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Preparation of a series of photoinitiators and their use in the thermal curing of epoxide and radical polymerization of acrylate

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Abstract

A series of photoinitiators, quaternary ammonium tetraphenylborate salts (QA Salts-BPh_4) with various chromophores, have been synthesized and characterized by elemental analysis (EA), ^1H NMR and IR. The photochemistry and photophysics of QA Salts-BPh_4 have been investigated by UV spectroscopy. The formation of triethylenediamine (TEDA) and phenyl free radical in the photolysis of QA Salts-BPh_4 was ascertained by mass spectrometric method. Their reactivity in the thermal curing of epoxide resin such as EPON827 and radical polymerization of acrylate monomers such as trimethylolpropane triacrylate (TMPTA) was studied. It is found that the relative initiator efficiency of QA Salts-BPh_4 is related to the structure of chromophore.

Keywords: Phtoinitiator; Epoxy thermal curing; Free radical polymerization

1. Introduction

There is more and more reports about free radical polymerization which is important in the fields of polymerization [1–3]. Triphenylbutylborate salts are well-known as the most effective photoinitiators compared to substituted di-, tri-, and tetraalkyl borates which are unstable [4–7]. The mechanism of photogenerating radicals from triphenylbutylborate salts involves photoinduced electron transfer from the borate anion to an excited state of the chromophore, likely forming a triphenylbutylborate radical, which in turn undergoes rapid cleavage to triphenylboron and butyl radical [8]. Tetraphenylborate salts have been thought to be inefficient because they contain no alkyl group while phenyl radical is poorer initiating species, less stable and easier to back electron transfer. However, Neckers, have reevaluated the applicability of tetraphenylborate salts as free radical photoinitiators, by measurement of relative initiation efficiency of borate salts contained the same chromophore as the cation and either tetraphenylborate and triphenylbutylborate as counteranion [9].

Recently, we have successfully prepared a series of quaternary ammonium tetraphenylborate salts bearing different chromophores (Scheme 1). They produce not only free radicals but also tertiary amines. The former can initiate rapidly free radical polymerization of acrylate or methylacrylate monomers. The latter as catalytic curing agent is found suitable for the thermal crosslinking of epoxy resin where nucleophilic attack on the epoxy ring is favorable. So they are anticipated to be applied in the hybrid UV curing which is attracting more and more attention [10,11]. Their photochemistry behaviors before and after irradiation were dependent on the structure of chromophore. Photolysis rate of both QA SaltII-BPh_4 and QA SaltIII-BPh_4 is faster than that of QA SaltI-BPh_4. Correspondingly, photo-initiating efficiency of both formers is better than that of the latter. It is responsible for this phenomenon that absorption spectra of QA SaltII-BPh_4 and QA SaltIII-BPh_4 can match with the emission wavelength of the medium pressure mercury lamp, whereas that of QA SaltI-BPh_4 cannot. It is worth pointing out that when QA SaltIII-BPh_4 is used as radical initiator, the inhibiting effect of oxygen for the radical polymerization of TMPTA has

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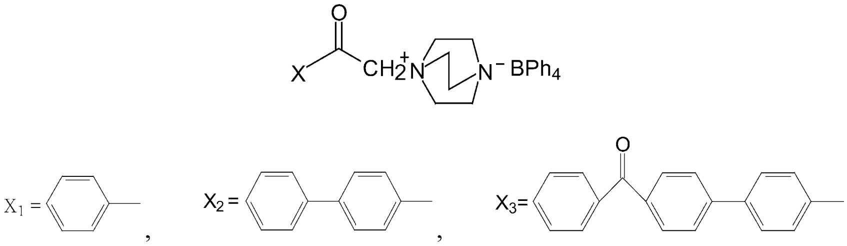


Scheme 1. The structure of quaternary ammoniums named QA SaltI-BPh$_4$, QA SaltII-BPh$_4$ and QA SaltIII-BPh$_4$ corresponding to the chromophore of X$_1$, X$_2$ and X$_3$, respectively.

been suppressed. This may be owned to the presence of tertiary amine and benzophenone.

2. Experimental section

2.1. Chemicals

Triethylenediamine (TEDA) from Alfa Aesar, Epoxide EPON827 from Shell, Trimethylolpropane triacrylate (TMPTA) from Cognis and Darocur 1173 from Ciba were used without further purification. 4-Acetylbiphenyl and 4-phenylbenzophenone were provided by Jintan Huashan Chemical Factory. Sodium tetraphenylboron was purchased from Shantou Guanghua Chemical Company. All other chemicals used were analytically pure.

2.2. Analysis

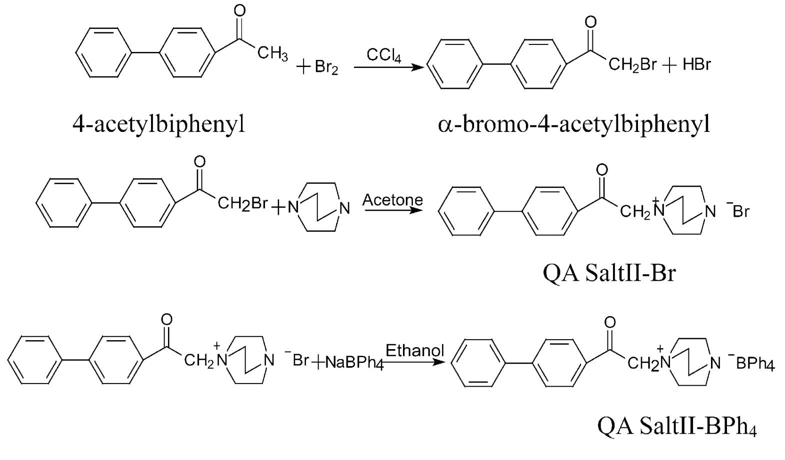
Melting point was measured on a Sanguang 248 X$_4$ instrument. Elemental analyses were carried out on an Elementar Vario EL instrument (Germany). ^{1}H NMR spectra were taken on a Varian Unity Inova 500 spectrometers. IR spectra were recorded on a Nexus 670 FT-IR. UV spectra were taken on a Shimadzu UV-240 UV–visible spectrophotometer. Mass spectrometry (MS) was taken on LCQ™ DECA XP liquid chromatography-mass spectrometry instrument. Thermogravimetric analysis (TGA) was carried out on a Netzsch TG 209C at a heating rate of 20 °C/min with a pure N$_2$ (or air) gas flow of 40 ml/min. DPC was taken on a modified CDR-4 model differential scanning calorimeter.

2.3. Synthesis of quaternary ammonium tetraphenylborate salts

Quaternary ammonium tetraphenylborate salt bearing acetylbiphenyl (QA SaltII-BPh$_4$), used as an example, was prepared as shown in Scheme 2. That is, 4-acetylbiphenyl was reacted with bromine in carbon tetrachloride to obtain α-bromo-4-acetylbiphenyl. QA SaltII-Br was prepared by the reaction between α-bromo-4-acetylbiphenyl and triethylenediamine (TEDA) in acetone at room temperature. The target product (QA SaltII-BPh$_4$) was obtained by the anion exchange of QA SaltII-Br with sodium tetraphenylboron in ethanol.

2.3.1. α-Bromo-4-acetylbiphenyl

Bromine (2.2 ml, 0.043 mol) was slowly added to the solution of 4-acetylbiphenyl (7.85 g, 0.04 mol) in carbon tetrachloride at room temperature and stirred for 6 h. The solvent was evaporated and the solid was dried under vaccum. After recrystallization from ethanol, α-bromo-4-acetylbiphenyl was obtained as white crystal (7.93 g, 72%). Mp: 108–110 °C. ^{1}H NMR (CDCl$_3$, δ ppm): 4.488 (s, 2H), 7.408 (dd, 1H), 7.471 (t, 2H), 7.616 (t, 1H), 7.639 (t, 1H),



Scheme 2. Preparation of the quaternary ammonium tetraphenylborate.

7.672 (t, 1H), 7.700 (t, 1H), 8.016 (t, 1H), 8.046 (t, 1H). Elem. Anal. Calcd for $C_{14}H_{11}OBr$: C 61.115, H 4.315. Found: C 61.025, H 4.406.

2.3.2. 4-Acetylbiphenyl-(1-azonia-4-azabicyclo[2,2,2]octane) bromide (QA SaltII-Br)

The solution of α-bromo-4-acetylbiphenyl (2.75 g, 0.01 mol), and triethylenediamine (1.12 g, 0.01 mol) in acetone was stirred at room temperature for 8 h. The resulting solution was filtered and precipitation was washed with acetone, then dried under vacuum. After recrystallization from ethanol, QA SaltII-Br was obtained as white crystal (2.63 g, 68%). Decompose at 210–212 °C without melting. ^1H NMR ($CDCl_3$, δ ppm): 3.276 (t, 6H), 4.154 (t, 6H), 5.859 (s, 2H), 7.421 (dd, 3H), 7.514 (t, 1H), 7.540 (t, 1H), 7.637 (t, 1H), 7.667 (t, 1H), 8.175 (t, 1H), 8.202 (t, 1H). Elem. Anal. Calcd for $C_{20}H_{23}ON_2Br$: C 62.021, H 5.985, N 7.233. Found: C 61.13, H 6.281, N 6.950.

2.3.3. 4-Acetylbiphenyl-(1-azonia-4-azabicyclo[2,2,2]octane) tetraphenylborate (QA SaltII-BPh4)

QA SaltII-Br (1.94 g, 0.005 mol) was dissolved in ethanol (100 ml) upon heating. The sodium salt of tetraphenyl borate (1.71 g, 0.005 mol) in a minimum 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 under vacuum. QA SaltII-BPh_4 was obtained as white powder (2.04 g, 65%). Mp: 202–204 °C. ^1H NMR (acetone, δ ppm): 3.364 (t, 6H), 3.909 (t, 6H), 5.293 (s, 2H), 6.774 (t, 4H), 6.922 (t, 8H), 7.309–7.366 (s, 8H), 7.443 (dd, 1H), 7.500 (t, 2H), 7.725 (t, 1H), 7.751 (t, 1H), 7.866 (t, 1H), 7.893 (t, 1H), 8.096 (t, 1H), 8.126 (t, 1H). Elem. Anal. Calcd for $C_{44}H_{43}ON_2B$: C 84.335, H 6.916, N 4.47. Found: C 83.84, H 7.101, N 4.488.

2.3.4. 1-Phenacyl-(1-azonia-4-azabicyclo[2,2,2]octane) bromide (QA SaltI-Br)

Yield: 42.3%. Decompose at 237 °C without melting. ^1H NMR ($CDCl_3$, δ ppm): 3.26 (t, 6H), 4.14 (t, 6H), 5.85 (s, 2H), 7.48 (t, 2H), 7.62 (t, 1H), 8.12 (d, 2H). Elem. Anal. Calcd for $C_{14}H_{19}N_2Obr$: C 54.04, H 6.111, N 9.006. Found: C 54.18, H 6.291, N, 9.192.

2.3.5. 1-Phenacyl-(1-azonia-4-azabicyclo[2,2,2]octane) tetraphenylborate (QA SaltI-BPh4)

Yield: 60.39%. Mp: 195–197 °C. ^1H NMR (acetone, δ ppm): 3.30 (t, 6H), 3.81 (t, 6H), 5.17 (s, 2H), 6.78 (t, 4H), 6.92 (t, 8H), 7.34 (s, 8H), 7.58 (t, 2H), 7.73 (t, 1H), 7.99 (d, 2H). Elem. Anal. Calcd for $C_{38}H_{39}N_2OBr$: C 82.94, H 7.093, N 5.093. Found: C 82.59, H 7.113, N 4.933.

2.3.6. α-Bromo-4-(4′-benzoylphenyl) acetophenone

Yield: 76%. Mp: 143–145 °C. IR (KBr, ν cm^{-1}): 3052, 1680, 1644, 1278, 829, 692, 655; ^1H NMR ($CDCl_3$, δ ppm): 4.477 (s, 2H), 7.493 (t, 2H, $J=14.7$ Hz), 7.603 (t, H, $J=14.7$ Hz), 7.741 (t, 4H, $J=17.1$ Hz), 7.822 (d, 2H, $J=6.9$ Hz), 7.906 (d, 2H, $J=8.1$ Hz), 8.086 (d, 2H, $J=8.4$ Hz). Elem. Anal. Calcd for $C_{21}H_{15}O_2Br$: C 66.49, H 3.958. Found: C 67.49, H 4.113.

2.3.7. 4-(4′-Benzoylphenyl)acetophenone-(1-azonia-4-azabicyclo[2,2,2]octane) bromide (QA SaltIII-Br)

Yield: 80%. Decompose at 176–178 °C without melting. IR (KBr, ν cm^{-1}): 3430, 2965, 2908, 1691, 1643, 1469, 1238, 1056, 792, 701; ^1H NMR ($CDCl_3$, δ ppm): 3.270 (t, 6H, $J=14.4$ Hz), 4.149 (t, 6H, $J=15$ Hz), 5.917 (s, 2H), 7.484 (t, 2H, $J=14.7$ Hz), 7.592 (t, 3H, $J=14.7$ Hz), 7.682 (d, 2H, $J=8.1$ Hz), 7.814 (dd, 4H, $J=22.2$ Hz), 8.228 (d, 2H, $J=8.4$ Hz). Elem. Anal. Calcd for $C_{27}H_{27}O_2N_2$: C 65.99, H 5.499, N 5.703. Found: C 65.34, H 6.000, N 5.127.

2.3.8. 4-(4′-Benzoylphenyl)acetophenone-(1-azonia-4-azabicyclo[2,2,2]octane) tetraphenylborate (QA SaltIII-BPh4)

Yield: 86%. Decompose at 210–212 °C without melting. IR (KBr, ν cm^{-1}): 3145, 3054, 2998, 2890, 1697, 1656, 1602, 1479, 1427, 1396, 1276, 831,705; ^1H NMR ($CDCl_3$, δ ppm): 3.353 (t, 6H, $J=14.7$ Hz), 3.903 (t, 6H, $J=15$ Hz), 5.309 (s, 2H), 6.749 (t, 4H, $J=14.4$ Hz), 6.897 (t, 8H, $J=14.7$ Hz), 7.284–7.342 (m, 8H), 7.557 (t, 2H, $J=14.7$ Hz), 7.671 (t, 1H, $J=14.7$ Hz), 7.800 (dd, 2H, $J=9.4$ Hz), 7.900 (d, 4H, $J=1.8$ Hz), 7.972 (d, 2H, $J=8.4$ Hz); 8.145 (d, 2H, $J=8.7$ Hz); LCMS (*m/z*): 411 (M^+), 319 (N^-). Elem. Anal. Calcd for $C_{51}H_{47}O_2N_2B$: C 83.80, H 6.438, N 3.835. Found: C 83.44, H 6.598, N 3.622.

2.4. Photolysis method

Photolysis was carried out by a medium-pressure mercury lamp. The light intensity was determined by a UV light illuminometer. An acetonitrile or ethanol solution containing QA Salts-BPh_4 (1.0×10^{-5} M) was put into a quartz cell. The solution in the quartz cell was irradiated for different times. Spectra of the solution before and after irradiation were measured respectively.

2.5. Photoinitiated free radical polymerization of different monomer

TMPTA was selected as the monomer for testing the efficiency of initiators. Content of initiator is 1 wt% in the mixture of monomer and initiator. Photoreactivity was respectively compared between QA Salts-BPh_4 synthesized and Darocur 1173. The photoreactivity was studied using a modified CDR-4 model differential scanning calorimeter. Sensitive wavelength is 360 and 313 nm and light intensity is 3.0 mW/cm^2.

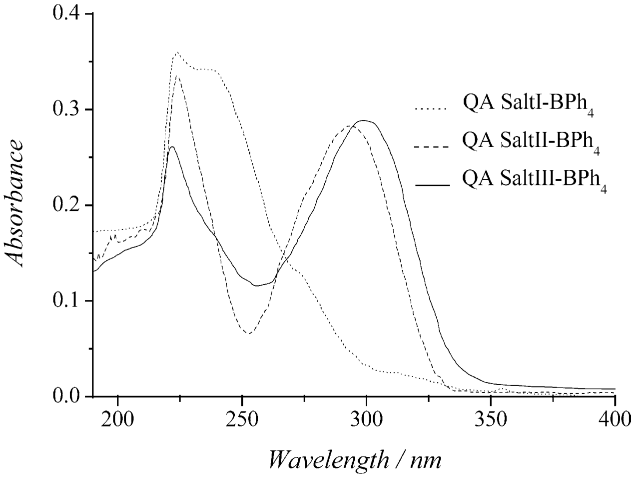


Fig. 1. Absorption spectra of QA Salts-BPh$_4$ in acetonitrile.

2.6. Photoinitiated thermal epoxide curing

Mixtures of QA Salt-BPh$_4$ and a commercial epoxide EPON827 (mass ratio epoxide/QA Salt-BPh$_4$=9:1) were spread on KBr plates. The mixtures were irradiated on the UV curing machine for 10 s (light intensity is 30 mW/cm^2 in the middle of machine). Then some of the mixtures posbaked at high temperature. The results were observed visually and measured quantitatively by FT-IR spectra.

3. Results and discussion

3.1. UV absorption spectroscopy

The absorption spectra of three QA Salts-BPh$_4$ in acetonitrile (1.0×10^{-5} M) were shown in the Fig. 1. The longer wavelength band (~300 nm) allows assignment of a $\pi\rightarrow\pi^*$ orbital transition to the band and the shorter wavelength band (~220 nm) allows assignment of a $n\rightarrow\pi^*$ orbital transition to the band. For QA SaltII-BPh$_4$ and QA SaltIII-BPh$_4$, both $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions are possible. While QA SaltI-BPh$_4$ is mainly $n\rightarrow\pi^*$ transition. This property is dependent on the characteristic of the chromophore. The higher conjugation level of QA SaltII-BPh$_4$ and QA SaltIII-BPh$_4$ than that of QA SaltI-BPh$_4$ is responsible for their longer absorption wavelength.

Figs. 2–4 show UV spectral changes of QA Salts-BPh$_4$ on irradiation of a medium pressure mercury lamp in acetonitrile and in ethanol. The irradiation energy was 3.0 mJ/cm^2. The arrows in the figures show the change tendencies of the peaks with increasing irradiation time. The quick decrease in absorption at ~300 nm in the UV spectral changes of QA SaltII-BPh$_4$ and QA SaltIII-BPh$_4$ was observed, and a new absorption at ~260 or ~280 nm appeared (Figs. 3 and 4). The decrease in absorption at ~300 nm is the result of photolysis and the new absorption can attribute to the formation of 4-acetylbiphenyl or 4-phenylbenzophenone. For QA SaltI-BPh$_4$, the photolysis rate is very slow (Fig. 2), which may attribute to the much shorter absorption wavelength of QA SaltI-BPh$_4$ than the emission wavelength of medium pressure mercury lamp. It is obvious that when absorption wavelength of chromophore can match well with emission wavelength of medium pressure mercury lamp, photolysis rate is quick, and vice versa.

3.2. The photolysis mechanism of QA Salts-BPh$_4$

In the photolysis of QA Salts-BPh$_4$, it had been suggested that tertiary amines and phenyl free radicals are generated [12,13]. The mechanism of radicals produced on irradiation involves electron transfer from the borate anion to the excited acceptor. Upon irradiation, the light absorbing

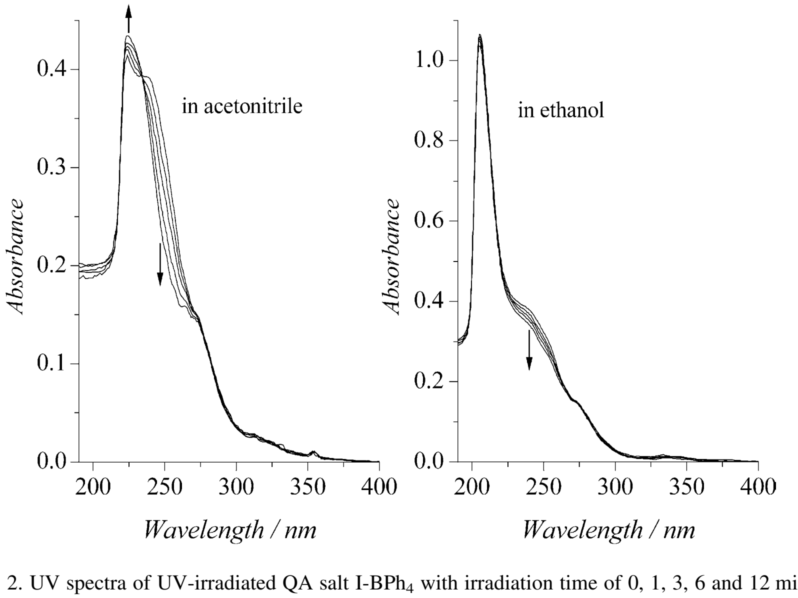


Fig. 2. UV spectra of UV-irradiated QA salt I-BPh$_4$ with irradiation time of 0, 1, 3, 6 and 12 min.

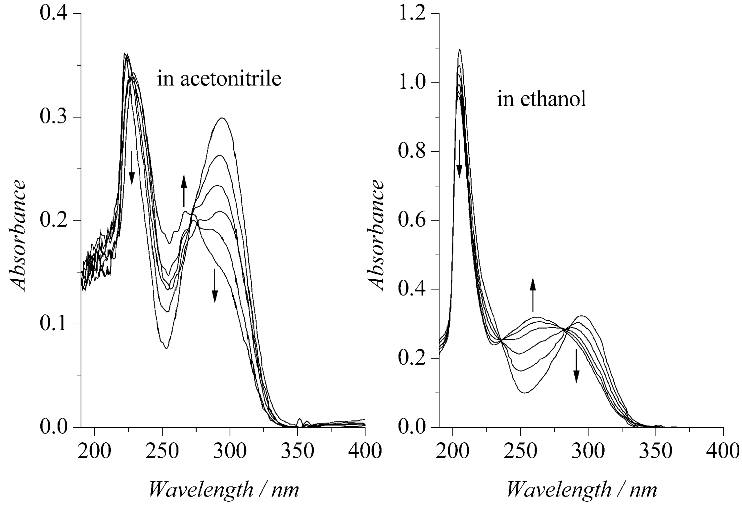


Fig. 3. UV spectra of UV-irradiated QA salt II-BPh$_4$ with irradiation time of 0, 1, 3, 5, 8 and 12 min.

chromophore (4-acetylbiphenyl) is promoted to its excited state, which is subsequently reduced by the tetraphenylborate anions. The resulting chromophore radical anion further fragments into a substituted alkyl radical and a free amine while the borate radical decomposes into phenyl free radicals and boron triphenyl (Scheme 3).

Mass spectrometric method for the photolysis of QA Salts-BPh$_4$ has been established, which is a more rapid and simple method compared with ^{1}H NMR. Take QA SaltII-BPh$_4$ for instance, MS of cation (*m*/*z* 307.2) and anion (*m*/*z* 319.3) of QA SaltII-BPh$_4$ before irradiation was shown in Fig. 5. While after irradiation, a decrease in relative abundance of *m*/*z* 307.2 cation was observed (Fig. 6). The decrease in this peak means the photo-decomposition of QA SaltII-BPh$_4$. At the same time, both figures show that photolysis of QA SaltII-BPh$_4$ by UV-induced electron transfer produces new fragments such as *m*/*z* 113.2, *m*/*z* 216.2, *m*/*z* 278.2 and *m*/*z* 292.3 etc. The appearance of *m*/*z* 113.2 indicates that TEDA is generated by the photolysis of QA SaltII-BPh$_4$. It is thought that fragment of *m*/*z* 242.3 is formed by coupling of the radicals, such dibenzoyl and phenyl radical. So the appearance of *m*/*z* 242.3 implies the formation of phenyl radical in the photolysis process, which can initiate free radical polymerization (refer to Table 1).

Based on the analysis above, the photolysis products of QA Salts-BPh$_4$ can be applied to the free radical polymerization of acrylate or methylacrylate and photo-induced thermal crosslinking of epoxy resin.

3.3. Free radical polymerization

Relative initiation efficiency of QA Salts-BPh$_4$ was studied using DPC technique on a modified CDR-4 model differential scanning calorimeter. The mass ratio is monomer/initiator = 99:1. Darocur 1173, as a widely used free radical photoinitiator with relatively high photoinitiating

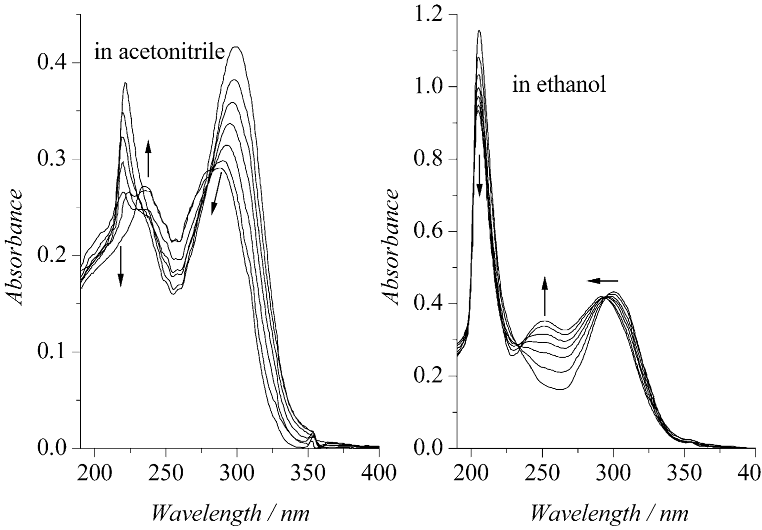
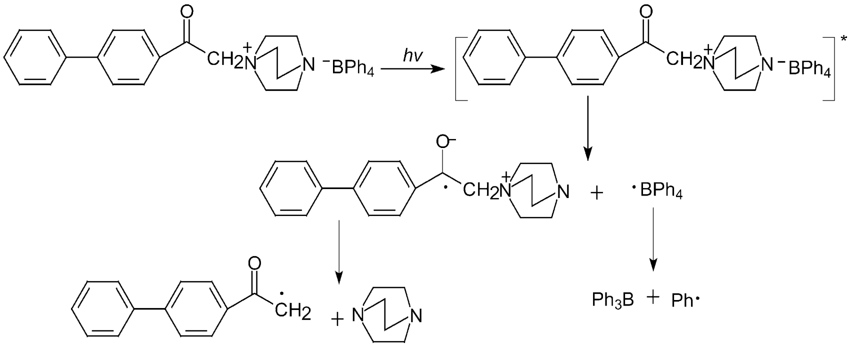


Fig. 4. UV spectra of UV-irradiated QA salt III-BPh$_4$ with irradiation time of 0, 1, 2, 3, 5, 8 and 12 min.



Scheme 3. Photolysis of QA SaltII-BPh$_4$.

activity, was used here for comparison. Scheme 4 shows the structure of Darocur 1173.

It is found from Fig. 7(a) that the initiation efficiency of QA saltI-BPh$_4$ was very poor and it only photoinitiated free radical polymerization of TMPTA in N$_2$. From Figs. 7(b) and 8(b) we can find that the initiation efficiency of QA saltII-BPh$_4$ was very high in N$_2$, while relatively low in air. At the beginning of polymerization, the polymerization rate of TMPTA increased more rapidly in N$_2$ than in air, and the final conversion was also obviously higher. Usually, both the rate and double bond conversion of free radical polymerization in N$_2$ are higher than that in air due to the inhibiting effect of oxygen. This suggests that the inhibiting effect of oxygen has been workable for free radical polymerization of TMPTA initiated by QA saltII-BPh$_4$.

It can also be found that the photoinitiating activity of QA saltII-BPh$_4$ and QA saltIII-BPh$_4$ approached that of Darocur 1173, the successful commercial photoinitiator.

From Figs. 7(c) and 8(c), we find that the polymerization profiles of TMPTA conducted in N$_2$ or in air are almost the same, which indicates that both in N$_2$ and in air, QA SaltIII-BPh$_4$ is a very effective photoinitiator in initiating the free radical polymerization of TMPTA. The result suggests that the inhibiting effect of oxygen has been suppressed, this may be due to the presence of 4-phenylbenzophenone and tertiary amine whose anti-oxygen effect in photopolymerzation is well documented.

QA SaltI-BPh$_4$ should give phenyl radical upon irradiation at ~250 nm whereas QA SaltII-BPh$_4$ and QA SaltIII-BPh$_4$ give phenyl radical upon irradiation at

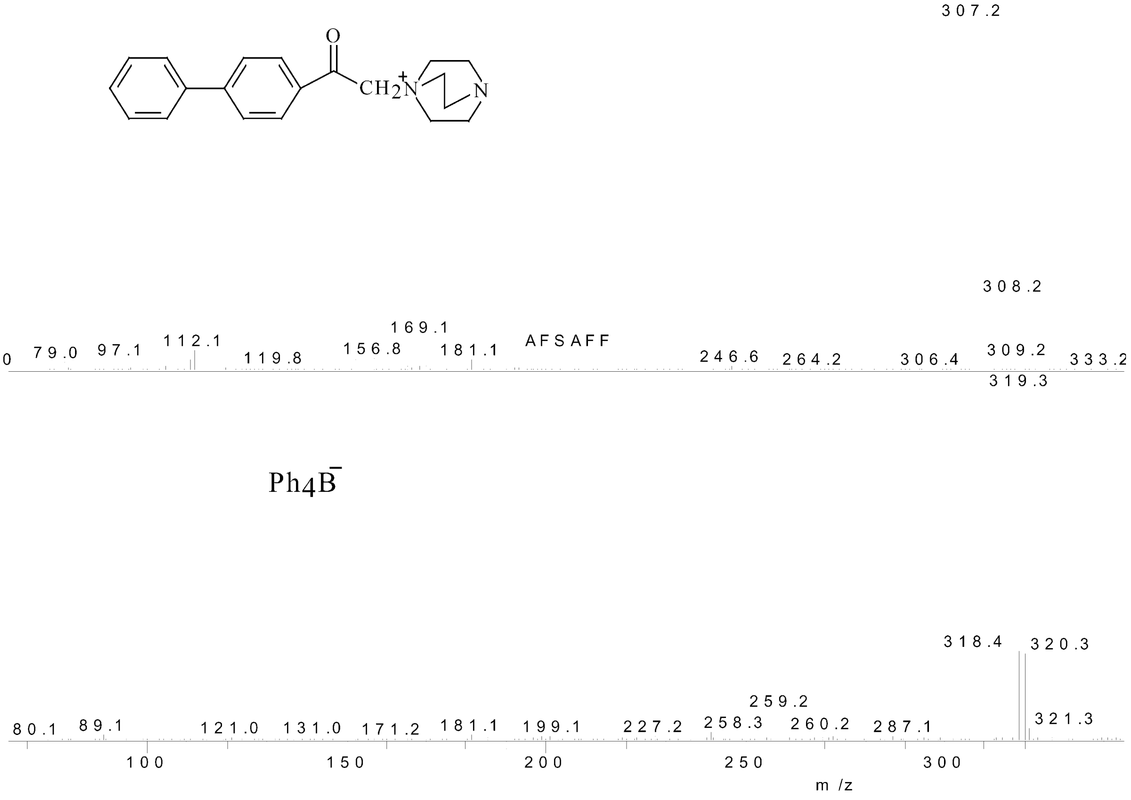


Fig. 5. MS of cation and anion in QA SaltII-BPh4 before irradiation.

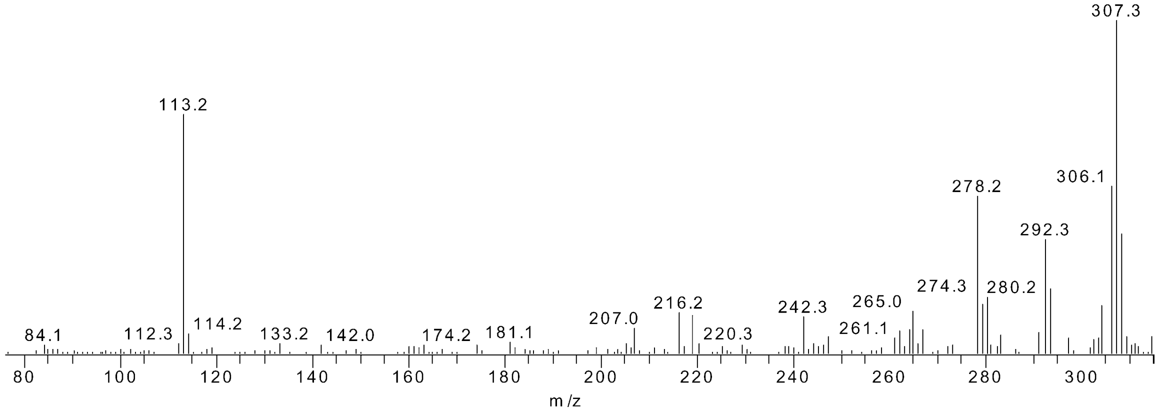
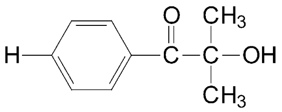


Fig. 6. MS changes of cation in QA SaltII-BPh4 after irradiation.



Scheme 4. Structure of Darocur 1173.

~300 nm according to their absorption spectra (Fig. 1). As we know, the emission wavelength of a medium pressure mercury lamp is mainly 365 and 313 nm. Both latter can match with wavelength of the medium pressure mercury lamp, so their initiation efficiency is better than that of the former. 4-Phenylbenzophenone and tertiary amine are formed in the photolysis products of QA SaltIII-BPh$_4$, so the inhibiting effect of oxygen for the free radical polymerization of TMPTA has been suppressed.

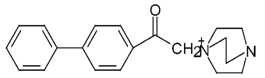
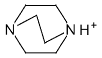
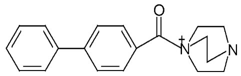
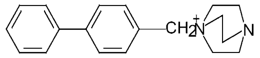
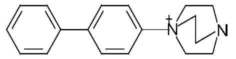
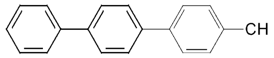
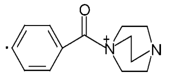
3.4. Tertiary amine catalyzed thermal curing of epoxide resin

Polymerization of epoxides with tertiary amines, as curing agents, is believe to be a two-stage process (Scheme 5). The initiating step involves nucleophilic attack of an amine on carbon which leads to the epoxy ring opening. The following chain reaction leads to a cross-linked product in case of the polyfunctional epoxides [14].

A commercial epoxide EPON827 was selected for the curing experiment. Take QA SaltII-BPh$_4$ for instance, mixture of QA SaltII-BPh$_4$ and EPON827 (mass ratio EPON827/QA SaltII-BPh$_4$ = 9:1) was spread on glass supports. Mixture only exposed to UV irradiation did not be cured besides yellowish. Heating the mixture at 130 °C for hours without irradiation can induce slightly curing due to the residual tertiary amine in TEDA unit. When the sample was exposed to UV light for thirty seconds and then heated at 130 °C for hours, a crosslinked polymer network was formed and was insoluble in acetone. It is obvious that the epoxy resin is cured by TEDA, one of the photolysis products of QA SaltII-BPh$_4$.

This curing process was clearly shown by the IR spectra of the mixtures (Fig. 9). There was a strong absorption band at 912 cm^{-1} assigned to the closed epoxide rings in the (a) which isn't irradiated and heated. IR spectrum (b) of

Table 1
MS date of fragments decomposed from *m/z* 307 cation

m/z	Fragment	Elemental constitution	Calcd for chemical formula
307.3		$C_{20}H_{23}N_2O$	307.42
113.2		$C_6H_{13}N_2$	113.18
292.3		$C_{19}H_{21}N_2O$	293.39
278.2		$C_{19}H_{23}N_2$	279.41
265.0		$C_{18}H_{21}N_2$	265.38
242.3		$C_{19}H_{14}$	242.32
216.0		$C_{13}H_{16}N_2$	216.28

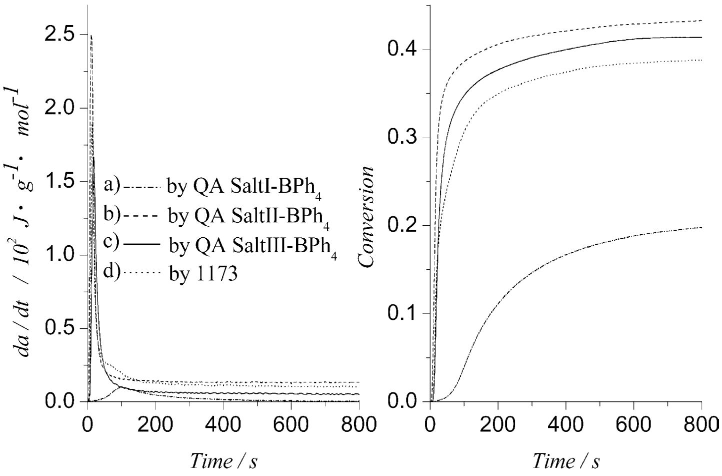


Fig. 7. Photopolymerization rate and double bond conversion of TMPTA in N_2.

mixture which was UV irradiated for 1 min and heated for 0.5 h have changed. There was a significant decrease in intensity of a band at 912 cm^{-1} and a significant increase in intensity of a band at 1110 cm^{-1} assigned to ether linkages formed by ring opening. Intensity of a band at 912 cm^{-1} kept on decreasing in the (c) which is irradiated for 1 min and heated for 1 h. Going ahead with heating, the band at 912 cm^{-1} almost disappeared in the (d) which is irradiated for 1 min and heated for 2.0 h. The behavior of QA SaltII-BPh$_4$ in effecting polymerization of epoxides proves to the proposed mechanism of its photolysis.

The curing kinetics of epoxy resin EPON827 cured by QA SaltII-BPh$_4$ was studied by DSC (Fig. 10). The results showed that the curing reaction carried through two stages: the first stage was addition reaction; the second stage was catalytic-polymerization.

Eq. (1) is Kissinger equation [15] which is the expression of relation between Φ and T_m:

$$\frac{d\left(\ln\dfrac{\Phi}{T_m^2}\right)}{d\left(\dfrac{1}{T_m}\right)} = -\frac{E}{R} \tag{1}$$

where Φ is the heating rate, T_m the temperature of peak, R the gas constant, E the activation energy. By integrating Eq. (1) we can obtain:

$$\ln\frac{\Phi}{T_m^2} = -\frac{E}{R}\frac{1}{T_m} + C \tag{2}$$

The activation energy E can be determined by DSC via Eq. (2). A series of T_m was obtained from DSC by changing the heating rate Φ, then the curve of $\ln(\Phi/T_m^2) \sim 1/T_m$ was made as shown in Fig. 11, and the values of E were calculated by the slope and found to be 78.55 and 111.02 kJ/mol for the first step and the second step, respectively.

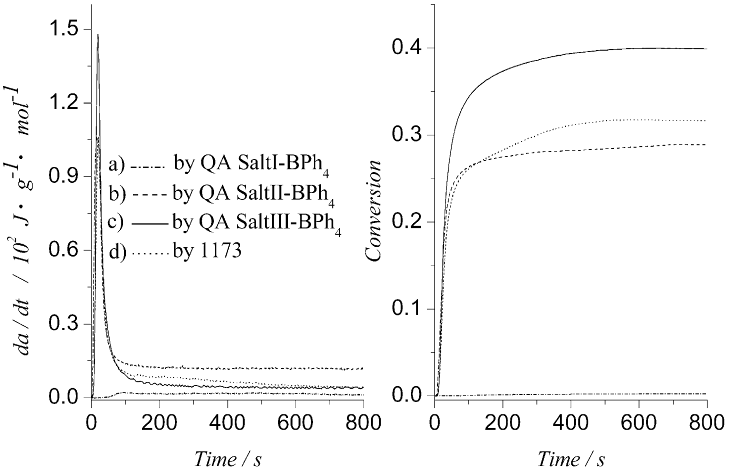
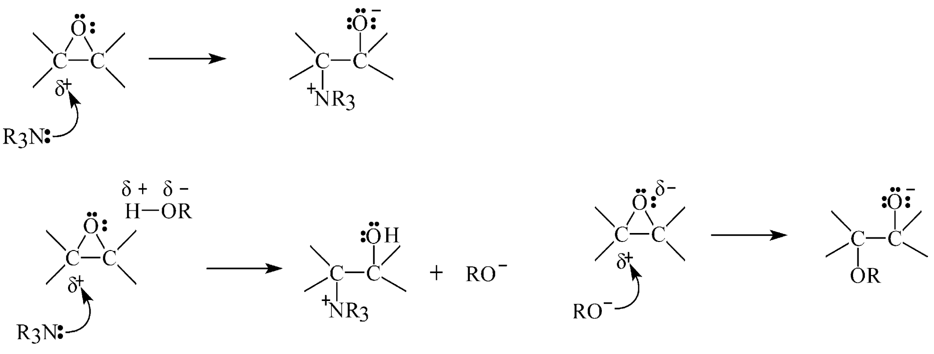


Fig. 8. Photopolymerization rate and double bond conversion of TMPTA in air.



Scheme 5. Mechanism of anionic polymerization of epoxides with tertiary amines as initiators.

3.5. Thermal stability of QA Salts-BPh$_4$

The thermal degradation temperature (T_d) of QA Salts-BPh$_4$ was measured with thermogravimetric analysis (TGA) to estimate their thermal stability (Fig. 12). The results show they all have quite high T_d. The initial thermal decomposing temperature of QA SaltI-BPh$_4$ is 190 °C, that of QA SaltII-BPh$_4$ is 205 °C and that of QA SaltIII-BPh$_4$ is 216 °C. They all show good thermal stability. In fact, they can be laid aside for one year or even longer time at room

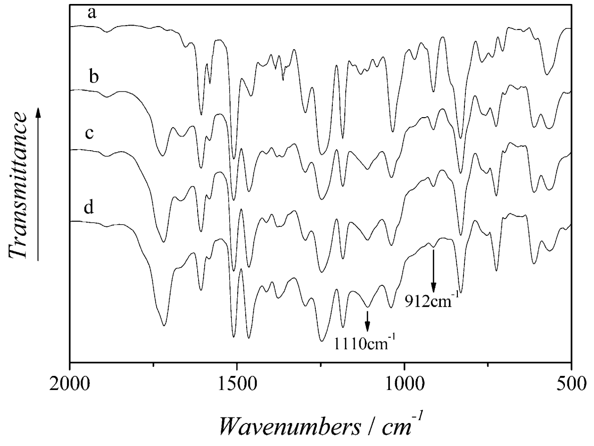


Fig. 9. IR spectra of mixture of QA SaltII-BPh$_4$ and EPON827. (a) No irradiation and no postbaking; (b) UV irradiation for 1 min and postbaking for 0.5 h; (c) UV irradiation for 1 min and postbaking for 1 h; (d) UV irradiation for 1 min and postbaking for 2.0 h.

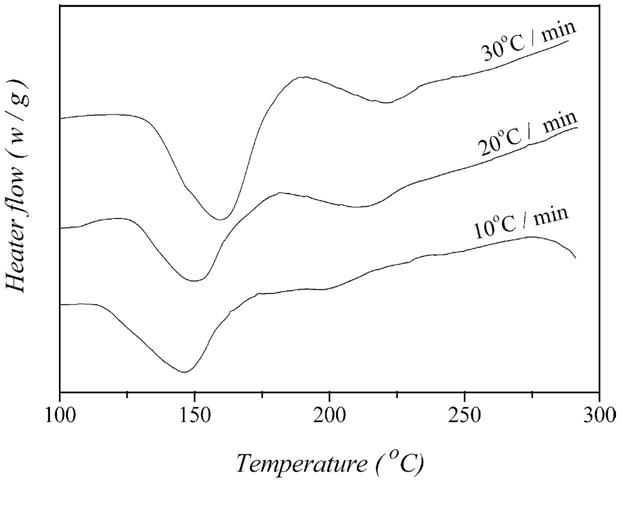


Fig. 10. The DSC curing curves of epoxy resin EPON827 with QA SaltII-BPh$_4$.

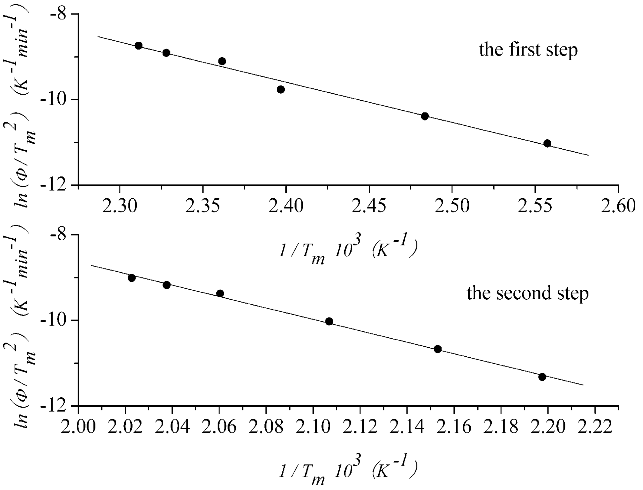


Fig. 11. Schematic diagram of $1/T_m \sim \ln(\Phi/T_m^2)$.

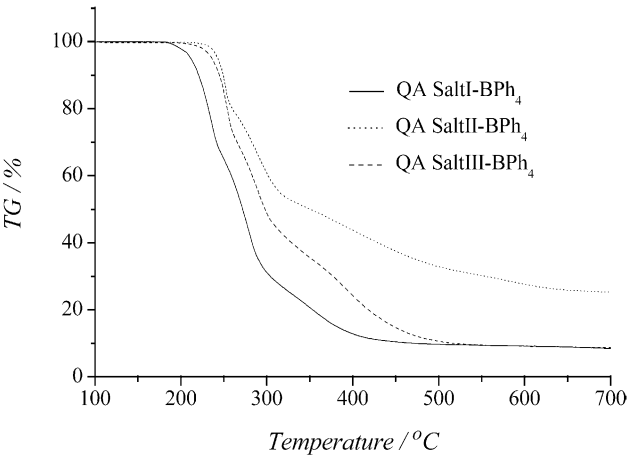


Fig. 12. TGA diagram of QA Salts-BPh$_4$ in N$_2$.

temperature avoiding irradiation. In the case of irradiation, they can immediately generate free radical. This is favorable to using as initiator.

4. Conclusion

A series of novel quaternary ammonium tetraphenylborate salts (QA Salts-BPh_4) bearing different chromophore have been prepared. The three QA Salts-BPh_4 are easily synthesized/purified and are stable. UV–visible spectra show the typical absorption wavelength of QA Salts-BPh_4 and the spectra will change on irradiation. The mass spectrometric results show that photolysis of QA Salts-BPh_4 produces TEDA and other fragments. In fact, the photolysis of QA Salts-BPh_4 resulted in the formation of TEDA and phenyl radical. Hence QA Salts-BPh_4 are not only an effective photoinitiated thermal crosslinker for epoxide such as EPON827 but also an excellent free radical initiator for acrylate such as TMPTA, this may be valuable for the synthesis of a hybrid material. Their photo-initiating efficiency was dependent on the structure of chromophore. It is worth pointing out that the inhibiting effect of oxygen for the free radical polymerization of TMPTA initiated by QA SaltIII-BPh_4 has been suppressed. We suppose that this is owned to the presence of tertiary amine and 4-phenylbenzophenone.

Acknowledgements

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