ESR and Kinetic Study of a Novel Polymerizable Photoinitiator Comprising the Structure of *N*-Phenylmaleimide and Benzophenone for Photopolymerization

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ABSTRACT: A novel polymerizable photoinitiator, 4-[(4-maleimido)phenoxy]benzophenone (MPBP) comprising the structure of *N*-phenylmaleimide and benzophenone was used for the photopolymerization with *N,N*-dimethylaminoethyl methacrylate (DMAEMA) as coinitiator. The ESR spectrum of this photoredox system was studied and compared with BP/DMAEMA; the results showed the same signals of them and verified that *N*-phenylmaleimide does not generate radicals. The kinetics for photopolymerization of methyl methacrylate (MMA) using such system was studied by dilatometer. It was found that the polymerization rate was proportional to the 0.3172th power of the MPBP concentration, the 0.7669th power and the 0.1765th power of MMA concentration and DMAEMA concentration respec-

tively; the overall apparent activation energy obtained was 31.88 kJ/mol. The polymerization kinetics of 1,6-hexanediol diacrylate (HDDA) initiated by such system was studied by photo-DSC. It showed that the increase in the MPBP concentration, light intensity, and temperature leads to increased polymerization rate and final conversion. The apparent activation energy was 11.25 kJ/mol. This polymerizable photoredox system was significantly favorable for reducing the migration of active species but owning high efficiency. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2347–2354, 2006

Key words: ESR; kinetics; photopolymerization; *N*-substituted maleimide; benzophenone

INTRODUCTION

Photoinitiated free radical polymerization is of enormous commercial importance due to extensive applications in the manufacture of printed circuits, encapsulation of electronic components, decorative coating, surface coating, etc.[1–3] Photoinitiated radical polymerization may be initiated by both cleavage (type II) and H-abstraction type (type II) initiators.[4] Among them, type II photoinitiators such as benzophenone (BP), thioxanthone, benzil, and quionone are the most studied, in which radicals are formed by a bimolecular process consisting of an excited chromophore and a tertiary amine as a coinitiator (H donor).[5–7] However, conventional photoinitiators, only a small amount of them being actually consumed during the polymerization, have problems associated with their poor compatibility and migration that result in undesirable effects in the postcured material. A possible way to

overcome such problems is to develop polymerizable and polymeric photoinitiators.[4,6,8–15]

Recently, there has been considerable activity dealing with the use of *N*-substituted maleimides (MIs) as photoinitiators for free-radical polymerization.[16–27] In each of these cases, the maleimide participates in producing radical species and also enjoys the unique advantage of being consumed by the free-radical chain processes that they initiate[28] (Scheme 1). Interestingly, *N*-aliphatic, alkyl, or twisted *N*-aryl MIs all initiate polymerization in the presence of transferable hydrogens, while planar *N*-aryl MIs do not. But it was found that the addition of any kind of the *N*-substituted MIs into BP system would increase the photoinitiating efficiency of both MIs and BPs to a level equivalent to that of conventional cleavage photoinitiators.[21,28,29]

In our previous work,[30] taking into account that there might be a significant interaction between MIs and BPs, which enhances both of their initiation rates, we have synthesized and investigated the photochemical behaviors of four kinds of polymerizable MIs comprising planar *N*-aryl MIs and benzophenone using *N,N*-dimethylaminoethyl methacrylate (DMAEMA) as the coinitiator. The results show that 4-[(4-maleimido)phenoxy]benzophenone (MPBP) is the most effi-
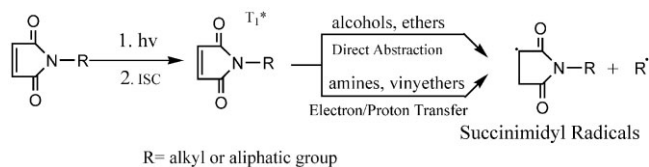
Scheme 1

cient photoinitiator, in which the photoinitiation rate is two times higher than that of BP system used in 1,6-hexanediol diacrylate (HDDA). Meanwhile, both MPBP and DMAEMA have the unique advantage of being consumed during the initiation process for the unsaturated double bond in their molecules, which is significantly favorable for the possibility in reducing the migration of active species. In this context, to know whether *N*-phenylmaleimide in the molecule of MPBP generates radicals and subsequently initiates the polymerization, we studied the ESR spectrum of MPBP in comparison with BP using DMAEMA as coinitiator. By dilatometer and photo differential scanning calorimetry (photo-DSC), the kinetics for photopolymerization of methyl methacrylate (MMA) and HDDA were also studied to further investigate the mechanism of such photoredox system.

EXPERIMENTAL

Materials

4-aminophenol, maleic anhydride, acetic anhydride, anhydrous potassium hydroxide, *N*-methyl-2-pyrrolidone (from Medicine group of China), 4-chlorobenzophenone (from Changzhou High-Tech Chemical Company), DMAEMA (from Shanghai Well Tone Material Company), HDDA, MDEA (from Kewang Chemical Reagent Company) were used as received. MMA was washed with 5 wt % NaOH aqueous solution, dried over anhydrous Na_2CO_3 and distilled. Other chemicals are of analytical grade except where noted.

Preparation of MPBP

MPBP was synthesized in our laboratory in three steps[30] (Scheme 2) and their ^{1}H NMR spectra were shown in Figure 1.
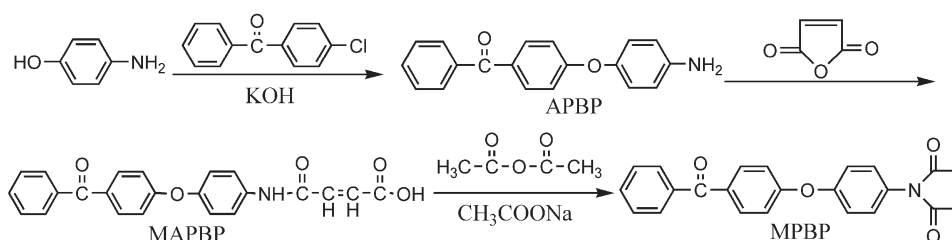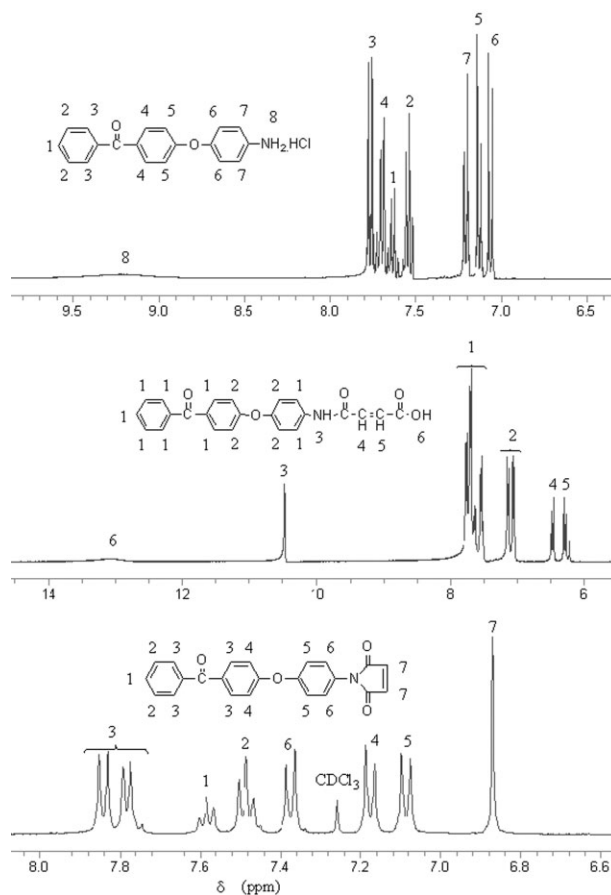

Figure 1　^{1}H NMR spectra of (a) APBP.HCl in [-d_6] DMSO; (b) MAPBP in [-d_6] DMSO; (c) MPBP in CDCl$_3$.

4-[(4-amino)phenoxy]benzophenone hydrochloride (APBP.HCl). M.p.: 143–145°C. EIMS (70eV) *m/e*: 289. ^{1}HNMR ([-d_6] DMSO, 400 MHz): δ = 9.21 (2H, NH$_2$), 7.78–7.52 (7H, aromatic), 7.22–7.05(6H, aromatic). FT-IR (KBr): 3420 (NH), 1648 (C=O), 1258 (C—O). Elemental analysis, calculated for $C_{19}H_{16}ClNO_2$: C, 70.70; H, 4.92; N, 4.30. Found: C, 71.96; H, 5.20; N, 3.91.

4-[(4-maleic acid)phenoxy]benzophenone (MAPBP). M.p.: 183–185°C. ^{1}H NMR ([-d_6] DMSO, 400 MHz): δ = 13.07 (1H, COOH), 10.47 (1H, NH), 7.77–7.51 (9H, aromatic), 7.15–7.05 (4H, aromatic), 6.49–6.46 (1H, —CH=), 6.31–6.28 (1H, —CH=). FT-IR (KBr): 3447 (NH), 3286

Scheme 2

(COOH), 1706 (—HN—$\overset{O}{\underset{C}{\|}}$—), 1656 (AR—$\overset{O}{\underset{C}{\|}}$—AR), 1595 (CH=CH), 1258 (C—O).

4-[(4-maleimido)phenoxy]benzophenone (MPBP).

UV: λ_{max} = 284 nm, logε (mol^{-1} cm^{-1} L) = 4.263. EIMS (70 eV) *m/e*: 369. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.85–7.78 (4H, aromatic), 7.57–7.60 (1H, aromatic), 7.50–7.47 (2H, aromatic), 7.39–7.36 (2H, aromatic), 7.19–7.16 (2H, aromatic), 7.10–7.07 (2H, aromatic), 6.49–6.46 (2H, CH=CH). FT-IR (KBr): 1714 (—N—$\overset{O}{\underset{C}{\|}}$—), 1651 (AR—$\overset{O}{\underset{C}{\|}}$—AR), 1593 (CH=CH), 1262 (C—O). Elemental analysis, Calculated for C$_{23}$H$_{15}$NO$_4$: C, 74.80; H, 4.07; N, 3.79. Found: C, 74.78; H, 4.01; N, 3.63.

Measurements

^{1}H NMR spectra were recorded on a Mercury Plus 400 MHz spectrometer with DMSO-d$_6$ or CDCl$_3$ as solvent.

FT-IR spectra were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrometer. The samples were prepared as KBr disc.

Mass spectra were recorded on a HP5989A mass spectrometer at 70eV.

Elemental analysis was conducted on an Elementary Varioel apparatus

UV–vis spectra were recorded in ethanol solution by Perkin–Elmer Lambda 20 UV–vis spectrophotometer.

ESR experiments were carried out with a Bruker EMX EPR spectrometer at 9.77 GHz with a modulation frequency of 100 kHz with 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as radical capturing agent. A high-pressure mercury lamp was used for irradiation in the ESR spectrometer cavity. Concentrations of photoinitiators and DMAEMA dissolved in dichloromethane were 1×10^{-3} M and 4×10^{-3} M, respectively. 0.5 mL of each sample was transformed into a quartz ESR tube and then purged with nitrogen to get rid of oxygen.

Photopolymerization

Photopolymerization of MMA was performed dilatometerically in a recording dilatometer by irradiating about 12 mL MMA solution in DMF at 40°C. The light source was a 400 W high-pressure Hg lamp, set at a distance of 30 cm from the sample. The polymerization rate (R_p) was determined below 10% conversion, where R_p is almost independent of the conversion.

Photocalorimetry (photo-DSC)

Photopolymerization of HDDA was carried out by DSC 6200 (Seiko Instrument) photo-DSC with high-pressure mercury lamp. Approximately 1.2 mg sample mixture was placed in the aluminum DSC pan.

Heat flow versus time (DSC thermogram) curves were recorded in an isothermal mode under a nitrogen flow of 50 mL/min. The reaction heat liberated in the polymerization was directly proportional to the number of vinyl groups reacted in the system (only a trace of polymerizable photoinitiator system was used compared with HDDA, which can be omitted here). By integrating the area under the exothermic peak, the conversion of the vinyl groups (C) or the extent of reaction could be determined according to

$$C = \Delta H_t / \Delta H_0^{theor} \qquad (1)$$

Where ΔH_t is the reaction heat evolved at time *t*, and ΔH_0^{theor} is the theoretical heat for complete conversion. ΔH_0^{theor} = 86 kJ/mol for an acrylic double bond.[5,31] The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by the following equation

$$R_p = dC/dt = (dH/dt)/\Delta H_0^{theor} \qquad (2)$$

RESULTS AND DISCUSSION

ESR spectroscopy

To reveal the photoinitiation mechanism of this polymerizable MPBP/DMAEMA system, the ESR spectra of BP/DMAEMA and MPBP/DMAEMA in dichloromethane using DMPO as radical trapper were recorded as shown in Figure 2, from which we can infer that their ESR spectra was not different from each other. Jiang et al.[32] had investigated the photopolymerization of BP/DMAEMA system and pointed out that such a system produced free radicals either by electron transfer from DMAEMA to excited triplet-state BP, followed by proton transfer, or by direct hydrogen-atom abstraction from DMAEMA by the excited triplet-state BP via charge-transfer interactions. According to the ESR results, it is proposed that the initiation mechanism of the MPBP/DMAEMA system is quite similar to that of the traditional benzophenone-amine system as the proposed mechanism shown in Scheme 3, which further certifies that planar *N*-phenylmaleimide in the molecule of MPBP does not generate radicals and subsequently initiate polymerization in the presence of transferable hydrogens.

In MPBP/DMAEMA system, according to the nuclear-electron spin coupling principle, there are two ways to abstract hydrogen for the excited triplet MPBP shown in Scheme 3. The ESR spectra show the existence of radicals (1) and (2). It should be noticed that the excited triplet MPBP abstracts hydrogen mainly from the methylene groups but not from the methyl groups of dimethylamino groups of DMAEMA. This
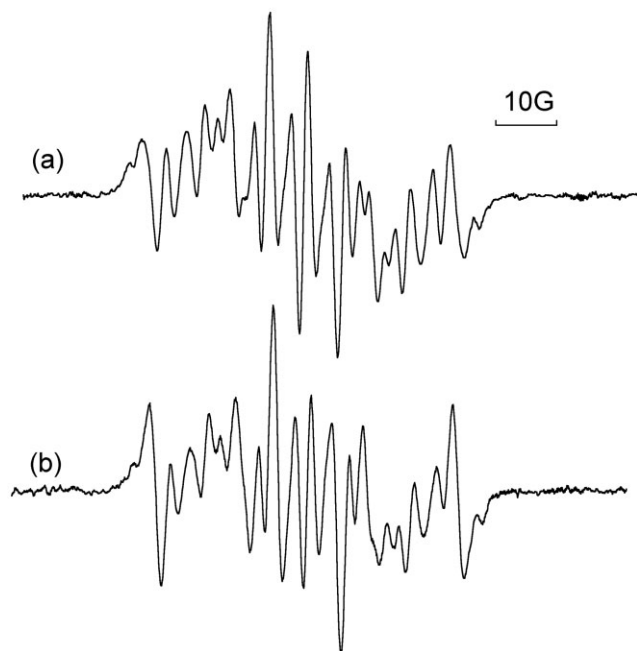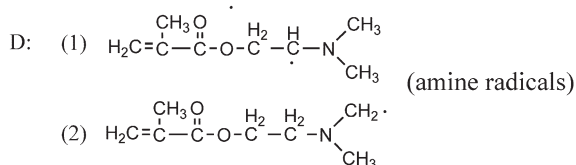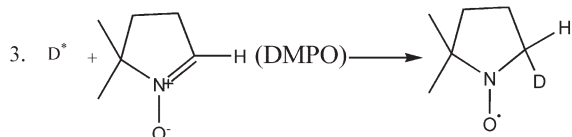
Figure 2 ESR spectra of (a) BP/DMAEMA; (b) MPBP/ DMAEMA in dichloromethane, irradiated for 10 min.

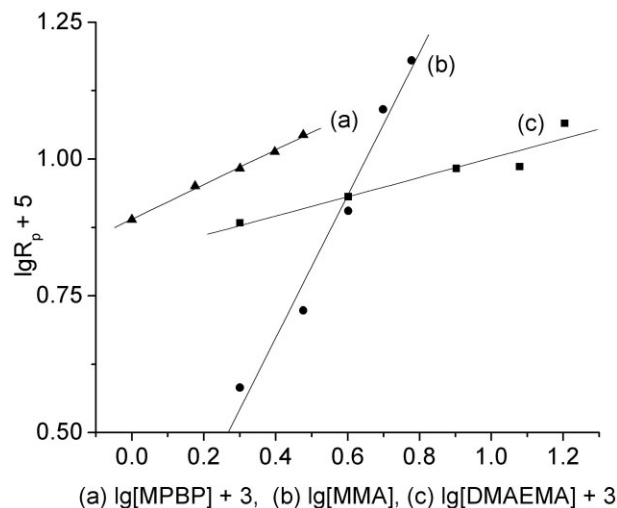**Figure 3** Relationship between R_p and the concentration of MPBP, MMA, or DMAEMA: (a) lgR_p versus lg[MPBP] plot, [MMA] = 4M, [DMAEMA] = 8 mM; (b) lgR_p versus lg[MMA] plot, [MPBP] = 2 mM, [DMAEMA] = 8 mM; (c) lgR_p versus lg[DMAEMA] plot, [MMA] = 4M, [MPBP] = 2 mM.

may be due to the stronger electron-donating ability of the ethyl groups relative to the methyl groups, which is similar to that of BP/DMAEMA system.[32]

Kinetic study on photopolymerization of MMA

The MPBP/DMAEMA system can initiate the photopolymerization of MMA as easily as the benzophenone-triethylamine system.[33] As described by Miller et al.,[28] planar *N*-aromatic MIs do not initiate photopolymerization. The photopolymerization of such polymerizable system should be addressed to the structure of BP. The photolysis of benzophenone, in the presence of DMAEMA, leads to the formation of a radical pro-

Scheme 3

duced from a carbonyl compound (ketyl-type radical) and another radical derived from DMAEMA.[32,34,35] The amine radicals usually initiate the photopolymerization of vinyl monomers. However, the ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron.

By varying the concentration of one of the three components (i.e., MPBP, MMA, or DMAEMA), and keeping the other two components constant, the relationships between the polymerization rate (R_p) and [MPBP], [MMA], [DMAEMA] can be obtained. The plots of lgR_p versus lg[MPBP], lgR_p versus lg[MMA], lgR_p versus lg[DMAEMA] are linear, as shown in Figure 3. From the slopes of the straight lines, we found the R_p is proportion to $[MPBP]^{0.3172}$, $[MMA]^{0.7669}$, and $[DMAEMA]^{0.1765}$ respectively. Hence, the relationship between R_p and concentration of MPBP, MMA, or DMAEMA can be expressed as

$$R_p \propto [MPBP]^{0.3172}[MMA]^{0.7669}[DMAEMA]^{0.1765}$$

This is close to that of the photopolymerization of MMA initiated by the benzophenone-triethylamine system,[36,37] which further confirms that the initiation mechanism is similar to the traditional benzophenone photoredox system.

Under low conversion, it is well known that lnR_p is proportion to $1/T$ according to Arrhenius equation, where A is a constant, E is apparent activation energy and R is gas constant
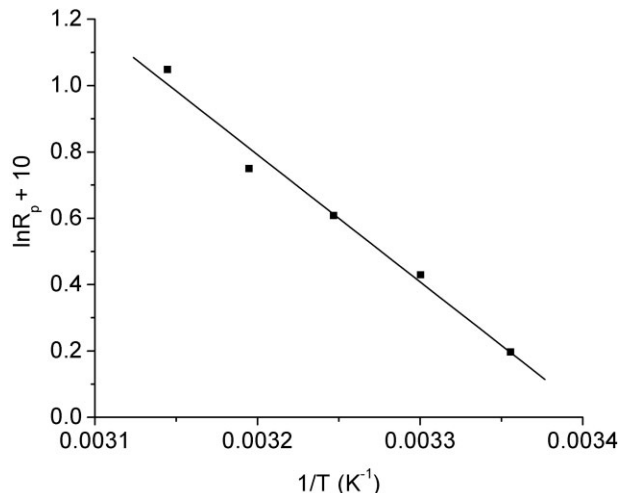
Figure 4 $\ln R_p$ versus $1/T$ plot for MMA photopolymerization initiated by MPBP-DMAEMA system: [MMA] = 4M, [MPBP] = 2 mM, [DMAEMA] = 8 mM.

$$R_p = A \exp\left[\frac{E}{RT}\right] \quad (3)$$

By varying the temperature from 298 to 318 K, the relationship between R_p and temperature can be obtained. Figure 4 shows the plot of $\ln R_p$ versus $1/T$, from which the overall apparent activation energy for the photopolymerization of MMA can be calculated. The result of E value is 31.88 kJ/mol, which is close to that of the conventional photoinitiated polymerization.[37]

Kinetic study on photopolymerization of HDDA

Photo-DSC is widely used in the photopolymerization of multifunctional monomers. The photopolymerization of multifunctional monomers has been the subject of many comprehensive review articles and books, which have appeared recently.[25,38–41] Our previous work[30] shows that MPBP/DMAEMA initiates photopolymerization of HDDA efficiently and the maximum initiation rate is almost three times as high as that of BP/DMAEMA system; therefore, it is significant to establish the kinetic parameters for such system. It is well known, at low conversion, that the rate of photopolymerization R_p can be expressed by the classical kinetics law[42]

$$R_p = -d[M]/dt = k_p/k_t^{1/2}[M](\phi \varepsilon I_0[A]_0)^{1/2} \quad (4)$$

Where k_p and k_t are the propagation and termination rate constants, [M] is the molar concentration of the monomers, ϕ is the initiation efficiency, ε is the absorption coefficient, I_0 is the incident light intensity, and [A] is the photoinitiator concentration.

Influence of initiator concentration

Comparisons of the rates of isothermal photopolymerization at different MPBP/DMAEMA concentrations are presented in Figure 5(a), from which we observe that higher concentration leads to higher maximum heat flow. Meanwhile, the time to reach the maximum polymerization rate decreases with increasing photoinitiator concentration [A]. At a very low [A] of 0.005M, it takes about 20 s to reach the maximum polymerization rate (R_{pmax}) when compared with that taken by others (<15 s). This was caused by the fact that a relatively low initiator concentration yields few radicals by the incident light, thus leads to the requirement of a long period to form the gel structure which restricts the movement of species to reach R_{pmax}.[5]

Figure 5(b) shows that as [A] is increased, R_{pmax} occurs at higher conversion and the final conversion increases. This may be attributed to the free volume
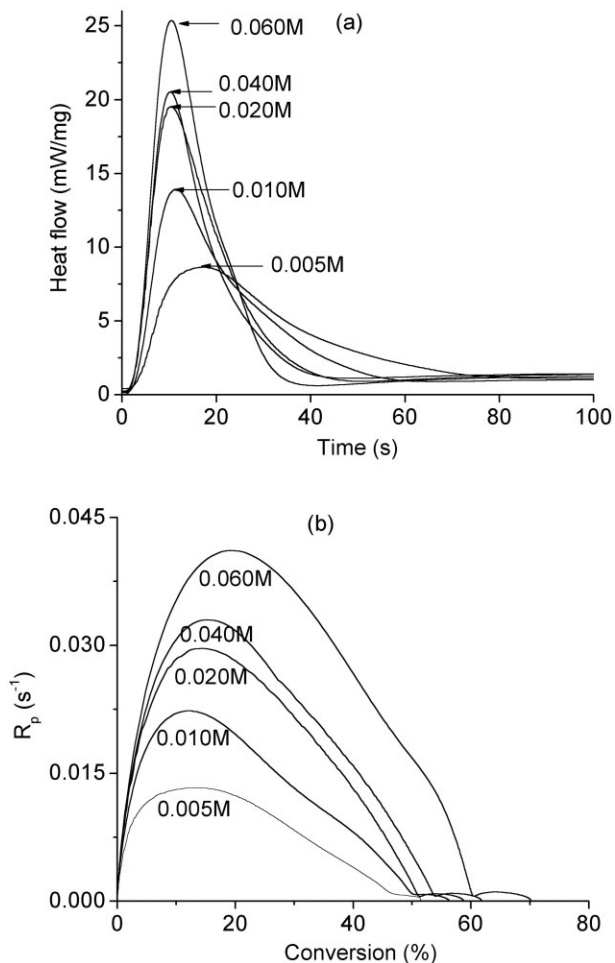

Figure 5 (a) Heat flow versus time; (b) Rate versus conversion of the Photo-DSC profiles for polymerization of HDDA with different MPBP/DMAEMA concentrations, cured at 25°C by UV light with an intensity of 50 mW/cm² (the concentration is in terms of MPBP, [DMAEMA] is always four times of [MPBP]).
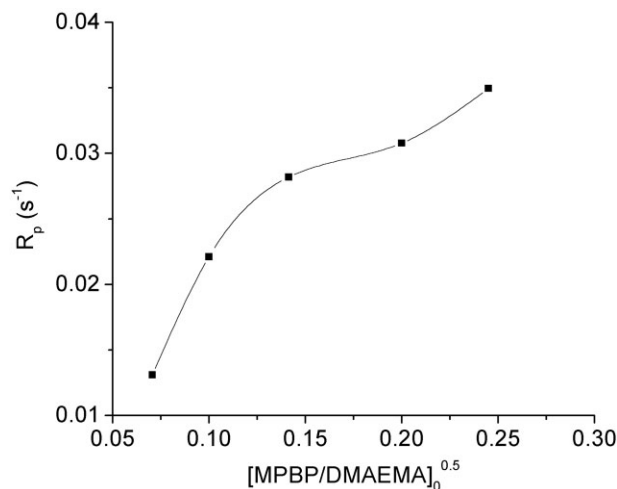
Figure 6 Polymerization rate (at 10% conversion) versus $[MPBP/DMAEMA]_0^{0.5}$ for HDDA, cured at 25°C by UV light with an intensity of 50 mw/cm² (the concentration is in terms of MPBP, [DMAEMA] is always four times of [MPBP]).

effect, which is caused by the delay in the volume shrinkage rate.[5,43,44] In the case of photoinitiated polymerization, initiation rate is very high. Thus, the polymerization of HDDA systems cannot be in volumic equilibrium because the volume shrinkage rate is much smaller than the chemical reaction rate. Such difference generates a temporary excess of free volume, which increases the mobility of the residual double bond and leads to a higher conversion.

Polymerization rate versus $[A]^{0.5}$ plot as shown in Figure 6 obviously deviates from the linearity when [A] increases, which is inconsistent with the eq. (4). This may be ascribed to the decrease of the initiation efficiency with the increase of photoinitiator concentration and the complicated bimolecular system of MPBP/DMAEMA. Similar behavior has been observed in other systems for photopolymerization.[5,43]

Influence of light intensity

Similar effect has been observed by varying the light intensity on the polymerization, as shown in Figure 7. The increase in the light intensity leads to the increase in the polymerization rate and final conversion. This similar result can be understood according to the eq. (4). In contrast to the deviation of linearity for conversion rate verus $[A]^{0.5}$ plots, however, the initial slope of the curves (R_p) is almost in agreement with the eq. (4) and proportional to $I_0^{0.5}$ as shown in Figure 8. This shows that the light intensity has no obvious effect on initiation efficiency ϕ, which is also confirmed in our laboratory by using thioxanthone on trimethylolpropane triacrylate (TMPTA).[5]

Influence of the temperature

Little difference was observed by varying the temperature when compared with the influence of light intensity and initiator concentration, as shown in Figure 9. The maximum polymerization rate of HDDA also occurs at a higher conversion as the polymerization temperature increases. This behavior is in agreement with the chemical-diffusion modeling of polymerization proposed by Cook.[45,46] On the other hand, raising the isothermal cure temperature also results in increased final conversion. This increase of the conversion is mainly due to the increased mobility of the reactive species. Since increasing temperature increases the mobility of the radicals, and the reaction systems can further polymerize and reach a higher level of conversion before the radicals lose their mobility.

However, it was shown that the time taken to reach the exothermic peak is almost independent of the isothermal curing temperature; meanwhile, the R_{pmax} only increases by less than one time even though the
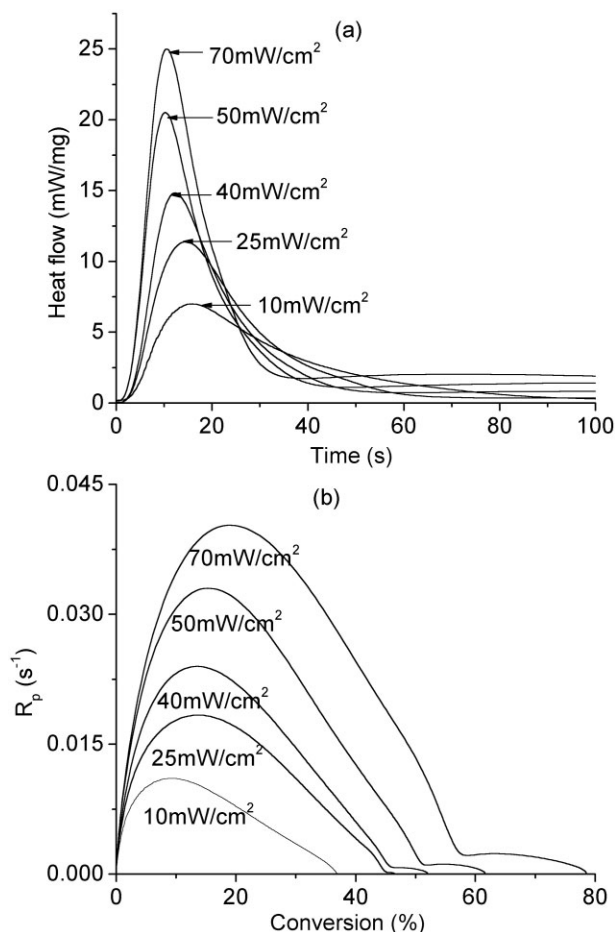

Figure 7 (a) Heat flow versus time; (b) Rate versus conversion of the Photo-DSC profiles for polymerization of HDDA with different light intensity, cured at 25°C with [MPBP] = 2 mM and [DMAEMA] = 8 mM.
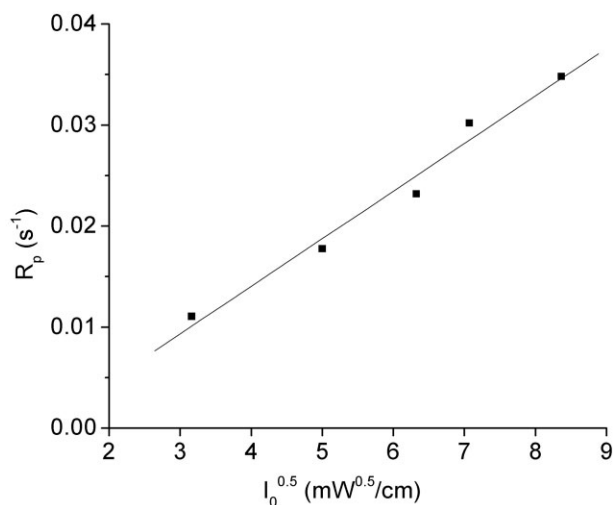
Figure 8 Polymerization rate (at 10% conversion) versus $I_0^{0.5}$ for HDDA, cured at 25°C by UV light with an intensity of 50 mw/cm² with [MPBP] = 2 mM and [DMAEMA] = 8 mM.

polymerization temperature is raised by 30°C. This indicates that the rate of decomposition of a photoinitiator is not dependent on the temperature quite different from thermal initiation. Scott[47] and Jiang[5] reported the similar results.

At a low conversion of 10%, the Arrhenius plot is linear as can be seen from Arrhenius plots of the rate data at different conversions shown in Figure 10. From the slope of the plot, we can obtain that the apparent activation energy is 11.25 kJ/mol. The Arrhenius plot is slightly curved at a higher conversion of 20%; however, such a plot seriously derivates from linearity at even higher conversion. This may be due to the diffusion-controlled kinetics for the late stage of polymerization. As the polymerization goes on, the viscosity of HDDA becomes higher, which eventually limits the molecular mobility, and then the propagation and termination steps become diffusion controlled. As the molecular mobility drops with the decrease of the polymerization temperature, the reaction rate becomes markedly slower than that predicted by the Arrhenius equation at higher conversion from Figure 10. However, as should be pointed out, HDDA possesses less viscosity when compared with TMPTA in which such effect would be smaller as depicted earlier in our laboratory.[5]

CONCLUSIONS

In this article, a novel polymerizable photoinitiator, 4-[(4-maleimido)phenoxy]benzophenone (MPBP), comprising the structure of N-phenylmaleimide and benzophenone was investigated for the photopolymerization of MMA and HDDA with N,N-dimethylaminoethyl methacrylate (DMAEMA) as coinitiator.

MPBP and DMAEMA could not only form the high efficient photoredox system to initiate the vinyl polymerization but also participate in the polymerization, which is significantly favorable for reducing the migration of active species.

1. ESR spectrum of this photoredox system shows the same signals when compared with BP/DMAEMA, which certifies that planar N-phenylmaleimide does not generate radicals and initiate polymerization in the presence of DMAEMA.

2. The kinetics for photopolymerization of MMA using such system was studied by dilatometer. The relationship between R_p and concentration of MPBP, MMA, or DMAEMA can be expressed as $R_p \propto [MPBP]^{0.3172}[MMA]^{0.7669}[DMAEMA]^{0.1765}$, and the apparent activation energy is 31.88 kJ/mol. This further verifies that the initiation mechanism is similar to the traditional H-abstraction type (type II) benzophenone initiators.

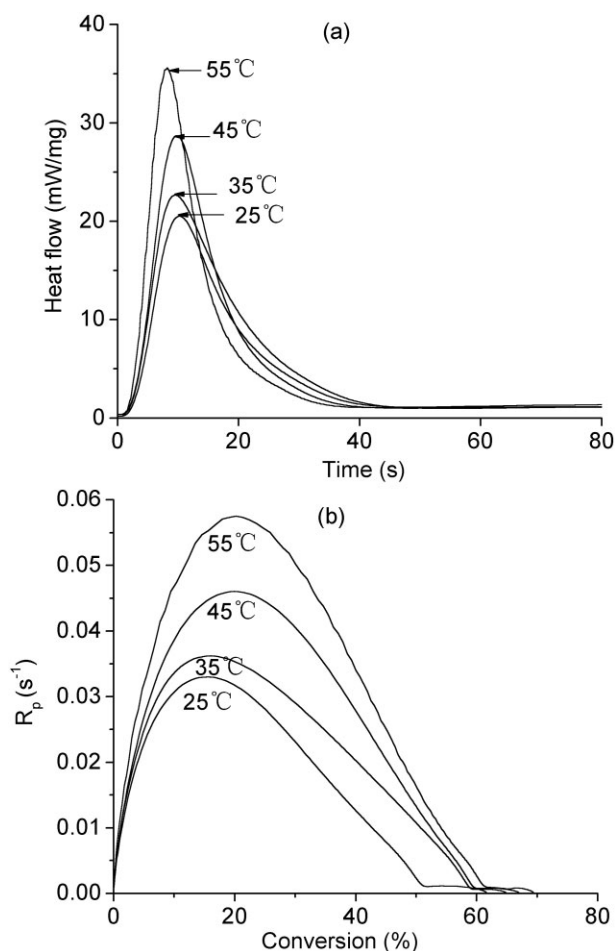3. The kinetics of HDDA initiated by such system was studied by photo-DSC. The results show that the in-

Figure 9 (a) Heat flow versus time; (b) Rate versus conversion of the Photo-DSC profiles for polymerization of HDDA measured at different temperatures with light intensity of 50 mw/cm², [MPBP] = 2 mM and [DMAEMA] = 8 mM.
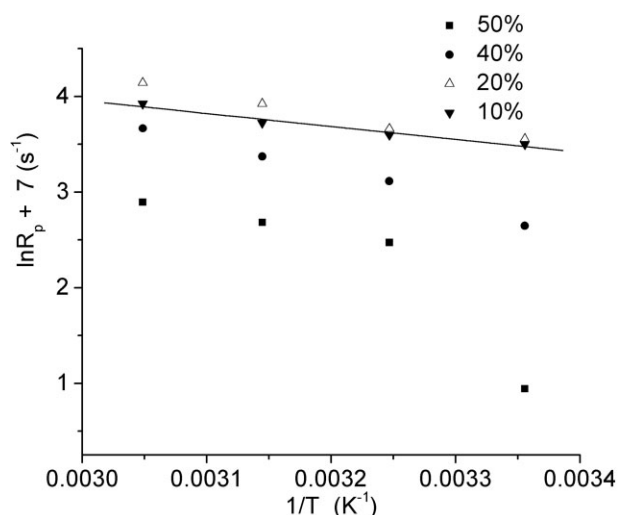
Figure 10 Polymerization rate versus $1/T$ plots for polymerization of HDDA at different conversion with light intensity of 50 mw/cm^2, [MPBP] = 2 mM and [DMAEMA] = 8 mM.

crease in the MPBP concentration ([A]), light intensity (I_0), and temperature leads to higher polymerization rate and final conversion. R_p is proportional to $I_0^{0.5}$ in contrast to the deviation of linearity for [A]$^{0.5}$. Light intensity has no obvious effect on initiation efficiency ϕ. The apparent activation energy for HDDA at 10% conversion is 11.25 kJ/mol.

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