Novel Benzoxazine Resins as Photoinitiator Comprising Benzophenone and Coinitiator Amine for Photopolymerization

Jing Bai, Zixing Shi

School of Chemistry and Chemical Technology, State Key Laboratory of Metal Matrix Composite Materials,
Shanghai Jiao Tong University, 200240 Shanghai, P. R. China
Correspondence to: Z. Shi (E-mail: zxshi@sjtu.edu.cn)

ABSTRACT: A novel kind of benzoxazine precursors made of 4-dihydroxybenzophenone (DHBP), formaldehyde and N, N'-diethylethylenediamine was developed. The striking feature of this class of precursors is that it can be acted as an effective photo initiator for polymerization of acrylate monomers. In addition, this kind of precursors could be directly dispersed in water and its aqueous solution exhibited very sharp response to temperature, with a well-defined cloud point. The structure of this precursor has been confirmed by Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR) and Fourier Transform Infrared spectroscopy (FTIR) and its curing behaviors are investigated by Differential Scanning Calorimetry (DSC). The photopolymerization of acylate monomers, initiated by this precursor, was studied through photo-DSC. The results show that this precursor is dramatically more efficient than benzophenone (BP), in which the polymerization rate is almost four times as high as that of the BP system. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

As a new member in the family of thermosetting resins, benzoxazine resin has attracted great attention over the past decade because they provide highly comprehensive physical and chemical properties[1-6] compared with more traditional thermoset materials like epoxy or phenolic resins. Benzoxazine resin can be prepared simply from inexpensive and commercially available phenols, primary amines, and formaldehyde,[7-11] as shown in Scheme 1. Therefore, the chemistry of benzoxazine synthesis offers a wide range of molecular design flexibility by using appropriate starting materials and polybenzoxazine properties can be tailored. Depending on the molecular design, benzoxazines can form highly cross-linked thermoset materials (in Scheme 2) after polymerization[12,13] with excellent mechanical and thermal properties like high modulus, high strength, high glass temperature, and good flame retardance. In addition, benzoxazine resins exhibit low dimensional shrinkage, true self-polymerization and no volatile small molecule by products during curing reaction.

The group of Ishida et al.[3,5,10,14-16] has made great contribution on the development of benzoxazine-based thermosetting resins. They have designed several kinds of benzoxazine resins by using different kinds of phenols and amines. Based on its curing behaviors and mechanical properties,[17] the relationship between the structure of benzoxazine and physical properties has been established. All these research works provide useful information on designing new kind of benzoxazine resins[18-20] to improve their properties in further. Generally, all the previous research works on the benzoxazine resins are almost focused on its application as polymer matrix for the fabrication of advanced composites with high performance,[6] printed circuit boards and brake adhesives. However, there is little work on benzoxazine resins for the other application.

In this article, the application of benzoxazine resins is transferred to the photopolymerization[21,22] science and technology based on its great flexibility in structure design. To our knowledge, benzoxazine resins acted as photo-initiators have seldom been reported before. Only Yagci[23] groups have investigated the photo-initiated behaviors based on the intermolecular reaction between thioxanthone as photo-initiator and benzoxazine as hydrogen donors. Through introducing the photoinitiator chromophore (benzophenone,[24-28] hydrogen abstracting type) unit into the benzoxazine structure, we have successfully synthesized novel kind of benzoxazine resins, which could be acted as an efficient photo-initiator. In the structure of this kind of benzoxazine resin, both photo initiator-benzophenone[29,30] and coinitiator amine[31,32] are incorporated into the same benzoxazine chain
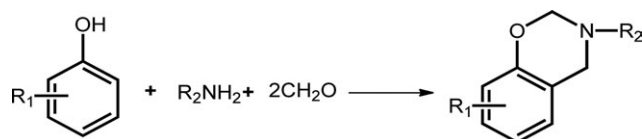
Scheme 1. Synthesis of benzoxazine monomers.

Scheme 2. Ring-opening polymerization reaction of the monomers.

and its mechanism of the photoinitiation is illustrated in Scheme 3. This kind of structure has obvious advantages such as intramolecular reactions responsible for the formation of more reactive species and protecting the active species by the benzoxazine chain.
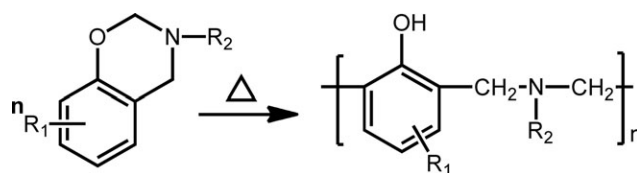
EXPERIMENTAL PART

Materials

1,4-Dioxane, ether, 4,4-dihydroxybenzophenone (DHBP), N, N'-diethylethylenediamine (Alfa AESAR), formaldehyde (Sinepharm Chemical Reagent), benzophenone (Sinepharm Chemical Reagent), 1,6-hexanediol diacrylate (HDDA) and trimethylopropane triacrylate (TMPTA) were obtained from Alfa Aesar. Phenoxy ethyleneglycol acrylate (AMP-10G) was from Shin-Nakamura Chemical. Polyethylene glycol methacrylate (PEGMA) and poly (ethylene glycol) diacrylate (PEGDA) were from Aldrich.

Synthesis of DE-DHBP-DE

Benzoxazine monomers were prepared from 4,4-dihydroxybenzophenone (DHBP), N, N'-diethylethylenediamine and paraformaldehyde as shown in Scheme 4. In a round-bottomed flask, 4,4-dihydroxybenzophenone (DHBP) (10 mmol), N, N'-diethylethylenediamine (20 mmol), and paraformaldehyde (40 mmol) were dissolved in 100 mL 1,4-dioxane and refluxed at 100°C for 6 h. The reaction mixture was evaporated in a rotary evaporator to remove 1, 4-dioxane. The resulting oily product was precipitated in ether to remove the remained solvent. Orange yellow oil was obtained.

Synthesis of Polybenzoxazine

As shown in Scheme 5, the thermally activated curing reaction occurs without the addition of catalysts or initiators.

The monomers are cured at elevated temperature. The monomers are placed into a self-made plate with aluminum foil then heated to cure from 80 to 220°C for increasing temperature 10°C per hour in oven.

MEASUREMENTS

^{1}H-NMR spectra were recorded on a Mercury Plus 400 MHz spectrometer with DMSO-d_6 as the solvent.

FTTR spectra were measured by Perkin-Elmer Spectrum 100 spectrophotometer. The samples were prepared with KBr plates.

UV-visible spectra were carried out in CHCl$_3$ solution by Shimadzu UV-2550 spectrophotometer. The concentration is 2.0×10^{-5} mol/l in terms of BP moiety.

Differential scanning calorimetry (DSC) analysis of DE-DHBP-DE was carried out with DSC 6200(Seiko Instrument) at a heating rate of 5°C/min from 50 to 300°C and nitrogen flow rate of 50 mL/min; 5 mg samples were sealed between aluminum hermetic pans and lids for all tests.

The optical transmittance of the polymer solutions were measured at 600 nm with a spectral-1.70 UV-visible spectrophotometer equipped with a thermo cell at a heating rate of 1°C/min.
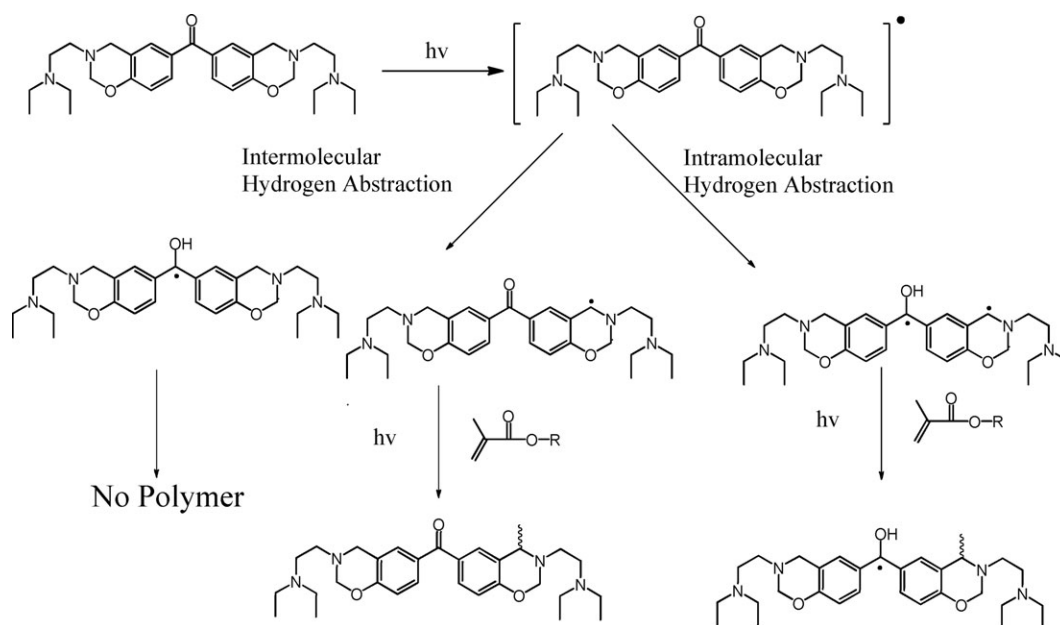

Scheme 3. the photoinitiation mechanism of DE-DHBP-DE.
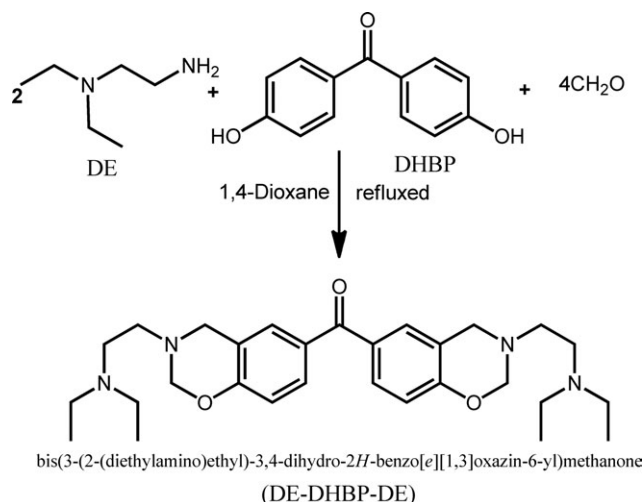
Scheme 4. Synthesis of the DE-DHBP-DE.

The temperature at 90% light transmittance of the solution was defined as the cloud point (CP). The DE-DHBP-DE aqueous solutions were prepared at 4 mg/mL concentration.

The photopolymerization of oil-soluble acylate monomers (AMP-10G, HDDA, and TMPTA) was monitoring surveyed by photo-DSC (DSC 6200, Seiko Instrument) with incident light 365 nm, whose intensity was 50 mW/cm^2. About 2.0 mg sample mixture was placed into an aluminum DSC pan. Heat flow versus time (DSC thermogram) curves were recorded in an isothermal mode at 25°C under the nitrogen flow of 50 mL/min. The reaction heat liberated in the polymerization was directly
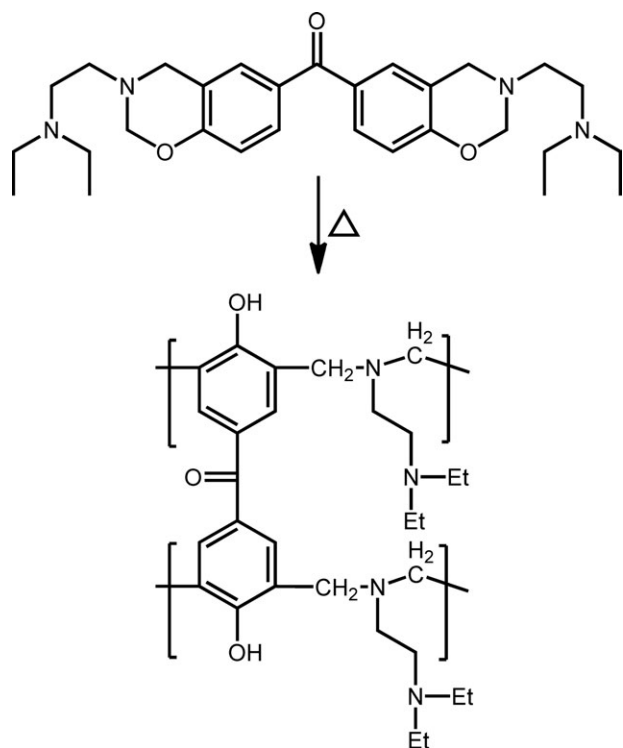
proportional to the number of vinyl groups related to the system. The conversion of the vinyl groups (C) or the extent of reaction could be determined by integrating the area under the exothermic peak, according to that for an acrylic double bond, when the reaction heat evolved at time t, t is the theoretical heat for complete conversation.[33]

RESULTS AND DISCUSSION

Synthesis and Characterization of the Benzoxazine Resins

Typically, bi-functional benzoxazine resins are synthesized by using phenol, formaldehyde, and amine (aliphatic or aromatic) as starting materials. As shown in Scheme 4, 4, 4-dihydroxybenzophenone (DHBP), formaldehyde and N, N'-diethylethylenediamine were selected to synthesize benzoxazine resins, where DHBP provides hydroxyl group as aromatic phenols molecules and N, N'-diethylethylenediamine offers amino group as amines molecules. The chemical structure of the benzoxazine was confirmed by both FTIR and ^{1}H-NMR spectroscopy. FTIR spectrum presented in Figure 1 shows characteristic absorptions of benzoxazine structure at 1226 cm^{-1} (asymmetric stretching of C—O—C), 1321 cm^{-1} (CH$_2$ wagging), and 921 and 1496 cm^{-1} (tri-substituted benzene ring). Absorption bands of 3443 cm^{-1} belonged to stretching of N—H and 1588 cm^{-1} to C=O. As shown in Figure 2, the ^{1}H-NMR spectrum also establishes the structure of DE-DHBP-DE. The characteristic protons of oxazine ring appeared at 4.8 and 4.0 ppm assigned to —Ar—CH$_2$—N— and —O—CH$_2$—N—, respectively. The aromatic protons of bisphenol appeared as multiplet in the region of 6.7–7 ppm. The protons of —CH$_2$— from N, N'-diethylethylenediamine could be found at about 1.0 ppm. The peaks at 3.5 ppm (1, 4-dioxaneresidues) can be assigned to solvent residues.

UV-vis spectra of BP and DE-DHBP-DE in chloroform were shown in Figure 3, BP possessed the characteristic absorption of (λ_{max} = 255 nm) and DE-DHBP-DE (λ_{max} = 302 nm),
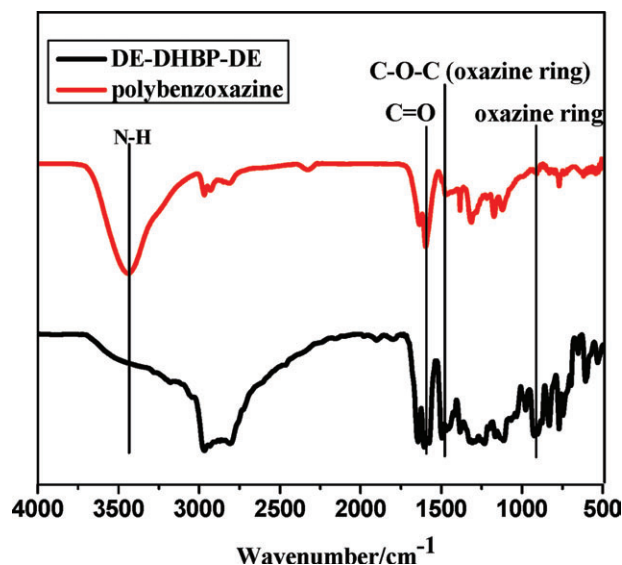

Scheme 5. Synthesis of the novel polybenzoxazine.

Figure 1. FTIR spectra of the DE-DHBP-DE and the polybenzoxazine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
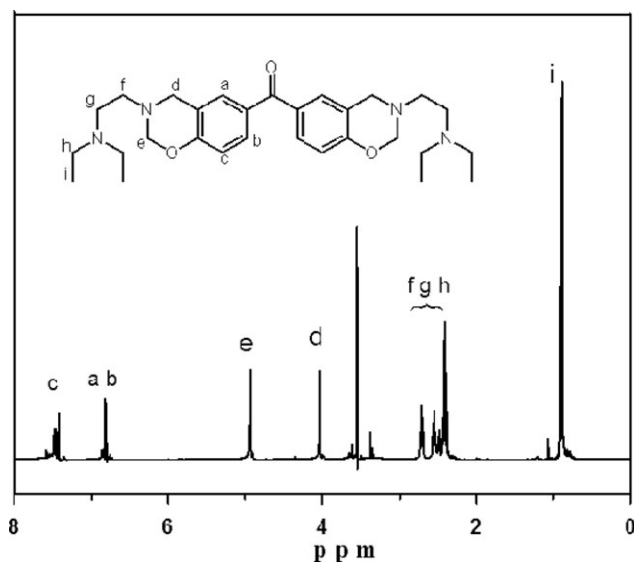
Figure 2. ^{1}H-NMR of DE-DHBP-DE.

Figure 4. DSC thermograms of DE-DHBP-DE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively. The UV-vis absorptions of the two different kinds of molecules were due to the carbonyl group on BP. It is well known that transitions in the region of 250–300 nm belong to the main $\pi-\pi^*$-type transitions of benzophenone.[34] Because of the appearance of the oxazine ring, DE-DHBP-DE exhibits a significantly red-shifted maximal absorption. These indicated that DE-DHBP-DE has been synthesized successfully, which is in good agreement with FTIR and H^1-NMR results.

The thermally activated polymerization behavior of oxazine ring was also studied by DSC. The nonisothermal polymerization thermogram is shown in Figure 4. An exothermic peak was observed due to the ring opening polymerization. The onset of the exotherm starts at 142°C and reaches the maximum at 173.7°C. FTIR also characterizes the change of structure after the curing reaction of benzoxazine resins. The absorbance bands
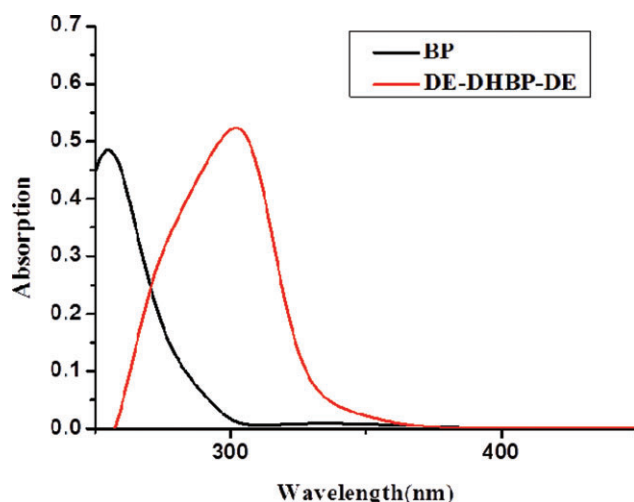
associated with the closed oxazine ring have been completely been consumed during the ring opening polymerization. These include the absorption contributed from the stretching modes of the cyclic aromatic ether at 1035 and 1228 cm^{-1}, as well as the characteristic band of the benzoxazine structure at 955 cm^{-1}. The DSC and FTIR results indicate that the polymerization of the monomer was effectively completed by the end of 213.3°C.

The solubility of DE-DHBP-DE in different solvents was tested here. There are the hydrophilic amino group and two hydrophobic ethyl groups in the structure of bi-functional benzoxazine resins. As shown in Figure 5, they can be readily dissolved in many selected different kinds of solvents such as H_2O, CH_2Cl_2, THF, and DMF and so on.

Previous studies have shown that the amphiphilic nature of these structures would endow the benzoxazine resins with a unique temperature-dependent dispersion behavior in water. It is observed that the benzoxazine resins can be dissolved in the water at room temperature with the concentration of 25 mg/mL. As shown in Figure 6 with the increase of temperature, hydrogen bonds between water molecules and hydrophilic amino parts of the DE-DHBP-DE are destroyed gradually and

Figure 3. UV–vis spectra of photoinitiator in (a) CHCl$_3$ (the concentration is 2.0 *10^{-5} mol/L in terms of BP). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
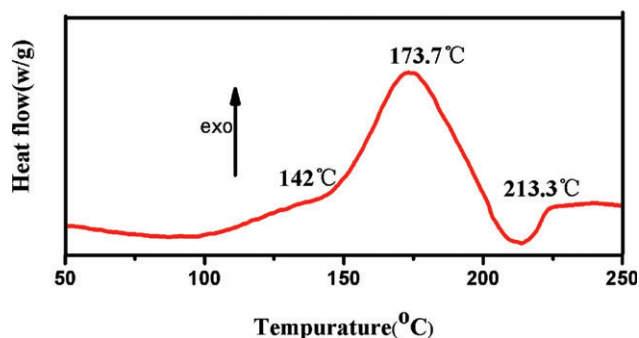

Figure 5. Photograph of dispersion of DE-DHBP-DE in different solvents from left to right: toluene, CH$_2$Cl$_2$, AcOEt, acetone, THF, EtOH, NMP, DMF, DMSO and H$_2$O. The concentration is 25 mg/ml in terms of DE-DHBP-DE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
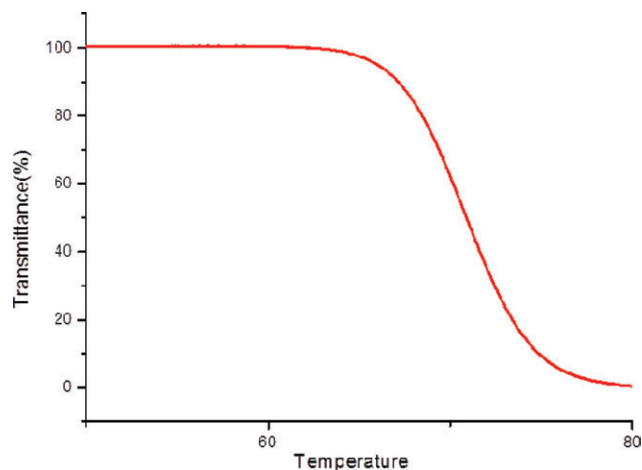
Figure 6. Temperature dependence of optical transmittance at 600 nm for DE-DHBP-DE aqueous solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. The thermally responsive aggregation behavior of DE-DHBP-DE, t<CP (left) and t>CP (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the benzoxazine resins become less hydrophilic, resulting in the aggregation of molecules and the turbidity of the aqueous solution. The thermally responsive aggregation behavior of DE-DHBP-DE was investigated by measuring the cloud points. A typical transmittance vs. temperature curve for DE-DHBP-DE solution is shown in Figure 6. The transparent DE-DHBP-DE solution at room temperature suddenly became turbid when the temperature was above the CP, as shown in Figure 7. The turbid solution should result from the aggregation of DE-DHBP-DE. The DE-DHBP-DE solution exhibited a sharp response to temperature and the range of transition temperature was less than 1.5°C. It should be noted that the thermally responsive aggregation of DE-DHBP-DE is completely reversible. The optical transmittance of the solution was also measured at 600 nm with UV-visible spectrophotometer equipped with a thermo cell at a heating rate of 1°C/min. The transmittance of the DE-DHBP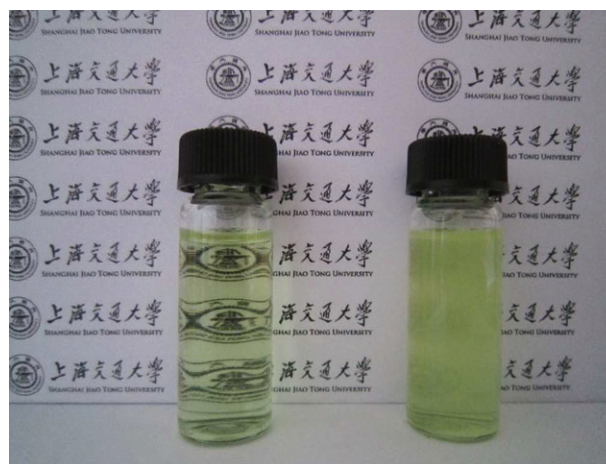-DE solution changed with increasing temperature and the temperature at 90% light transmittance of the solution was defined as the cloud point (CP). It can be seen in Figure 6 that CP of DE-DHBP-DE solution was 67.2°C.

Photopolymerization of Acylate Monomers

As shown in Scheme 6, three commercial acylate monomers with different functionalities were selected to investigate the photoinitiation behavior of the obtained DE-DHBP-DE. BP was also under investigation as photointiator while triethylamine as coinitiator for comparison.

Among these monomers, AMP-10G is a monofunctional monomer with low viscosity and can release high heat flow during polymerization. HDDA is the bifunctional monomers used, while TMPTA is trifunctional. It is known that the double bond content of TMPTA is much higher than the bifunctional monomers which results in high viscosity and crosslinking densities in polymerization. Therefore, the mobility of the radicals for
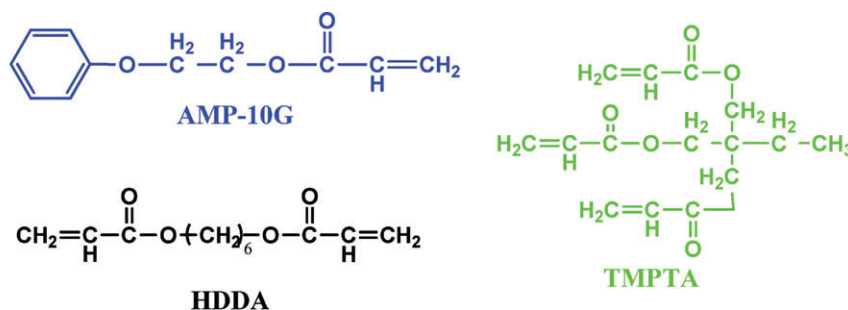
Monomers	AMP-10G	HDDA	TMPTA
Molecular weight	192g/mol	776 g/mol	296g/mol
ΔH_o^{theor} (kJ/mol)	447.9 J/g	221.6J/g	871.6J/g

Scheme 6. Properties and structures of acrylate monomers with different functionality (AMP-10G, HDDA, TMPTA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
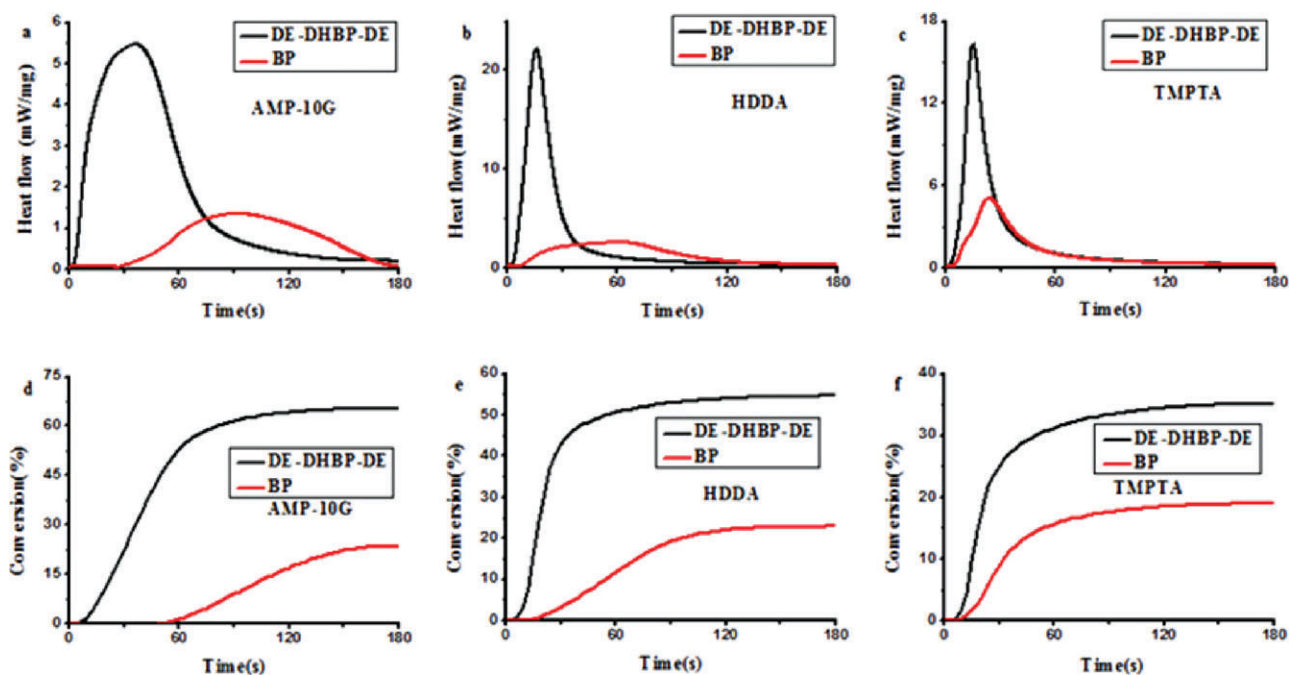
Figure 8. Photo-DSC profile for polymerization of AMP-10G (a), HDDA (b) and TMPTA (c); conversion versus time curves for polymerization of AMP-10G (d), HDDA (e) and TMPTA (f) initiated by BP and DE-DHBP-DE cured at 25°C by UV light with intensity of 50 mW/cm^2 (The photoinitiator concentration is 0.01M in terms of BP moiety). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

these three monomers is relatively different. The conversions are expected to be lower for TMPTA due to high viscosity and crosslinking densities in the initial polymerization stage.

The photo-DSC profiles of the photopolymerization of AMP-10G, HDDA, and TMPTA initiated by BP and DE-DHBP-DE were presented in Figure 8. Figure 8 shows that the time to reach maximal heat flow (t_{max}) is dependent on the photoinitiator used. The data for t_{max} and final conversion of acylate monomers is shown in Table I. For the monofunctional monomer AMP-10G, the time to reach maximal heat flow (t_{max}) is 36.1s and the maximal heat flow (H_{max}) is 5.47 mW/mg when DE-DHBP-DE is used as photo-initiator. However, T_{max} is prolonged to 91.5 s (2.5 times increase) and H_{max} is decreased to 1.35 mW/mg (three times reduction) as BP is used as photo-initiator. As a result, the final conversion for AMP-10G with DE-DHBP-DE as photo-initiator is approaching 65.42% and the final conversion is reduced greatly to 23.44% for AMP-10G photo initiated by BP. For the other two monomers (HDDA and TMPTA), similar results (t_{max}, H_{max} and final conversion) are also obtained based on the comparison of two the polymerization behavior photo initiated by DE-DHBP-DE and BP.

Therefore, DE-DHBP-DE showed more efficient photo initiative behavior than BP in the photo-polymerization of these monomers based on the results obtained from photo-DSC.

Two factors may be responsible for these differences between two photo-initiators. For DE-DHBP-DE, the initiator units (benzophone) and coinitiator amine (from PBZ and DE) are incorporated into the same molecular. The photolysis of DE-DHBP-DE leads to the formation of a radical produced from a carbonyl compound (ketyl-type radical) and another radical derived from coinitiator amine. The photo-polymerization of vinyl monomers is usually initiated by the amine radicals and not by the ketyl radicals due to its unreactive toward vinyl monomers because of steric hindrance and the delocalization of an unpaired electron. So the number of active amine radicals determines the photopolymerization rate. The larger local concentration of coinitiator amine of DE-DHBP-DE makes the energy transition along the chain between the excited triplet state of amine more rapid, which results in a larger amount of amine radicals which facilitate the fast photopolymerization rate. For BP system, benzophenone and coinitiator amine have to collide each other to attain efficient electron and proton

Table I. Data of Photopolymerization of Three Oil-Soluble Acylate Monomers

Acylate monomer	AMP-10G		HDDA		TMPTA	
Initiator	BP	DE-DHBP-DE	BP	DE-DHBP-DE	BP	DE-DHBP-DE
t_{max} (s)	91.5	36.1	61.2	16.2	24.3	15
H_{max} (mW/mg)	1.35	5.47	2.60	22.22	5.10	16.31
Final conversion (%)	23	65	23	54	19	35

transfer between two different molecules, which slow down the photopolymerization rate. The other factor is that both intramolecular and intermolecular hydrogen abstraction exits in DE-DHBP-DE, while only intermolecular hydrogen abstraction in the BP.

DE-DHBP-DE can disperse in the three kinds of acylate monomers well, radicals are easy to approach acylate monomers and initiate them to polymerize.

CONCLUSIONS

We have obtained a new kind of benzoxazine resin, synthesized from the mixture of 4,4-dihydroxybenzophenone (DHBP), N, N'-diethylethylenediamine, and paraformaldehyde. The structure of this resin has been confirmed by FTIR, and ^{1}H-NMR analyses. Its curing behavior was also investigated by DSC with the maximum curing temperature around 173°C. Because both the benzophenone and tertiary amines units are incorporated into in the chain of benzoxazine resin, DE-DHBP-DE was found as effective photo-initiator to initiate polymerization of acrylic monomers. It is not only soluble in water and other selected solvents but also possesses good compatibility with multiple functional acrylate (TMPTA). Such characters would make DE-DHBP-DE find wide potential application in the field of UV-curing.

REFERENCES

1. Riess, G.; Schwob, J. M.; Guth, M.; Roche, M.; Laude, B. *Polym. Prep. (Am. Chem. Soc. Div. Polym. Chem.)* **1984,** 41.

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

3. Ishida, H.; Low, H. Y. *Macromolecules* **1997,** *30*, 1099.

4. Ning, X.; Ishida, H. *J. Polym. Sci. Part A: Polym. Chem.* **1994,** *32*, 1121.

5. Ishida, H.; Allen, D. J. *J. Polym. Sci. Part B: Polym. Phys.* **1996,** *34*, 1019.

6. Wang, C.-F.; Su, Y.-C.; Kuo, S.-W.; Huang, C.-F.; Sheen, Y.-C.; Chang, F.-C. *Angew. Chem. Int. Ed.* **2006,** *45*, 2248.

7. Yagci, Y.; Kiskan, B.; Koz, B. *J. Polym. Sci. Pol. Chem.* **2009,** *47*, 6955.

8. Liu, Y.-L.; Yu, J.-M.; Chou, C.-I. *J. Polym. Sci. Part A: Polym. Chem.* **2004,** *42*, 5954.

9. Agag, T.; Takeichi, T. *J. Polym. Sci. Part A: Polym. Chem.* **2006,** *44*, 1424.

10. Ishida, H.; Ohba, S. *Polymer* **2005,** *46*, 5588.

11. Andreu, R.; Espinosa, M. A.; Galià, M.; Cádiz, V.; Ronda, J. C.; Reina, J. A. *J. Polym. Sci. Part A: Polym. Chem.* **2006,** *44*, 1529.

12. Sudo, A.; Kudoh, R.; Nakayama, H.; Arima, K.; Endo, T. *Macromolecules* **2008,** *41*, 9030.

13. Chutayothin, P.; Ishida, H. *Macromolecules* **2010,** *43*, 4562.

14. Ishida, H.; Low, H. Y. *J. Appl. Polym. Sci.* **1998,** *69*, 2559.

15. Ishida, H.; McCoy, M.; Bando, T.; Hatta, H. *Polym. Compos.* **2010,** *31*, 1995.

16. Ishida, H.; Kisanuki, A.; Endo, K. *Polym. J.* **2009,** *41*, 110.

17. Takeichi, T.; Kano, T.; Agag, T. *Polymer* **2005,** *46*, 12172.

18. Velez-Herrera, P.; Doyama, K.; Abe, H.; Ishida, H. *Macromolecules* **2008,** *41*, 9704.

19. Chernykh, A.; Agag, T.; Ishida, H. *Polymer* **2009,** *50*, 382.

20. Wang, L.; Gong, W.; Zheng, S. *Polym. Int.* **2009,** *58*, 124.

21. Norman S. A. *J. Photochem. Photobiol. A: Chem.* **1996,** *100*, 101.

22. Fouassier, J. P.; Morlet-Savary, F.; Yamashita, K.; Imahashi, S. *J. Appl. Polym. Sci.* **1996,** *62*, 1877.

23. Tunc, D.; Yagci, Y. *Polym. Chem.-Uk* **2011,** *2*, 2557.

24. George, B.; Dhamodharan, R. *Polym. Int.* **2001,** *50*, 897.

25. Wrzyszczynski, A.; Bartoszewicz, J.; Hug, G. L.; Marciniak, B.; Paczkowski, J. *J. Photochem. Photobiol. A: Chem.* **2003,** *155*, 253.

26. Tasis, D. A.; Siskos, M. G.; Zarkadis, A. K. *Macromol. Chem. Phys.* **1998,** *199*, 1981.

27. Costela, A.; Dabrio, J.; Figuera, J. M.; García-Moreno, I.; Gsponer, H.; Sastre, R. *J. Photochem. Photobiol. A: Chem.* **1995,** *92*, 213.

28. Allen, N. S.; Salleh, N. G.; Edge, M.; Corrales, T.; Shah, M.; Weddell, I.; Catalina, F.; Green, A. *J. Photochem. Photobiol. A: Chem.* **1996,** *99*, 191.

29. Allen, N. S.; Corrales, T.; Edge, M.; Catalina, F.; Blanco-Pina, M.; Green, A. *Polymer* **1998,** *39*, 903.

30. Wang, H.; Wei, J.; Jiang, X.; Yin, J. *J. Polym. Sci. Part A: Polym. Chem.* **2006,** *44*, 3738.

31. Gacal, B.; Akat, H.; Balta, D. K.; Arsu, N.; Yagci, Y. *Macromolecules* **2008,** *41*, 2401.

32. Yates, S. F.; Schuster, G. B. *J. Organic Chem.* **1984,** *49*, 3349.

33. Andrzejewska, E.; Andrzejewski, M. *J. Polym. Sci. Part A: Polym. Chem.* **1998,** *36*, 665.

34. Liska, R. *J. Polym. Sci. Part A: Polym. Chem.* **2002,** *40*, 1504.