Synthesis and Photoinitiation Properties of a Novel Quaternary Ammonium Tetraphenylborate Salt

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ABSTRACT: Quaternary ammonium salts are photobase generators. Recently, we prepared a novel quaternary ammonium tetraphenylborate salt bearing a 6-methoxynaphthoylmethyl group. The structure of the products was confirmed by elemental analysis and ^{1}H-NMR. Thermogravimetry showed its good thermostability. UV spectra and fluorescence emission spectra of the samples were studied. A mass spectrometry method for the analysis of the tertiary amine and other fragments produced by photolysis was established. Photolysis was found to produce both tertiary amine and free radicals. Therefore, the products of photolysis not only could cause thermal curing of epoxide but also could initiate the free-radical polymerization of acrylate or methyl acrylate monomer. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 399–405, 2006

Key words: photochemistry; UV-vis spectroscopy; radical polymerization; quaternary ammonium salt

INTRODUCTION

Photobase generators (PBGs) are compounds that can generate basic compounds such as amine upon UV irradiation.[1] Since the first publication on PBGs appeared in the latter half of the 1980s, studies have been increasing. Actually, they are a continuation of photoacid generators (PAGs), which are widely used in the field of polymeric photosensitive systems (e.g., photoinitiated polymerization and photoresist systems) because of their good initiating effect. However, PAGs may cause corrosion of the substrate through resultant acids in electronics-related fields. PBGs can overcome this defect of PAGs and do not have such unfavorable properties. Cobalt–amine complexes,[2,3] acyl oximes,[1,4–8] carbamates,[1,9,10] formamides,[11] and quaternary ammonium salts have been used as PBGs.[12–16] Among these PBGs, quaternary ammonium salts have been develop recently. As we know, arylalkylborate salts are also free-radical chain initiators, so quaternary ammonium arylalkylborate salts can produce not only amines but also free radicals. They are expected to be applied to hybrid UV curing.

In our previous work, we found that a quaternary ammonium tetraphenylborate salt bearing a phenacyl group gives a phenyl radical upon irradiation at 250 nm, the typical absorption band of the phenacyl chromophore. The formation of the phenyl radical takes place because the phenacyl triplet state oxidizes the borate anion. Because the main emission wavelengths of a medium-pressure mercury lamp are 365, 313, and 303 nm, to match these longer wavelengths, we modified the chromophore and proposed that 6-methoxynaphthoylmethyl as a chromophore would better match these wavelengths. On the basis of this idea, recently we synthesized a quaternary ammonium tetraphenylborate salt bearing a 6-methoxynaphthoylmethyl group that was expected to improve the initiation activity because of the absorption properties of this compound. UV spectra have shown that its typical absorption band is 270–380 nm, and it can match the main emission wavelength of a medium-pressure mercury lamp. The formation of triethylenediamine (TEDA) in the photolysis of quaternary ammonium salt BPh$_4$ was ascertained by a mass spectrometry method, which is a more rapid and simple method than ^{1}H-NMR. In fact, its photolysis by UV-induced electron transfer produces both a tertiary amine (TEDA) and a phenyl radical; therefore, it can be used as a PBG and photoradical generator. The former has been found suitable for the thermal crosslinking of an epoxy resin. The latter can rapidly initiate the free-radical polymerization of acrylate or methyl acrylate monomers such as trimethylolpropane triacrylate (TMPTA). Mixtures of the quaternary ammonium tetraphenylborate salt with a monomer or resin have good stability in the dark. Because the tetraphenyl compound is more stable and more easily synthesized and purified and has good photoinitiation properties, it is more attractive for particular applications.
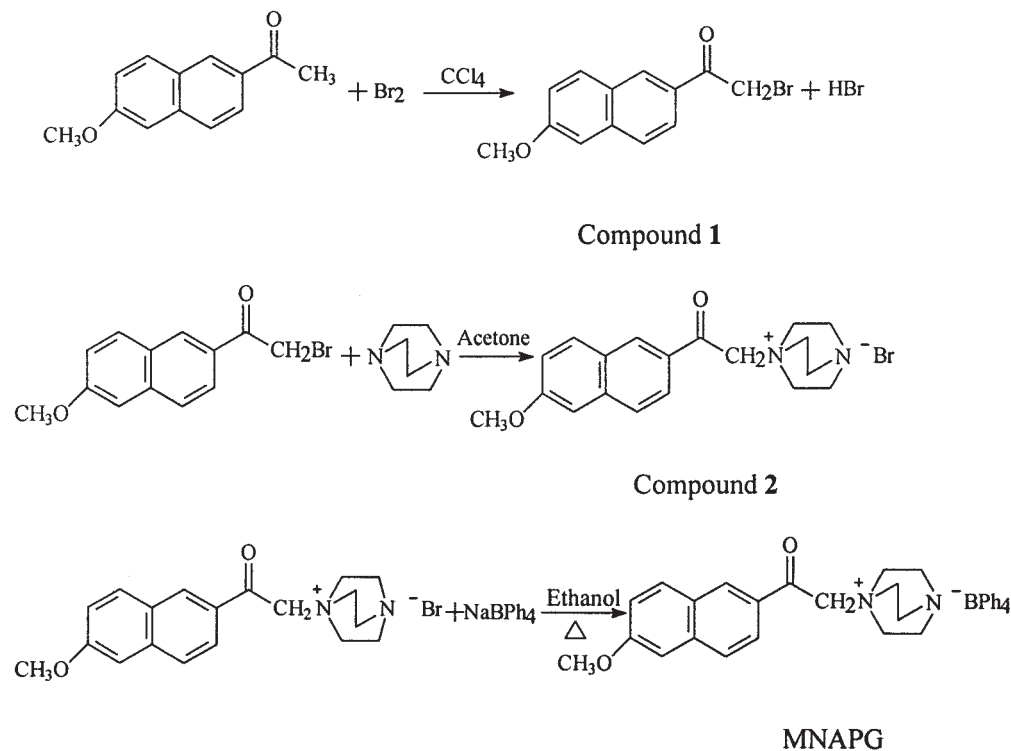
EXPERIMENTAL

Materials

Ethanol, carbon tetrachloride (CCl$_4$), acetone, acetonitrile, and bromine were used as purchased from

Scheme 1   Preparation of the quaternary ammonium tetraphenylborate salt.

Guangzhou Chemical Co. (Guangzhou, China) 6-Methoxynaphthoylmethane was purchased from Chongqing Chuandong Chemical (Group) Co. (Chongqing, China) TEDA was purchased from Alfa Aesar (Herts, UK) and was used without further purification. Sodium tetraphenylboron was purchased from Shantou Guanghua Chemical Co. (Shantou, China) Epoxide EPON827 was purchased from Shell Co. (Beijing, China) TMPTA was provided by Cognis Corp. (Cincinnati, OH) Darocur 1173 was obtained from Ciba Co. (Guangzhou, China)

Analysis

The melting point was measured on a Sanguang 248 X_4 instrument (Beijing, China). Elemental analyses were carried out on an Elementar (Hanau, Germany) Vario EL instrument. ^{1}H-NMR spectra were taken on a Varian Unity Inova 500 spectrometer (Palo Alto, CA). IR spectra were recorded on a Nexus 670 Fourier transform infrared spectrometer (USA). UV spectra were taken on a Shimadzu UV-240 UV–vis spectrophotometer (Kyoto, Japan). Fluorescence spectra were taken on an FLS 920 fluorescence spectrometer (Edinburth, UK). Mass spectrometry was taken on an LCQ DECA XP liquid chromatography/mass spectrometry instrument (Thermo Electron Corp., San Jose, CA). Thermogravimetric analysis (TGA) was carried out on a Netzsch TG 209C (Bavaria, Germany) at a heating rate of 20°C/min with a pure N_2 gas flow of 40 mL/min. Differential photocalorimetry (DPC) was taken on a modified homemade

CDR-1 model differential scanning calorimeter (Shanghai Balance Instrument Plant, China).

Synthesis of the quaternary ammonium tetraphenylborate salt

The quaternary ammonium tetraphenylborate salt bearing a 6-methoxynaphthoylmethyl group was prepared as shown in Scheme 1. 6-Methoxynaphthoylmethane was reacted with bromine in CCl_4 to obtain 6-methoxynaphthoylmethyl bromide (compound **1**). 6-Methoxynaphthoylmethyl-(1-azonia-4-azabicyclo[2,2,2]-octane)bromide (compound **2**) was prepared by the reaction between compound **1** and TEDA in acetone at room temperature. The target product, 6-methoxynaphthoylmethyl-(1-azonia-4-azabicyclo[2,2,2]octane) tetraphenylborate (MNAPG), was obtained by the anion exchange of compound **2** with sodium tetraphenylboron in alcohol upon heating.

Compound 1

Bromine (2.2 mL, 42.6 mmol) was slowly added to a solution of 6-methoxynaphthoylmethane (8 g, 40 mmol) in 300 mL of CCl_4 at room temperature and was stirred for 6 h. The resulting solution was filtered, and the solid product was subsequently washed with CCl_4 and dried *in vacuo*. After recrystallization from ethanol, compound **1** was obtained as white needles (8.48 g, 76% yield).

mp: 95–97°C. ^{1}H-NMR (CDCl$_3$, δ, ppm): 3.970 (s, 3H), 4.568 (s, 2H), 7.169 (s, 1H), 7.237 (d, 1H), 7.808 (d, 1H), 7.885 (d, 1H), 8.015 (d, 1H), 8.438 (s, 1H). ANAL. Calcd for C$_{13}$H$_{11}$O$_2$Br: C, 55.95%; H, 3.941%. Found: C, 57.32%; H, 4.046%.

Compound 2

A solution of compound **1** (2.79 g, 10 mmol), and TEDA (1.12 g, 10 mmol) in acetone (250 mL) was stirred at room temperature for 8 h. The resulting solution was filtered, washed with acetone, and dried *in vacuo*. After recrystallization from ethanol, compound **2** was obtained as pale brown, needlelike crystals (3.13 g, 80% yield). It decomposed at 155°C without melting.

^{1}H-NMR (CDCl$_3$, δ, ppm): 3.280 (t, 6H), 4.159 (t, 6H), 3.917 (s, 3H), 5.945 (d, 2H), 7.032 (s, 1H), 7.141 (d, 1H), 7.504 (d, 1H), 7.684 (d, 1H), 8.216 (d, 1H), 8.958 (s, 1H). ANAL. Calcd. for C$_{19}$H$_{23}$O$_2$N$_2$Br: C, 58.35%; H, 5.880%; N, 7.159%. Found: C, 57.30%; H, 6.081%; N, 6.950%.

MNAPG

Compound **2** (1.96 g, 5 mmol) was dissolved in ethanol (100 mL) upon heating. The sodium salt of tetraphenylborate (1.72 g, 5 mmol) in a minimum amount of ethanol was added dropwise over 15 min. Then, the solution was stirred for 8 h and filtered. The resulting solid was washed with ethanol several times and dried *in vacuo*. MNAPG was obtained as a white powder (2.71 g, 86% yield). It decomposed at 205°C without melting.

^{1}H-NMR (acetone, δ, ppm): 3.339 (t, 6H), 3.887 (t, 6H), 3.966 (s, 3H), 5.316 (d, 2H), 6.758 (t, 4H), 6.906 (t, 8H), 7.322 (s, 8H), 7.509 (t, 1H), 7.680 (t, 1H), 7.855 (t, 1H), 7.903 (t, 1H), 8.230 (t, 1H), 8.596 (s, 1H). ANAL. Calcd. for C$_{43}$H$_{43}$O$_2$N$_2$B: C, 81.92%; H, 6.820%; N, 4.440%. Found: C, 80.94%; H, 6.901%; N, 4.438%.

Analysis of the photolysis products of MNAPG by mass spectrometry

An acetone solution containing MNAPG (1.0 × 10^{-5}M) was put into a quartz cell. The solution in the quartz cell was irradiated on a UV curing machine (UV/262, Yee Fung Electric Equipment Ltd., Hong Kong, China) for 10 s (light intensity = 30 mW/cm^2 in the middle of the machine), and then the irradiation was repeated three times to complete the photolysis of MNAPG. Brief irradiation many times can prevent a thermal influence. Mass spectra of the solution before and after irradiation were measured.

Photoinitiated thermal curing of epoxide EPON827

A mixture of MNAPG and a commercial epoxide EPON827 (epoxide/MNAPG mass ratio = 9:1) was spread on KBr plates. Curing was observed visually and measured quantitatively with Fourier transform infrared spectra of mixtures that were irradiated with UV light with or without postbaking at 120°C.

Photoinitiated free-radical polymerization of TMPTA

The free-radical photopolymerization of a TMPTA/MNAPG mixture (TMPTA/MNAPG mass ratio = 99:1) was studied with the DPC technique on a modified homemade CDR-1 model differential scanning calorimeter. The light source was a medium-pressure mercury lamp, and the light intensity measured by a UV light illuminometer (type UV-A, Photoelectric Instrument Factory, Beijing, China) was 3.0 mW/cm^2. A widely used photoinitiator, Darocur 1173, was used in place of MNAPG for comparison.

RESULTS AND DISCUSSION

Thermal stability of MNAPG

The thermal degradation temperature (T_d) of MNAPG was measured with TGA to estimate the thermal stability. The results show that MNAPG has a quite high T_d value (200°C) and good thermal stability. In fact, it can be put aside for 1 year or even longer at room temperature if irradiation is avoided. In the case of irradiation, it can immediately generate a tertiary amine and a phenyl radical. Therefore, MNAPG is a photoinitiator with good properties.

UV–vis spectra ofMNAPG

The absorption spectra of compound **2** and MNAPG in acetonitrile (1.0 × 10^{-5}M) show a broad band at 270–380 nm that is independent of the structure of the anion. This absorption maximum is redshifted (10 nm) without a change in the shape in comparison with that of the starting material, 6-methoxynaphthoylmethane (Fig. 1). This suggests that a substantial interaction exists between the nitrogen cation and boron anion in the acetonitrile solvent. The spectral shape of MNAPG at 220–270 nm changes because of the addition of sodium tetraphenylborate.

Compared with the quaternary ammonium tetraphenylborate salt bearing a phenacyl group, whose typical absorption wavelength is at 250 nm, MNAPG shows a new absorption band at 270–380 nm. This property is dependent on the characteristics of the chromophore. The conjugation level of 6-methoxynaphthoylmethyl, higher than that of phenacyl, is responsible for its longer absorption wavelength.

Figure 2 shows UV spectral changes of MNAPG upon the irradiation of a medium-pressure mercury lamp in acetonitrile. The light intensity is 3.0 mW/
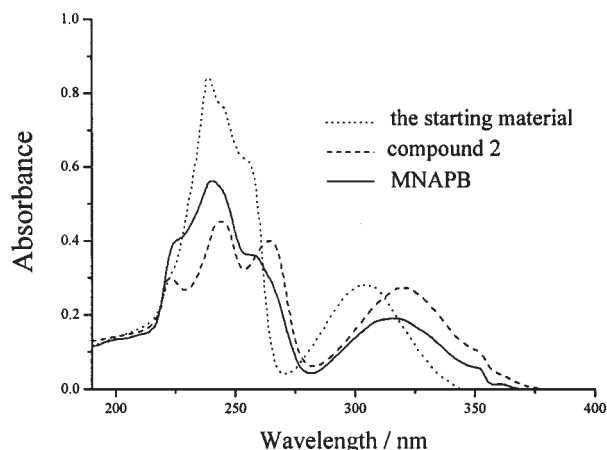
**Figure 1** Absorption spectra of the starting material, compound **2**, and MNAPG in acetonitrile.

cm². A decrease in absorption at ~320 nm in the UV spectral changes of MNAPG can be observed, and yet an increase in absorption at ~240 nm can also be observed. Both absorption maxima are blueshifted (~10 nm) after irradiation in acetonitrile.

Emission spectra of MNAPG

Figure 3 shows the fluorescence of MNAPG in ethanol as a function of the concentration. At a concentration of about $10^{-6}M$ or less, the fluorescence is concentration-independent and is close to the emission of the pure MNAPG monomer. As the concentration increases, two effects can be observed: (1) the intensity of the MNAPG monomer emission decreases, and (2) a new fluorescent emission as a broad, structureless band, due to the MNAPG excimer, appears on the red side (i.e., longer wavelengths or lower energies) of the monomer emission and increases in intensity. The
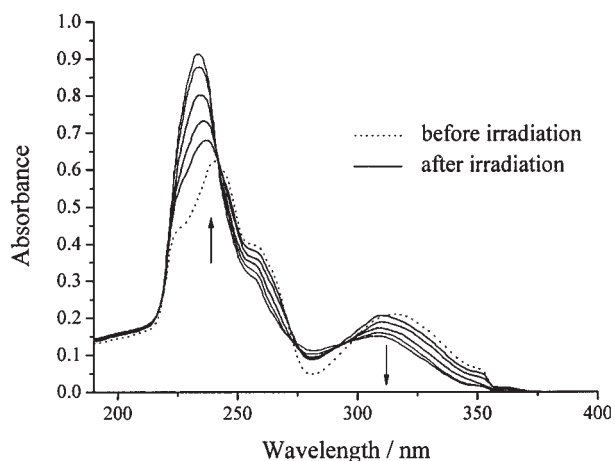
**Figure 2** UV spectral changes in MNAPG upon irradiation in acetonitrile.
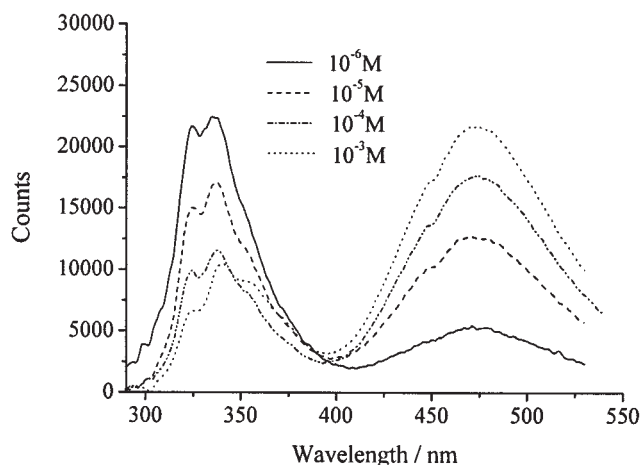
Figure 3 Fluorescence emission spectra of MNAPG in ethanol.

aforementioned phenomenon can be explained by the following process (Scheme 2). The occurrence of an isoemissive point is consistent with the excimer in the observed fluorescence. As we see, the excimer emission is structureless and is a redshifted broad peak.
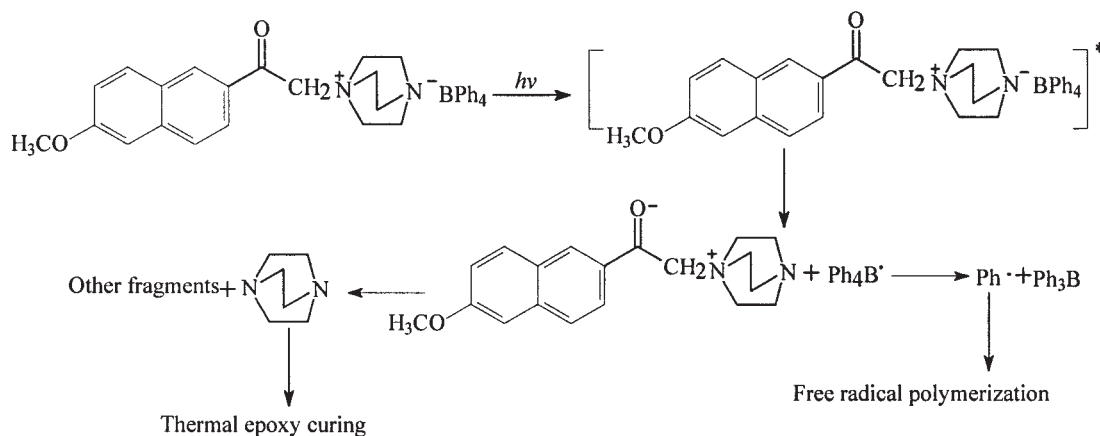
Photolysis of MNAPG

In the photolysis of quaternary ammonium borate salt, it has been suggested that tertiary amines and free radicals are generated.[13,16] Scheme 3 shows the proposed photolysis mechanism of MNAPG. First, electron transfer from the borate anion to the excited acceptor occurs. This generates radical pairs that can decompose by rapid carbon–nitrogen and carbon–boron bond fragmentation. TEDA is formed as a result of reductive carbon–nitrogen bond scission. The tetraboranyl radical formed by electron transfer cleaves to generate a phenyl radical. TEDA as a catalytic curing agent has been proved suitable for the thermal crosslinking of an epoxy resin (EPON827), for which nucleophilic attack on the epoxy ring is favorable. Meanwhile, the phenyl radical can rapidly initiate the free-radical polymerization of acrylate or methyl acrylate monomers such as TMPTA.

A mass spectrometry method for the photolysis of MNAPG has been established. Compared with the relative abundance of the $m/z = 311$ cation before irradiation, that of $m/z = 311$ decreases after irradiation. The results show that the photolysis of MNAPG
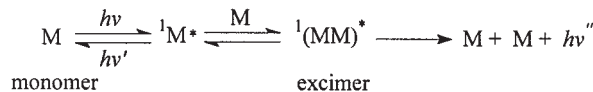
Scheme 2 Mechanism of the formation of excimer of MNAPG (M=MNAPG).

Scheme 3 Photolysis of quaternary ammonium tetraphenylborate salt.

by UV-induced electron transfer produces fragments such as $m/z = 311$, $m/z = 169.3$, $m/z = 254.2$, and $m/z = 295.1$ (Table I). The appearance of $m/z = 113$ indicates that TEDA is generated by the photolysis of MNAPG, whereas the formation of fragments of $m/z = 169.3$ and $m/z = 295.1$ shows that the carbon–nitrogen bond and carbon–oxygen bond have decomposed. Furthermore, fragments of $m/z = 127.2$ and $m/z = 254.2$ are formed from those of $m/z = 169.3$ and $m/z = 295.1$ by the loss of an acetyl. The fragment of $m/z = 376.1$ is thought to be formed by the coupling of radicals, such as 6-methoxynaphthyl, naphthyloxyl, and phenyl radicals, implying the formation of a phe-

nyl radical in the photolysis process, which can initiate free-radical polymerization.

Tertiary-amine-catalyzed thermal curing of epoxide (EPON827)

A commercial epoxide, EPON827, was selected for the curing experiment. A mixture of MNAPG and EPON827 (epoxide/MNAPG mass ratio = 9:1) was spread on glass supports. The mixture, exposed to UV irradiation only, was not cured, besides becoming yellowish. Heating the mixture at 120°C for hours without irradiation could slightly induce curing because of

TABLE I
MS Data of Fragments Decomposed from the $m/z = 311$ Cation

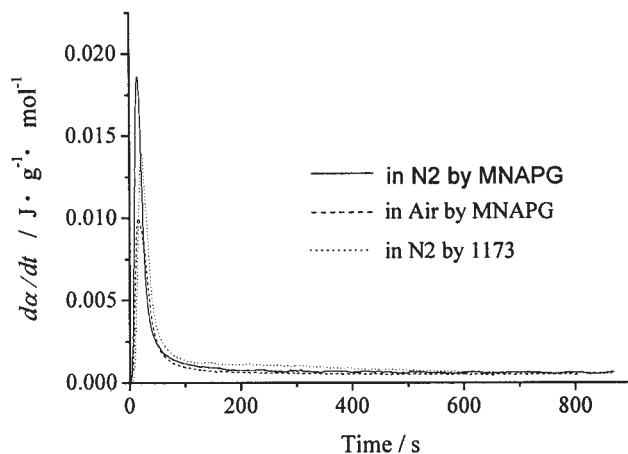| m/z	Relative abundance (%)	Fragment	Elemental composition	Calcd. for the chemical formula
311.3	100		$C_{19}H_{23}N_2O_2$	311.40
113.2	11.5		$C_6H_{13}N_2$	113.18
127.2	13.2		$C_{10}H_7$	127.17
169.3	38.5		$C_{12}H_9O$	169.20
254.2	65.0		$C_{20}H_{14}$	254.33
295.1	23.0		$C_{22}H_{15}O$	295.36
376.1	55.2		$C_{27}H_{20}O_2$	376.45
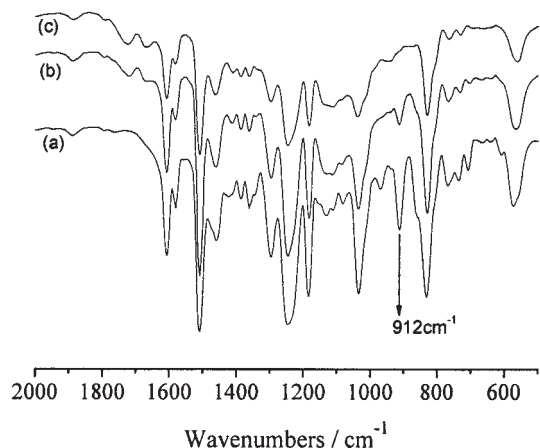
Figure 4 IR spectra of a mixture of MNAPG and EPON827 resin: (a) no irradiation and no postbaking, (b) UV irradiation for 1 min and postbaking for 1 h, and (c) UV irradiation for 1 min and postbaking for 2 h.

Figure 5 Photopolymerization rate ($d\alpha/dt$) of TMPTA in different atmospheres initiated by MNAPG and Darocur 1173.

the residual tertiary amine in the TEDA unit. When the sample was exposed to UV light for 30 s and then heated at 120°C for hours, a crosslinked polymer network was formed, and it was insoluble in acetone. The epoxy resin was obviously cured by TEDA, one of the photolysis products of MNAPG. This curing process was clearly shown by the IR spectra of the mixture (Fig. 4). There was a significant decrease in the intensity of a band at 912 cm^{-1} assigned to the closed epoxide rings and a significant increase in the intensity of a band at 1120–1140 cm^{-1} assigned to ether linkages formed by ring opening. A further thermal treatment led to the disappearance of the IR band at 912 cm^{-1}.

Free-radical polymerization

In addition to the ability of a quaternary ammonium tetraphenylborate salt bearing a 6-methoxynaphthoylmethyl group to cure an epoxy resin, its performance as a free-radical photoinitiator is also good. We have found that MNAPG is a very effective photoinitiator in initiating free-radical polymerization. Figures 5 and 6 compare the efficiencies of MNAPG and Darocur 1173 (a widely used free-radical initiator) in the photopolymerization of TMPTA. The mass ratio was TMPTA/initiator = 99:1. Compared with that of Darocur 1173, the polymerization rate of TMPTA initiated by MNAPG in N$_2$ increased more rapidly at the beginning of the polymerization, and the final conversion was higher. It is presumed that the initiation efficiency was improved by the 6-methoxynaphthoylmethyl chromophore, whose typical absorption band is 270–380 nm and can better match the main emission wavelength of a medium-pressure mercury lamp. The polymerization profiles conducted in N$_2$ with

MNAPG were higher than those in air with MNAPG, and this suggests that the inhibiting effect of oxygen is workable.

CONCLUSIONS

A quaternary ammonium tetraphenylborate salt bearing a 6-methoxynaphthoylmethyl group (MNAPG) has been prepared. MNAPG has good thermal stability. UV–vis spectra show a typical absorption wavelength of MNAPG at 270–380 nm. The mass spectrometry results show that the photolysis of MNAPG produces TEDA and other fragments. In fact, the photolysis of MNAPG results in the formation of TEDA and a free radical. Therefore, MNAPG is not only an effective photoinitiated thermal crosslinker for an epoxide such as EPON827 but also an excellent free-radical initiator for acrylate or methyl acrylate
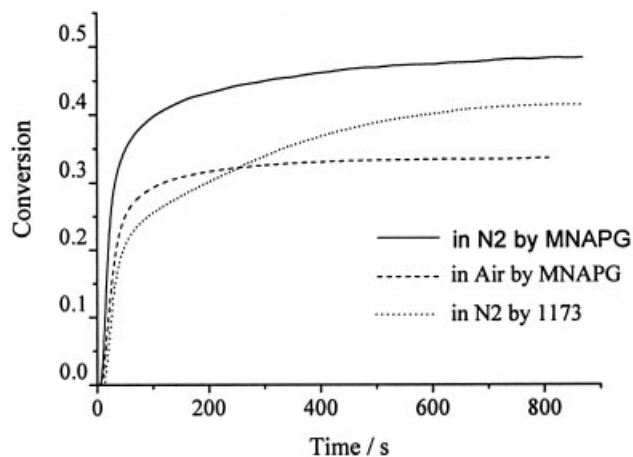
Figure 6 Double-bond conversion of TMPTA in different atmospheres initiated by MNAPG and Darocur 1173.

monomers such as TMPTA, and it may be valuable for the synthesis of a hybrid material.

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