# Synthesis and Photopolymerization Characterization of a Novel Difunctional Photoinitiator

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**ABSTRACT:** A novel difunctional photoinitiator HBP-TDI-HBP based on 4-hydroxybenzophenone (HBP) and toluene-2,4-diisocyanate (TDI) was synthesized and characterized by $^1$H NMR and UV–Vis absorption spectroscopy. The kinetics of photopolymerization was studied by real-time infrared spectroscopy. It showed that HBP-TDI-HBP was a more effective photoinitiator than benzophenone. When this photointiator and amine were used to efficiently initiate polymerization of acrylates and methacrylates, both rate of polymerization and final conversion increased with increase of HBP-TDI-HBP concentration, light intensity, and amine concentration. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 665–670, 2008

**Key words:** initiators; UV–Vis spectroscopy; FTIR; kinetics; photopolymerization

## INTRODUCTION

Photopolymerization is a well-accepted technology that finds industrial application in coatings on various materials, adhesives, printing inks, photoresists, and biomaterials.[1,2] In photopolymerization, a typical formulation consists of a vinyl monomer and a photoinitiator. The most commonly used monomers are acrylates, which have rapid cure speed and low viscosity. Methacrylates are less reactive than acrylates and are used in special applications.[3] This technology is based on the use of photoinitiator systems suited to absorb a light radiation of the appropriate wavelength and to produce primary radical species to convert a multifunctional monomer into a cross-linked network. All photoinitiators for free-radical polymerization proceed by either a cleavage mechanism (Type I photoinitiator) or a hydrogen abstraction mechanism (Type II photoinitiator).[1] Typical hydrogen abstraction photoinitiators include benzophenone (BP), thioxanthones, benzil, quinones, and organic dyes, while amines, alcohols, ethers, and thiols are used as hydrogen donors.[4]

Benzophenone has been shown to initiate free-radical polymerization of (meth)acrylic systems effectively in the presence of amines. The photoreduction of triplet-state benzophenone by tertiary amines has been extensively investigated[5–7] and found to result in the formation of the radical anion of benzophenone followed by a proton transfer from the radical cation of the amine to form the semipinacol radical and a radical derived from the amine (R-aminoalkyl radical). The amine-derived radical initiates polymerization while the ketyl radical is inefficient in initiating free-radical polymerization,[8,9] serving as a terminating species only.

Benzophenone is by far one of the most widely used photoinitiators for photopolymerization as it has low yellowing, good surface curing, and solubility. But benzophenone is also known for its relatively strong odor and exceptional ability to migrate and be extracted from cured products.[10] It is clear that there is a need for a low odor benzophenone derivative with good reactivity, particularly good surface curing, good solubility, and a limited tendency to migrate and be extracted and which does not yellow on cure and so can be used in UV formulations. The development of difunctional photoinitiators is possible to reduce the risk of migration because of the rather high molecular weight. The cure speed of benzophenone derivatives can be related to some degree to their UV absorption spectra.[11] 4-Hydroxybenzophenone is highly efficient and has a strong absorption band in the mid-UVB region. Despite being widely used in photopolymerization, it cannot be used as a benzophenone alternative in UV formulations as it has insufficient solubility and excessive yellowing on cure.[10]

In this research, a novel hydrogen abstraction difunctional photoinitiator was synthesized based on 4-hydroxybenzophenone and toluene-2,4-diisocyanate, and the kinetics of photopolymerization of the photoinitiator in different conditions was studied by real-time infrared spectroscopy. The results indicated that HBP-TDI-HBP is an effective initiator.

## EXPERIMENTAL

### Materials

4-Hydroxybenzophenone (HBP) was obtained from Runtec Co. (Jintan, Jiangsu, China) and used as received. Toluene-2,4-diisocyanate (2,4-TDI) was purchased from Shanghai Chemical Reagent Co. (Shanghai, China). Dibutyltin dilaurate (DBTDL) was purchased from Beijing Chemical Co. (Beijing, China). All the monomers were obtained from Sartomer Company (Warrington, PA). Triethanolamine (TEOHA), $N$-methyldiethanolamine (MDEA), $N,N$-dimethyl ethanolamine (DMEA), triethylamine (TEA), 2-(dimethylamino) ethyl methacrylate (DMEM), $N,N$-dimethylaniline (DMA), ethyl 4-dimethylaminobenzoate (EDAB), 2-ethylhexyl 4-dimethylaminobenzoate (ODAB), and hydroxyethyl methacrylate (HEMA) were purchased from Sinopharm Group Chemical Reagent Co. (Beijing, China). Ethyl acetate and acetonitrile were dried and purified according to standard laboratory methods. All other reagents were of analytical grade and used as received unless otherwise specified.

### Instrumentation

The $^1$H NMR spectra were recorded on a Bruker AV600 unity spectrometer operated at 600 MHz using DMSO-d$_6$ as deuterated solvent.

FTIR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA).

UV–Vis Absorption spectra were recorded in acetonitrile solution on a Hitachi U-3010 UV–Vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). A cell path length of 1 cm was employed.

UV spot source (EFOS Lite, 50 W miniature arc lamp, with 5-mm crystal optical fiber, Canada) was employed.

Light intensity was recorded by the UV light radiometer (Photoelectric Instrument Factory, Beijing Normal University, Beijing, China).

### Synthesis of HBP-TDI-HBP

2,4-TDI (5.2 g, 30 mmol), 1 mL of DBTDL, and 150 mL of ethyl acetate were added into a 500-mL

four-necked round bottom flask fitted with a condenser, a overhead stirring, a thermometer, and an addition funnel containing HBP (11.9 g, 60 mmol) and 120 mL of ethyl acetate mixture. The solution was stirred and heated to 50°C, and then the HBP solution was dropped to the flask. Once all the HBP solution was added, the temperature was raised to 60°C and maintained for about 4 h. Infrared spectroscopy was used to monitor disappearance of —NCO peak at about 2250 cm$^{-1}$. The absence of this peak indicated a level of residual —NCO below the detection limits of the spectrophotometer, and the reaction was complete.[3] The organic layer was washed twice with 10% aqueous NaOH solution and deionized water, respectively, and then dried overnight by sodium sulfate. The solvent was removed by vacuum distillation. A white powder product was obtained. Yield: 12.3 g, 71.9%.

### Real-time infrared spectroscopy

The initiation efficiency of the novel difunctional photoinitiator was studied by real-time infrared spectroscopy (RTIR), which had become an important method for obtaining kinetics data. The basic principle of RTIR spectroscopy consists in exposing the sample simultaneously to the UV light, which induces the polymerization, and to the infrared beam which serves to measure the monomer concentration at any given time. The resulting decrease in the IR absorption band characteristic of that monomer is monitored continuously on a transient memory recorder. Since the absorbance increment ($A_o - A_t$) is always proportional to the amount of monomer that has polymerized after a given exposure, and thus to the degree of conversion, the recorded RTIR trace actually corresponds to a conversion versus time curve.[12,13] Conversion data were obtained by monitoring the decay of the (meth)acrylate double bond =C—H peak at about 6165 cm$^{-1}$. Upon irradiation, the decrease of the =C—H absorption peak area from 6101.84 to 6247.95 cm$^{-1}$ accurately reflects the extent of the polymerization, since the change of the absorption peak area was directly proportional to the number of the (meth)acrylate that had polymerized. After baseline correction, conversion of the functional groups could be calculated by measuring the peak area at each time of the reaction and determined as following:

$$DC(\%) = (A_0 - A_t)/A_0 \times 100 \qquad (1)$$

where DC is the degree of (meth)acrylate double bond conversion at $t$ time, $A_0$ is the initial peak area before irradiation and $A_t$ is the peak area of the double bonds at $t$ time.
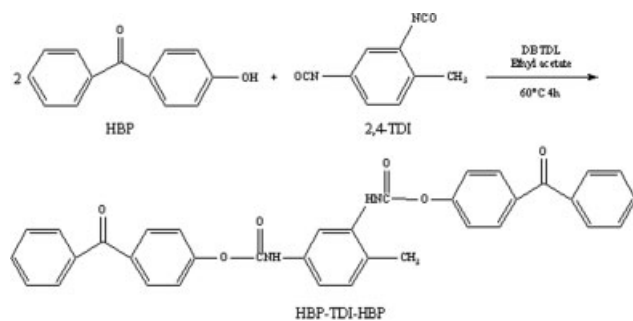
**Scheme 1** The synthesis process of HBP-TDI-HBP.

All samples were photocured in 1.6-mm thick plastic molds with an 11-mm central diameter. The molds were clamped between two glass slides with spring-loaded binder clips.[14] The samples were irradiated with a UV spot source. Each spectrum was signal of 1 scan with the resolution of 4 cm$^{-1}$ at room temperature. For each sample, the series RTIR runs were repeated three times.

## RESULTS AND DISCUSSION

### Synthesis of HBP-TDI-HBP

The HBP-TDI-HBP was synthesized according to Scheme 1. The reaction was carried out by controlling the stoichiometry of the reagents in ethyl acetate solution at 60°C with DBTDL as the effective catalyst. All residual trace of isocyanate must be removed, because isocyanate is highly reactive and is a potential health hazard. To eliminate the last residual traces of isocyanate, excess HBP could be added. The disappearance of —NCO peak at about 2250 cm$^{-1}$ indicates that the reaction is complete.[3] After the reaction, the excess HBP can be removed by washing the product with 10% aqueous NaOH solution. The structure of the photoinitiator was confirmed by $^1$H NMR.

$^1$H NMR (DMSO-d$_6$): δ: 2.23 (CH$_3$); 7.81 (NH); 7.42, 7.53, 7.58, 7.62, 7.67, 7.76 (CH, Ar).

### UV–Vis absorption of HBP-TDI-HBP and benzophenone

UV–Vis absorption spectra of HBP-TDI-HBP and BP in acetonitrile were showed in Figure 1. Values for the wavelength of maximum absorption ($\lambda_{max}$) and the molar extinction coefficient at $\lambda_{max}$ ($\epsilon_{max}$) are summarized in Table I. Compared with BP, HBP-TDI-HBP possesses a maximal absorption of 282 nm, which exhibits a significant red-shift of the π–π* type (32 nm). It may be ascribed to the electron effect via phenoxy group. Therefore, the n–π* transition was overlaid by the shoulder of the more intense π–π* transition at higher concentrations. This red-shifted
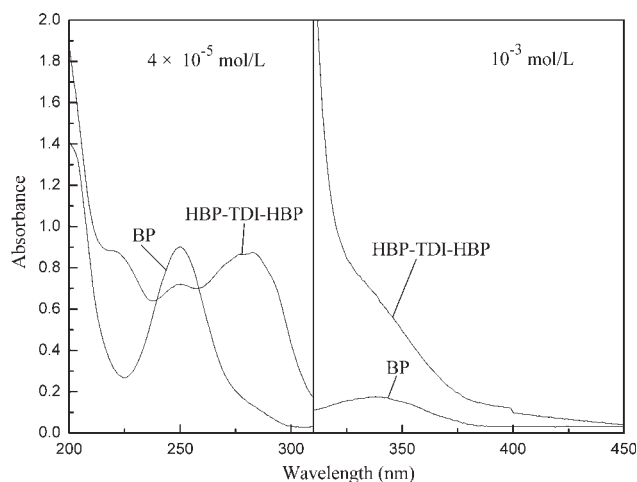


**Figure 1** UV–Vis absorption spectra of HBP-TDI-HBP and BP in acetonitrile solution (concentration = $4 \times 10^{-5}$ mol L$^{-1}$).

maximal absorption makes HBP-TDI-HBP attractive as photoinitiator, because it could absorb longer wavelength light effectively than BP at used UV source, thus more free radical could produce and the cure speed of the novel difunctional photoinitiator would be higher than BP in the same condition. It is clearly shown in Figure 2.

### Kinetic study of photopolymerization initiated by HBP-TDI-HBP

The kinetics of photopolymerization of the photoinitiator in different conditions was studied by real-time infrared spectroscopy.

The conversion vs. time plots for the polymerization of TPGDA induced by HBP-TDI-HBP and BP systems were shown in Figure 2. At the beginning, the polymerization rate of BP was slightly faster than HBP-TDI-HBP, this was because the chromophore content per gram of BP was higher than HBP-TDI-HBP. But the final conversion and latter rate of polymerization of HBP-TDI-HBP were higher than BP, which meant HBP-TDI-HBP was a more effective photoinitiator compared with BP.

Figure 3 showed the conversion vs. time plots for different monomers. Tripropylene glycol diacrylate (TPGDA), 2(2-ethoxyethoxy) ethylacrylate (EOEOEA), trimethylolpropane triacrylate (TMPTA), dipentaerythritol pentaacrylate (DPEPA) are acrylates, and

**TABLE I**
**UV Spectroscopy of Photoinitiators (PI) in Acetonitrile**

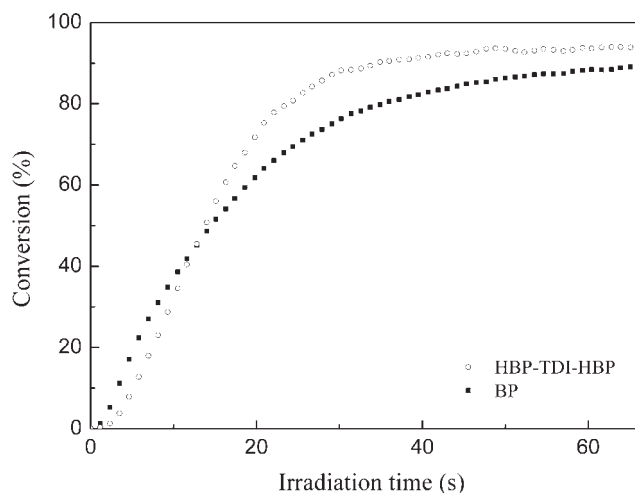| PI | $\lambda_{max}$ (nm) | $\epsilon_{max}$ (L mol$^{-1}$ cm$^{-1}$) |
|---|---|---|
| HBP-TDI-HBP | 282 | 21,706 |
| BP | 250 | 22,547 |
|  | 338 | 136 |

**Figure 2** Conversion vs. irradiation time plot of TPGDA initiated by 1.0 wt % HBP-TDI-HBP and 1.0 wt % BP in the presence of 1.0 wt % EDAB ($I$ = 55 mW/cm$^2$).



**Figure 3** Double-bond conversation of different monomers ([HBP-TDI-HBP] = 1.0 wt %, [EDAB] = 1.0 wt %, $I$ = 55 mW/cm$^2$).

hydroxyethyl methacrylate (HEMA), tetraethylene glycol dimethacrylate (TTEGDMA), trimethylolpropane trimethacrylate (TMPTMA) are methacrylates. The results indicated that the rate of polymerization for acrylates was significantly higher than that of methacrylates, and the functionality of acrylates had a strong influence on both the polymerization rate and the residual monomer content. With increasing acrylate functionality, the content of residual unsaturations rose. As the functionality increased, the viscosity of the resin increased, with the resulting gel effect and the higher crosslink density set a limit to the extent of conversion.[15] It was the same to the methacrylates. As to HEMA, the conversion was higher than that of nonhydroxylated monomers, because the hydrogen bonding could lead to preorganization of the molecules or to decrease in the rate constant of termination, causing an increase in final conversion.[16]

TPGDA could be chosen as the monomer to the further studies of the novel difunctional photoinitiator because it had the higher final conversion compared with others. The plots of conversion vs. irradiation time of TPGDA incorporating different HBP-TDI-HBP concentrations in the presence of 1.0 wt % of EDAB as the initiating system were shown in Figure 4. The polymerization rate and final conversion increased with increase of HBP-TDI-HBP concentration. Because the higher the HBP-TDI-HBP concentration, the more the free radical could produce during irradiation, which caused the higher rate of polymerization. On the other hand, this might be due to the free-volume effect, which was caused by the volume shrinkage.[17] The volume shrinkage occurred at very fast rate of polymerization and resulted in an increase in free-volume formation, which increased the mobility of the residual double bond and led to a higher final conversion.
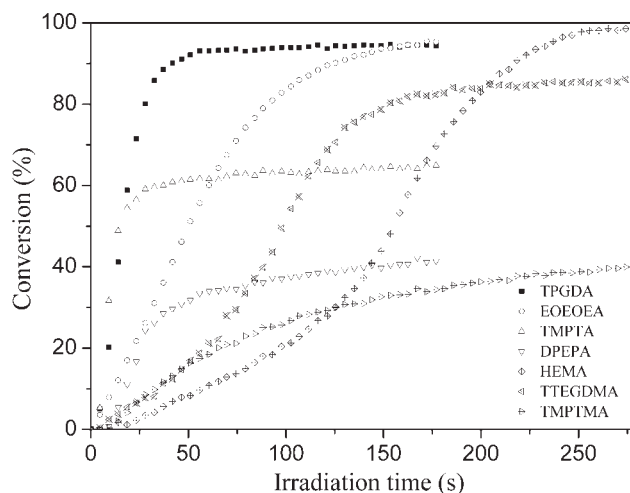
Figure 5 showed the conversion vs. time plots of TPGDA initiated by 1.0 wt % HBP-TDI-HBP in the presence of 1.0 wt % EDAB at different light intensity. It had the similar effect on the polymerization to the photoinitiator concentration. The polymerization rate and final conversion increased with increase in light intensity. This was because the higher light intensity could yield more radicals, which led to the increase in polymerization rate and final conversion. At the same time, the higher number of radicals yielded by the increase of light intensity could overcome oxygen inhibition more efficiently, resulting in the shortening of the induction period.

The plots of conversion vs. irradiation time of TPGDA incorporating HBP-TDI-HBP in the presence of five aliphatic tertiary amines as the initiating system were recorded in Figure 6(a). The HBP-TDI-
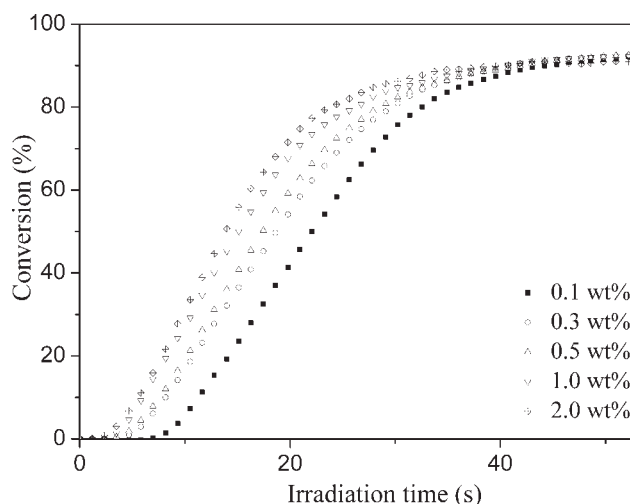


**Figure 4** Effect of HBP-TDI-HBP concentration on the polymerization of TPGDA ([EDAB] = 1.0 wt %).
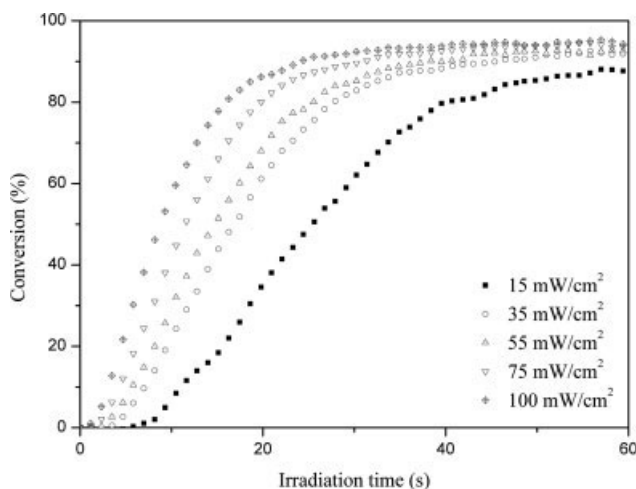
**Figure 5** Effect of light intensity on polymerization of TPGDA ([HBP-TDI-HBP] = 1.0 wt %, [EDAB] = 1.0 wt %).

HBP/TEOHA combination in TPGDA exhibited the highest polymerization rates. The hydroxy-substituted amines were more efficient than the corresponding alkyl derivative (TEA), because alcohols can also be used as hydrogen donors; the efficiency of amines would be enhanced as the number of substituted hydroxy groups increased on them. On the other hand, the radical yield was higher for the TEOHA; this was the amine that behaved as a better coinitiator.[18] As to the three aromatic tertiary amines [Fig. 6(b)], DMA was the most efficient coinitiator. The initiation efficiency of EDAB and ODAB was lower than DMA, it may be due to the ester group attached directly to the phenyl ring. The larger radical had more steric hindrance and slower diffusion rate. So ODAB had the lower activity. On the other hand, the lower photopolymerization rate of ODAB owed to its higher molecular weight, which meant less weight percentage of radicals generated when its concentration was the same to that of EDAB.

Figure 7 showed the conversion vs. time plots of TPGDA initiated by 0.5 wt % HBP-TDI-HBP with different EDAB concentrations. The polymerization rate and final conversion increased with increase in EDAB concentration. This was because high coinitiator concentration yielded more radicals by the light irradiation, thus led to the large polymerization rate and final conversion. The polymerization rate of EDAB equal to 2.0 wt % was only slightly higher than that of EDAB equal to 1.0 wt %, which meant 1.0 wt % of EDAB was enough for inducing the polymerization. As shown in Figure 7, the induction period was shortened with the increase of the EDAB concentration. It is because photopolymerization is carried out in the presence of air, and the initiating radicals are scavenged by oxygen molecules dissolved in the formulation. As the oxygen is con-

sumed, the monomer molecules become capable of successfully reacting with the initiator radicals, thus initiating polymerization. Thus, increasing the EDAB concentration could produce rapidly large amounts of free radicals to overcome oxygen inhibition.[12]

## CONCLUSIONS

A novel hydrogen abstraction photoinitiator HBP-TDI-HBP based on 4-hydroxybenzophenone and toluene-2,4-diisocyanate was synthesized and characterized by $^1$H NMR and UV–Vis absorption spectroscopy. The kinetics of photopolymerization of the photoinitiator was studied by real-time infrared spectroscopy. It showed that HBP-TDI-HBP was a more effective photoinitiator compared to BP. The rate of polymerization of acrylates was significantly higher than that of methacrylates at the same polymerization situation, and the functionality of acryl-
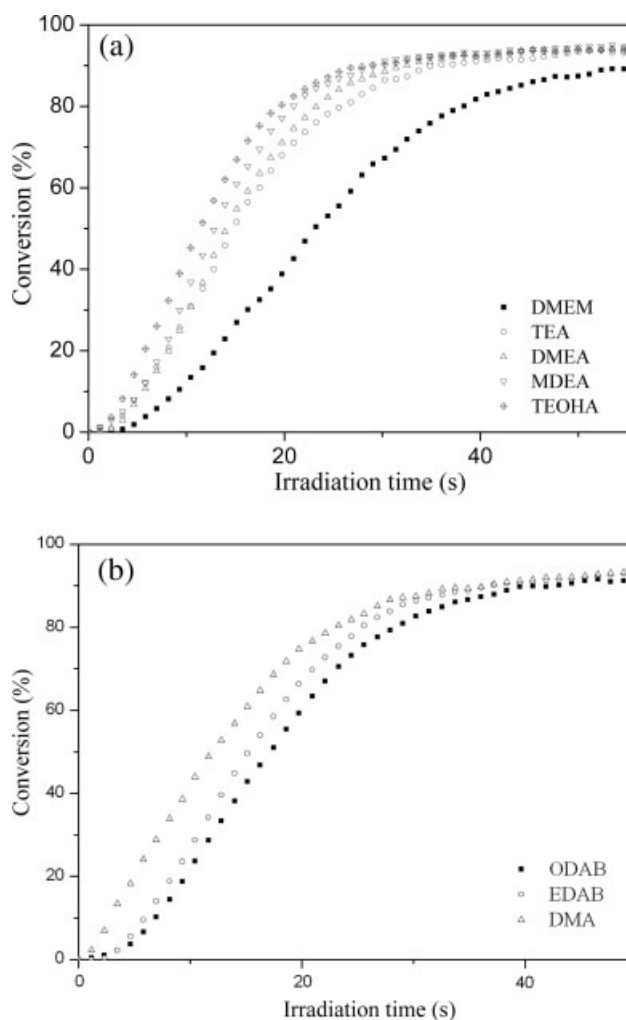


**Figure 6** Effect of amine structure on the photopolymerization of TPGDA: (a) different aliphatic tertiary amines, and (b) different aromatic tertiary amines ([HBP-TDI-HBP] = 1.0 wt %, [amine] = 1.0 wt %, $I$ = 55 mW/cm$^2$).
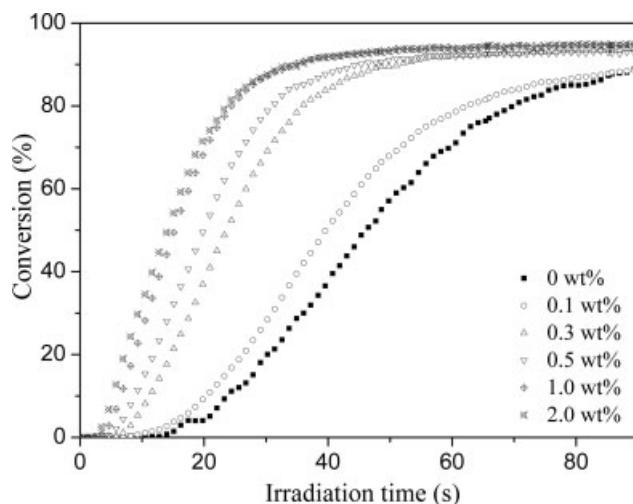
**Figure 7** Effect of EDAB concentration on the polymerization of TPGDA ([HBP-TDI-HBP] = 0.5 wt %, $I$ = 55 mW/cm$^2$).

ates had a strong influence on both the polymerization rate and the residual monomer content. With increasing (meth)acrylate functionality, the content of residual unsaturations increased and the final conversion decreased. The kinetics of photopolymerization for TPGDA incorporating HBP-TDI-HBP in the presence of different tertiary amines as the initiating system were also studied; the HBP-TDI-HBP/ TEOHA combination exhibited the highest polymerization rates among the HBP-TDI-HBP/aliphatic amines combinations. As to the aromatic tertiary amines, DMA was the most efficient coinitiator. Amine concentration, HBP-TDI-HBP concentration, and light intensity had similar effect on the polymerization process. The increase in amine concentration, HBP-TDI-HBP concentration, and light intensity re-

sulted in the increase in the polymerization rate and the final conversion.

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