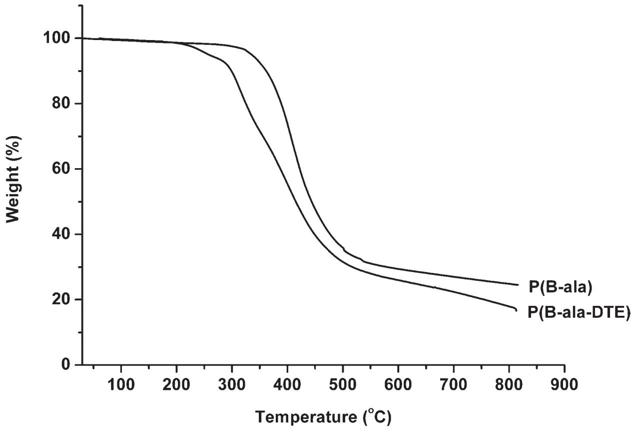


FIGURE 8 TGA thermograms of P(B-ala) and P(B-ala-DTE).

ACKNOWLEDGMENTS

The authors thank Istanbul Technical University for financial support. One of the authors (M. U. Kahveci) thanks TUBITAK (Turkish Scientific and Technological Council) for the financial support by means of a graduate program.

REFERENCES AND NOTES

1 Ghosh, N. N.; Kiskan, B.; Yagci, Y. *Prog. Polym. Sci.* **2007,** *32*, 1344–1391.

2 Andreu, R.; Reina, J. A.; Ronda, J. C. *J. Polym. Sci. A:Polym. Chem.* **2008,** *46*, 3353–3366.

3 Lu, Y.; Li, M.; Zhang, Y.; Hu, D.; Me, L.; Xu, W. *Thermochim. Acta* **2011,** *515*, 32–37.

4 Sudo, A.; Du, L.-C.; Hirayama, S.; Endo, T. *J. Polym. Sci. A Polym. Chem.* **2010,** *48*, 2777–2782.

5 Agag, T.; Arza, C. R.; Maurer, F. H. J.; Ishida, H. *Macromolecules* **2010,** *43*, 2748–2758.

6 Endo, T.; Sudo, A. *J. Polym. Sci. A Polym. Chem.* **2009,** *47*, 4847–4858.

7 Agag, T.; Takeichi, T. *Macromolecules* **2003,** *36*, 6010–6017.

8 Kim, H. J.; Brunovska, Z.; Ishida, H. *Polymer* **1999,** *40*, 6565–6573.

9 Brunovska, Z.; Liu, J. P.; Ishida, H. *Macromol. Chem. Phys.* **1999,** *200*, 1745–1752.

10 Pei, D. F.; Gu, Y.; Cai, X. X. *Acta Polym. Sin.* **1998, 595**–598.

11 Ning, X.; Ishida, H. *J. Polym. Sci. A Polym. Chem.* **1994,** *32*, 1121–1129.

12 Burke, W. J.; Glennie, E. L. M.; Weatherbee, C. *J. Org. Chem.* **1964,** *29*, 909–912.

13 Burke, W. J. *J. Am. Chem. Soc.* **1949,** *71*, 609–612.

14 Kiskan, B.; Koz, B.; Yagci, Y. *J. Polym. Sci. A Polym. Chem.* **2009,** *47*, 6955–6961.

15 Kiskan, B.; Yagci, Y. *J. Polym. Sci. A Polym. Chem.* **2007,** *45*, 1670–1676.

16 Ishida, H.; Rodriguez, Y. *Polymer* **1995,** *36*, 3151–3158.

17 Ning, X.; Ishida, H. *J. Polym. Sci. B Polym. Phys.* **1994,** *32*, 921–927.

18 Schreiber H. German Patent **1973,** 2,323,936.

19 Schreiber H. German Patent **1973,** 2,255,504.

20 Jubsilp, C.; Takeichi, T.; Rimdusit, S. In Handbook of Benzoxazine Resins; Hatsuo, I.; Tarek, A., Eds.; Elsevier: Amsterdam, **2011,** pp 157–174.

21 Baqar, M.; Agag, T.; Qutubuddin, S.; Ishida, H. In Handbook of Benzoxazine Resins; Hatsuo, I.; Tarek, A., Eds.; Elsevier: Amsterdam, **2011,** pp 193–210.

22 Takeichi, T.; Nakamura, K.; Agag, T.; Muto, H. *Des. Monomers. Polym.* **2004,** *7*, 727–740.

23 Chernykh, A.; Agag, T.; Ishida, H. *Macromolecules* **2009,** *42*, 5121–5127.

24 Kiskan, B.; Yagci, Y. *Polymer* **2008,** *49*, 2455–2460.

25 Agag, T.; Takeichi, T. *Macromolecules* **2001,** *34*, 7257–7263.

26 Kim, H. J.; Brunovska, Z.; Ishida, H. *J. Appl. Polym. Sci.* **1999,** *73*, 857–862.

27 Chaisuwan, T.; Ishida, H. *J. Appl. Polym. Sci.* **2006,** *101*, 548–558.

28 Nagai, A.; Kamei, Y.; Wang, X. S.; Omura, M.; Sudo, A.; Nishida, H.; Kawamoto, E.; Endo, T. *J. Polym. Sci. A Polym. Chem.* **2008,** *46*, 2316–2325.

29 Takeichi, T.; Kano, T.; Agag, T. *Polymer* **2005,** *46*, 12172–12180.

30 Chernykh, A.; Liu, J. P.; Ishida, H. *Polymer* **2006,** *47*, 7664–7669.

31 Koz, B.; Kiskan, B.; Yagci, Y. *Polym. Bull.* **2011,** *66*, 165–174.

32 Demir, K. D.; Kiskan, B.; Yagci, Y. *Macromolecules* **2011,** *44*, 1801–1807.

33 Tuzun, A.; Kiskan, B.; Alemdar, N.; Erciyes, A. T.; Yagci, Y. *J. Polym. Sci. A Polym. Chem.* **2010,** *48*, 4279–4284.

34 Yagci, Y.; Kiskan, B.; Ghosh, N. N. *J. Polym. Sci. A Polym. Chem.* **2009,** *47*, 5565–5576.

35 Kiskan, B.; Yagci, Y.; Ishida, H. *J. Polym. Sci. A Polym. Chem.* **2008,** *46*, 414–420.

36 Altinkok, C.; Kiskan, B.; Yagci, Y. *J. Polym. Sci. A Polym. Chem.* **2011,** *49*, 2445–2450.

37 Yeganeh, H.; Jangi, A. *Polym. Int.* **2010,** *59*, 1375–1383.

38 Aydogan, B.; Sureka, D.; Kiskan, B.; Yagci, Y. *J. Polym. Sci. A Polym. Chem.* **2010,** *48*, 5156–5162.

39 Kiskan B.; Aydogan, B.; Yagci, Y. *J. Polym. Sci. A Polym. Chem.* **2009,** *47*, 804–811.

40 Sawaryn, C.; Landfester, K.; Taden, A. *Macromolecules* **2011,** *44*, 5650–5658.

41 Sawaryn, C.; Landfester, K.; Taden, A. *Macromolecules* **2010,** *43*, 8933–8941.

42 Alhassan, S.; Schiraldi, D.; Qutubuddin, S.; Agag, T.; Ishida, H. In Handbook of Benzoxazine Resins; Hatsuo, I.; Tarek, A., Eds.; Elsevier: Amsterdam, **2011,** pp 309–318.

43 Kiskan, B.; Ghosh, N. N.; Yagci, Y. *Polym. Int.* **2011,** *60*, 167–177.

44 Kukut, M.; Kiskan, B.; Yagci, Y. *Des. Mon. Polym.* **2009,** *12*, 167–176.

45 Kiskan, B.; Demiray, G.; Yagci, Y. *J. Polym. Sci. A Polym. Chem.* **2008,** *46*, 3512–3518.

46 Gress, A.; Volkel, A.; Schlaad, H. *Macromolecules* **2007,** *40*, 7928–7933.

47 Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci. A Polym. Chem.* **2004,** *42*, 5301–5338.

48 Morgan, C. R.; Magnotta, F.; Ketley, A. D. *J. Polym. Sci. A Polym. Chem.* **1977,** *15*, 627–645.

49 Hoyle, C. E.; Bowman, C. N. *Angew. Chem. Int. Edit.* **2010,** *49*, 1540–1573.

50 Nurmi, L.; Lindqvist, J.; Randev, R.; Syrett, J.; Haddleton, D. M. *Chem. Commun.* **2009,** 2727–2729.

51 Connal, L. A.; Kinnane, C. R.; Zelikin, A. N.; Caruso, F. *Chem. Mater.* **2009,** *21*, 576–578.

52 ten Brummelhuis, N.; Diehl, C.; Schlaad, H. *Macromolecules* **2008,** *41*, 9946–9947.

53 Killops, K. L.; Campos, L. M.; Hawker, C. J. *J. Am. Chem. Soc.* **2008,** *130*, 5062–5064.

54 Campos, L. M.; Meinel, I.; Guino, R. G.; Schierhorn, M.; Gupta, N.; Stucky, G. D.; Hawker, C. J. *Adv. Mater.* **2008,** *20*, 3728–3733.

55 Campos, L. M.; Killops, K. L.; Sakai, R.; Paulusse, J. M. J.; Damiron, D.; Drockenmuller, E.; Messmore, B. W.; Hawker, C. *J. Macromol.* **2008,** *41*, 7063–7070.

56 Kiskan, B.; Weber, J. *ACS Macro Lett.* **2012,** *1*, 37–40.

57 Gorodisher, I.; DeVoe, R. J.; Webb, R. J. In Handbook of Benzoxazine Resins; Hatsuo, I.; Tarek, A., Eds.; Elsevier: Amsterdam, **2011, pp 211–234.**

58 Baqar, M.; Agag, T.; Ishida, H.; Qutubuddin, S. *J. Polym. Sci. A Polym. Chem.* **2012,** *50*, 2275–2285.

59 Tasdelen, M. A.; Kiskan, B.; Yagci, Y. *Macromol. Rapid. Commun.* **2006,** *27*, 1539–1544.