Synthesis and Photopolymerization of 4-(1-Propenyl)oxybutyl Acrylate

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ABSTRACT: Hybrid monomer, 4-(1-propenyl)oxybutyl acrylate, with cationic and free radical polymerizable group was synthesized. Real-time Fourier transform infrared spectroscopy (FTIR) was used to monitor the photopolymerization kinetics of the monomer. Photopolymerization processing conditions, such as light intensity, photoinitiator concentrations have been evaluated. It was found that hybrid monomer showed higher efficiency of photopolymerization in comparison with the blend system. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3388–3394, 2008

Key words: hybrid monomer; cationic photopolymerization; free radical photopolymerization; FTIR; kinetics

INTRODUCTION

In recent years, radiation curing has become an important technique for the application and curing of coatings, inks, and adhesives. There are two major basic chemistries that are employed in radiation curing: photoinitiated free radical polymerization and photoinitiated cationic polymerization.

Photoinitiated free radical polymerization is typically composed of mono-, di-, and multifunctional (meth)acrylate monomers and photoinitiator which are available in commercial quantities. The advantages of free radical polymerization includes: high rates of polymerization, low energy requirements, and environment friendly. But there are some disadvantages as well, which are atmospheric oxygen inhibition, volume shrinkage during polymerization, and high monomer residue.[1,2]

Photoinduced cationic polymerization requires a photoinitiator such as diaryliodonium, triarylsulfonium, or ferrocenium, and monomer such as epoxides, vinyl ethers. Photoinduced cationic polymerization show no oxygen inhibition, lower volume shrinkage, and less irritating to the skin, but recently, lack of suitable high reactivity monomer, sensitive to water and other impurities has retarded its application.[3,4]

To overcome the disadvantages of photoinitiated free radical polymerization and photoinduced cationic polymerization, sequential or simultaneous increase in the properties of the materials; hybrid photoinduced polymerization system has been developed. Decker[5,6] reported photopolymerization of (meth)acrylate/epoxide blend systems by using different wavelength ranges or by removal of a filter from a single source. This provided temporally controlled dual wavelength initiation. Lin and Stansbury[7] examined how variations in initiation conditions could impact the photopolymerization kinetics of blend systems. In recent years, one-step, one-pot methodology has been introduced to prepare hybrid polymers from comonomers that polymerize by different chemistries.[8–11]

In this article, a hybrid monomer with acrylate and propenyl ether groups was synthesized and the photopolymerization kinetics was investigated by FTIR. Photopolymerization processing conditions was studied as well.

EXPERIMENTAL

Materials and methods

1,4-butanediol, allyl bromide, and other agents were of analytical grade (Beijing Chemistry Company) and were used without further purification. Acryloyl chloride was prepared as described in the literature.[12] Triethyleneglycol divinyl ether (DVE-3, ISP Technologies), ethyl propenyl ether (EPE, Acros Organics), and *n*-butyl acrylate (BA, Beijing Chemical Reagent Company) were used as received. The
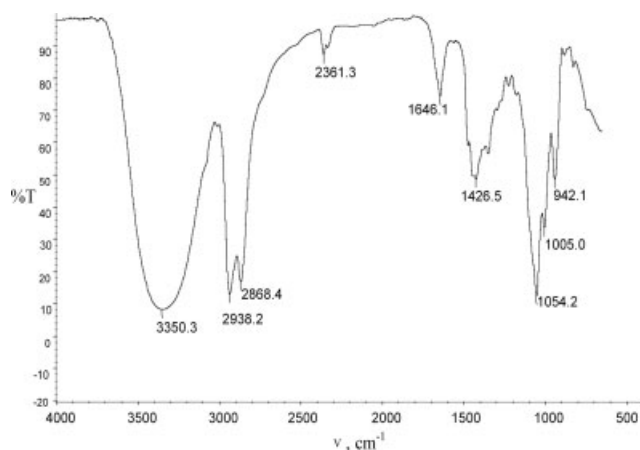
Figure 1 The FTIR spectra of 4-hydroxybutyl allyl ether.

photoinitiators, triarylsulfonium salt (45 wt % solution in propylene carbonate, UVI-6976, $\lambda_{max} = 280$ and 320 nm), and 2-hydroxy-2-methyl-1-phenyl-1-propanone (1173, $\lambda_{max} = 331$ nm) were donated by Runtec Chemical Company (Changzhou, China).

NMR

^{1}H-NMR spectra were recorded on a Bruker AV600 unity spectrometer operated at 600 MHz using TMS as an internal reference, with CDCl$_3$ as the solvent.

FTIR

Fourier transform infrared spectra (FTIR) were obtained on a Nicolet 5700 instrument (Thermo Electron Corp., Madison, WI). Series real time Fourier transform infrared spectroscopy (RTIR) was used to determine the conversion of double bond.[13] A mixture of monomer and initiator was applied between two KBr crystals, and a UV spot light source (Rolence-100 UV, Taiwan, China, dominant wavelength at 365 nm) was directed to the sample with light intensity of 15–70 mW/cm^2 (UV light Radiometer, Beijing Normal University, China) at room temperature. A horizontal transmission accessory (HTA) was designed to enable mounting of samples in a horizontal orientation for RTIR measurements.[14]

Synthesis of monomer

Synthesis of 4-hydroxybutyl allyl ether

Twenty-seven grams of 1,4-butanediol and 100 mL of toluene were placed into a 250-mL four-necked flask equipped with a magnetic stirrer, a thermometer, a nitrogen inlet, and dropping funnel. The reaction mixture was slowly heated to 40°C under magnetic stirring. 0.4 g of tetrabutyl ammonium bromide and 4 g of sodium hydroxide was added.

When the reaction mixture was heated to 65°C, a mixture of 12.1 g of allyl bromide dissolved in 20 mL toluene was added dropwise during 6 h. Then, the mixture was cooled to room temperature and the precipitate was filtered off and washed twice with 20 mL of toluene. The toluene was removed by rotary evaporation, and crude product was purified by vacuum distillation. Yield: 7.3 g (56%). The FTIR spectrum was shown in Figure 1.

IR (cm^{-1}): 3365.4 (v_{O-H}), 3081.3 ($v_{=C-H}$), 2937.9, 2864.2 (v_{c-H2}), 1646.2 ($v_{C=C}$), 1060.1 (v_{C-O}).

Synthesis of 4-hydroxybutyl 1-propenyl ether

A well-stirred solution of 4-hydroxybutyl allyl ether (13 g) and potassium *tert*-butoxide (3.54 g) in 100 mL of dimethyl sulfoxide (DMSO) was heated to 100–110°C for 2 h. When the mixture was cooled to room temperature, it was poured into 50 mL of water, then extracted with diethyl ether/hexane (1/1, v/v) for three times. The organic layer was dried overnight by anhydrous magnesium sulfate, and the solvent was removed by rotary evaporation. Then 4-hydroxybutyl 1-propenyl ether was obtained. Yield: 7.5 g (58%). The FTIR spectrum was shown in Figure 2 (see also Fig. 3).

IR (cm^{-1}): 3370.2(v_{O-H}), 3039.8 ($v_{=C-H}$), 2933.9, 2861.6 (v_{c-H2}), 1667.7 ($v_{C=C}$), 1097.3 (v_{C-O}).

Synthesis of 4-(1-propenyl)oxybutyl acrylate (POBA)

A mixture of 13 g of 4-hydroxybutyl 1-propenyl ether and 14 g of triethylamine dissolved in 100 mL of toluene was added into a three-necked flask equipped with stirrer, thermometer, and dropping funnel. Under cooling condition (0–5°C) by ice-salt bath, 9.05 g of acryloyl chloride dissolved in 20 mL of toluene was added over 2 h. The precipitate was
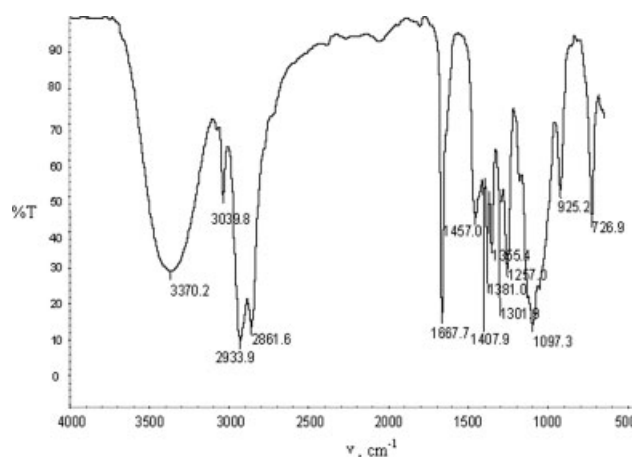

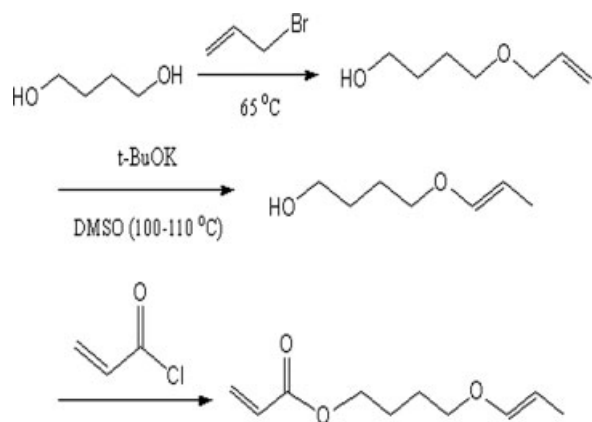**Figure 2** The FTIR spectra of 4-hydroxybutyl 1-propenyl ether.

Figure 3 Synthetic route of 4-(1-propenyl)oxybutyl acrylate.

Figure 5 The ^{1}H-NMR spectra of 4-(1-propenyl)oxybutyl acrylate (POBA).

filtered off and washed twice with 20 mL of toluene. Then the organic layers were combined and washed with water, 1 mol/L hydrochloric acid and 1 mol/L NaHCO$_3$ and dried over night with anhydrous sodium sulfate. The toluene was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (10/1, m/m) as eluent. Yield: 8.8 g (48%). The syntheses process has been shown in Figure 4. The product was identified by FTIR and ^{1}H-NMR (Fig. 5).

IR (cm^{-1}): 3040.5 ($\nu_{=C-H}$), 2954.0, 2917.79, 2872.7 ($\nu_{C-H2,C-H3}$),1725.9 ($\nu_{C=O}$), 1667.9 ($\nu_{C=C}$), 1637.1($\nu_{C=C}$), 1192.0 (ν_{C-O}), 810.2 ($\nu_{C=C}$).

^{1}H-NMR:δ (ppm) 6.39, 5.80 (d,2H,CH$_2$=),6.10 (m,1H,CH$_2$=CH—), 5.91 (d,1H, —OCH=CH—),4.36 (m,1H, —OCH=CH—), 4.16 (t,2H, —COOCH$_2$—), 3.73 (t,2H, —CH$_2$OCH=), 1.75 (m,2H, —CH$_2$CH$_2$OCH=), 1.67 (m,2H, —COOCH$_2$—CH$_2$—), 1.54 (d,3H, —CH$_3$).

RESULTS AND DISCUSSION

Effect of concentration of photoinitiator and light intensity

During UV irradiation, triarylsulfonium salt[15,16] produced both free radical and cationic reactive species, which could induce the polymerization of acrylate double bond (ADB) and propenyl ether double bond (PEDB), respectively.[17] Real time FTIR spectroscopic method could be used to directly measure the decrease of the acrylate double bond peak around 810 cm^{-1} and the 1-propenyl ether double bond (PEDB) peak around 1668 cm^{-1}. Upon irradiation, the decrease of the acrylate double bond absorption peak area from 792.61 to 829.25 cm^{-1} (Fig. 6) and the PEDB absorption peak area from 1650.79 to 1693.22 cm^{-1} accurately reflect the extent of free radical and cationic polymerization, respectively. Because the decrease of absorption of the peak area was directly proportional to the number of double bond functionalities that had been polymerized. Various kinetics parameters could be derived from the origin curve of absorbance peak area as a function of irradiation time.[18,19]

Figure 7 showed the relationship of double bond conversion and irradiation time. At the light intensity of 15 mW/cm^2, when the concentration of UVI-6976 increased from 0.5 wt % to 2.0 wt %, the rate of polymerization increased, but the acrylate double bond conversion decrease from almost 100% to about 90%, further increased the UVI-6976 concentration from 2.0 to 4.0 wt %, the rate of polymerization almost kept the same, double bond conversion slightly decreased [Fig. 7(a)]. At the light intensity of 70 mW/cm^2, when the concentration of UVI-9676 increased from 0.5 wt % to 2.0 wt %, the rate of polymerization increased, the final acrylate double bond conversion could reach the same (99%), further
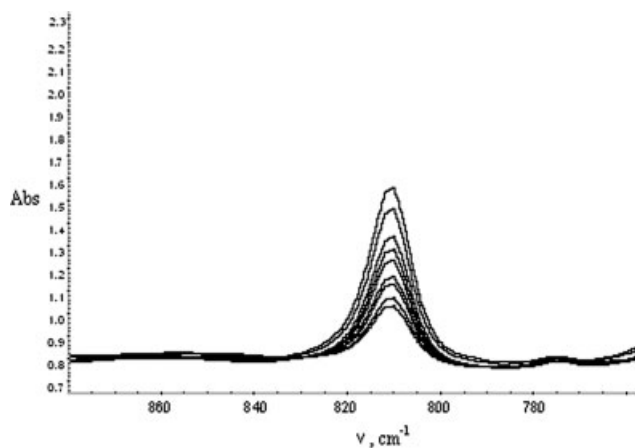

Figure 4 The FTIR spectra of 4-(1-propenyl)oxybutyl acrylate (POBA).

Figure 6 FTIR spectra of acrylate double bond recorded at various time intervals after irradiation.

increased the concentration of initiator from 2.0 to 4.0 wt %, the rate of polymerization almost kept the same, but the final double bond conversion slightly decreased from 99% to about 94% [Fig. 7(b)]. It could assume that when the initiator concentration increased, the concentration of free radical reactive species increased during irradiation, then the polymerization rate increased, but when the initiator

concentration reached certain level, the concentration of free radical species was high enough to quickly induce the polymerization of acrylate double bond. On the other hand, during the increase of polymerization rate, the microgel in the polymer is formed at the earlier stage of polymerization, which decreases the mobility of the double bond and thereby some of the double bond even could not be polymerized, then the final double bond conversion decreased. When the light intensity increased, the concentration of free radical reactive species increased, which caused the increase of rate of polymerization and double bond conversion. But the high light intensity minimized the difference of polymerization rate and double bond conversion which results from the increasing of initiator concentration.

The results for the polymerization of propenyl ether double bond are shown in Figure 7(c,d). It can be seen that at lower light intensity, when the concentration of UVI-6976 less than 1.0 wt %, the rate of polymerization and double bond conversion were very low, when the concentration of UVI-6976 higher than 2.0 wt %, the rate of polymerization and double bond conversion increased rapidly, the conversion was even higher than 90%. It can be attributed to that increasing the light intensity and concentration of initiator would produce more
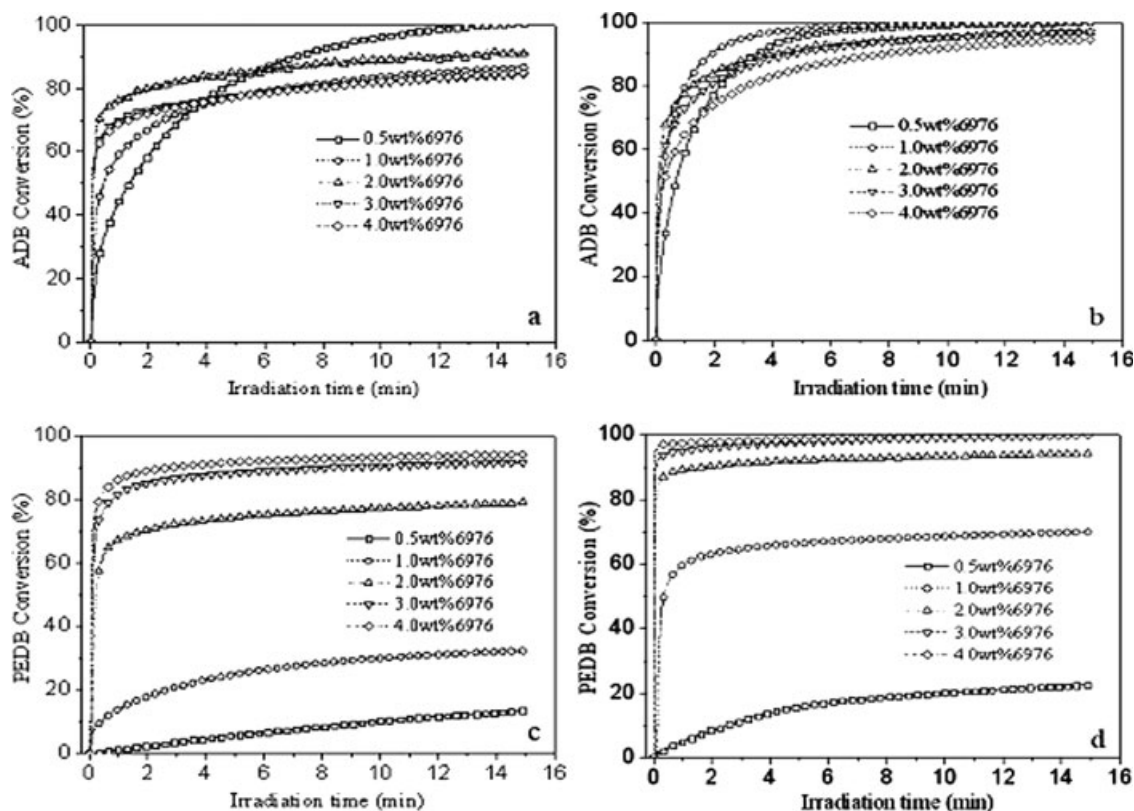

Figure 7 Effect of photoinitiator concentration and light intensity on photopolymerization of POBA. Acrylate Double Bond (ADB), (a): $I = 15$ mW/cm^2, (b) $I = 70$ mW/cm^2; Propenyl Ether Double Bond (PEDB), (c): $I = 15$ mW/cm^2, (d): $I = 70$ mW/cm^2.
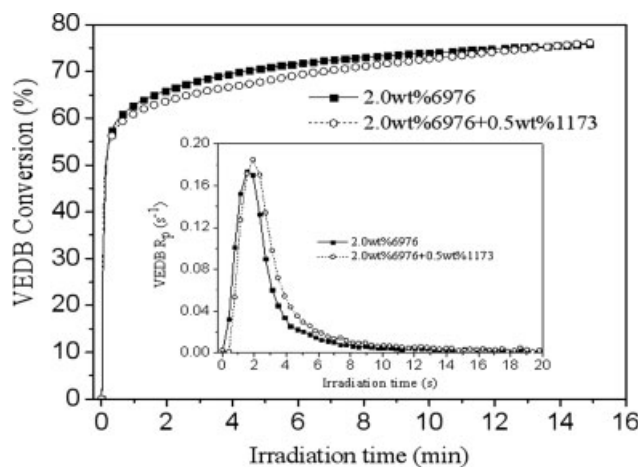
Figure 8 Vinyl ether double bond (VEDB) conversion of DVE-3 photopolymerized by UVI-6976 and 1173 ($I = 50$ mW/cm^2, Inner figure: reaction rate plots).

cationic species that cause the increase of double bond conversion and rate of polymerization. Because the initiator was very expensive, increase in light intensity would be the better way to improve the polymerization extent when the initiator concentration reached only necessary level e.g., 2.0 wt % in this research.

For POBA, free radical and cationic polymerization active group in one molecule could accelerate with each other. When faster polymerized free radical process proceeded, the propenyl ether double bond could exist as side group and lead to faster polymerize rate due to their closer and more orderly arrangement. At the same time, the proceeding of cationic polymerization can form the crosslinked surface more easily for its insensibility to oxygen, which could decrease the oxygen inhibition effect to radical process of hybrid monomer because the oxygen penetration was hindered.

Effect of addition of free radical photoinitiator

Onium salts, their excellent photosensitivity and good thermal stability made them ideal photoinitiators for the polymerization of many types of cationically polymerizable monomers. Their shortcoming was their poor spectral sensitivity at the wavelengths where high-pressure mercury lamps emit light. Photosensitizers[20,21] and free-radical photoinitiators[22] have been successfully employed to extend their spectral response to longer wavelengths. However, this mechanism is effective mainly for iodonium and some special structure sulfonium and disabling for simple structure triarylsulfonium due
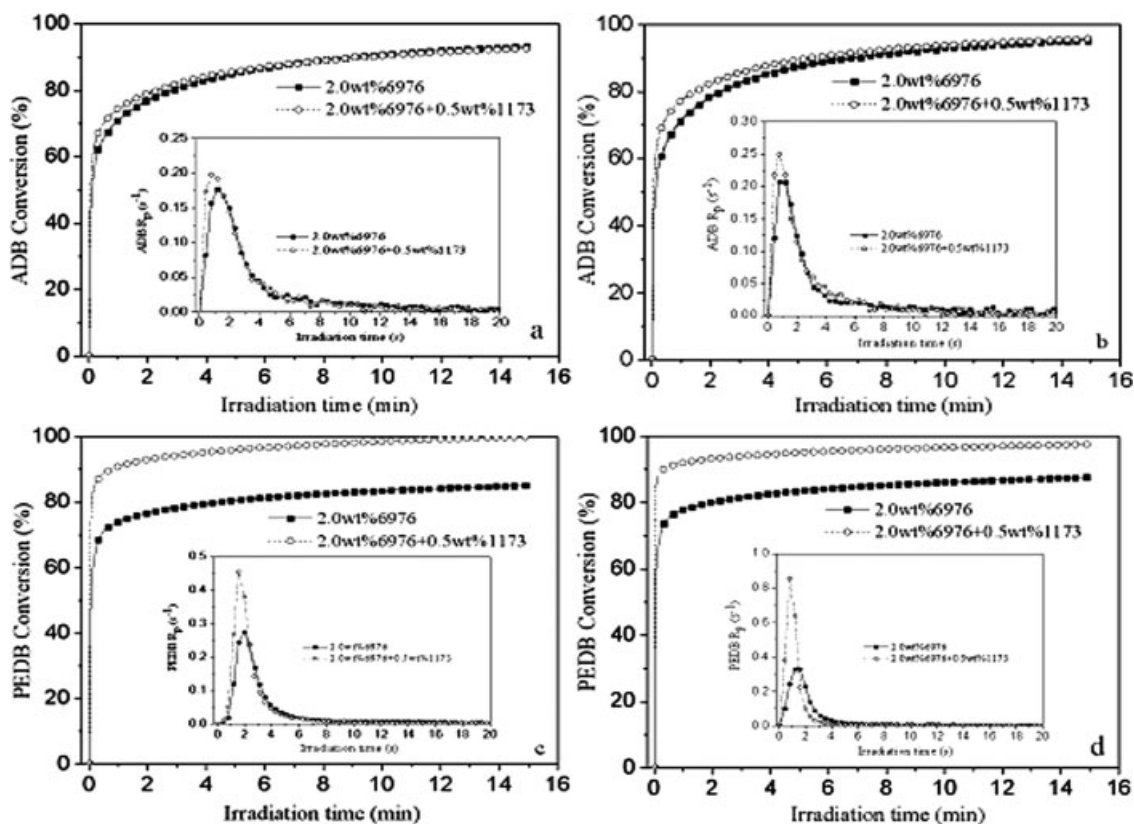

Figure 9 Double bond conversion of POBA photopolymerizated by UVI-6976 and 1173 (Inner figure: reaction rate plots). Acrylate Double Bond (ADB): (a) $I = 30$ mW/cm^2, (b) $I = 50$ mW/cm^2; Propenyl Ether Double Bond (PEDB): (c) $I = 30$ mW/cm^2, (d) $I = 50$ mW/cm^2.
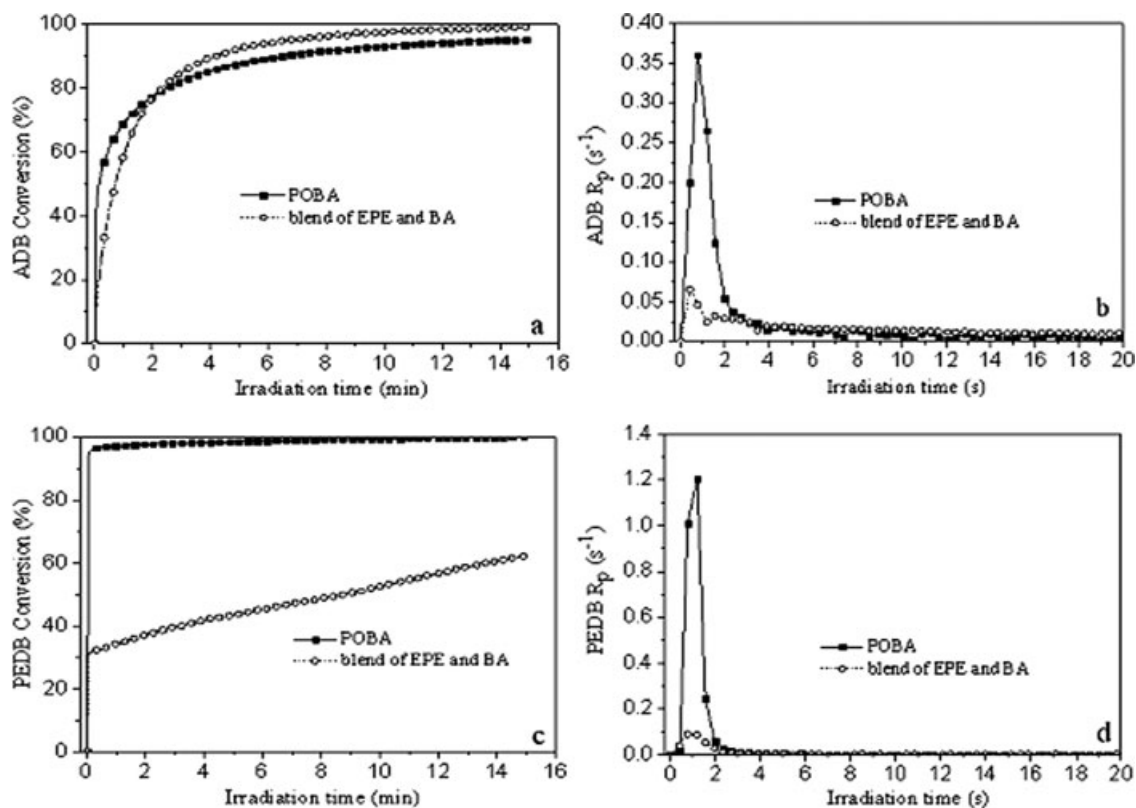
Figure 10 Double bond conversion and rate of polymerization (R_p) of POBA and blend system. Blend system: $M_{EPE}/M_{BA} = 1/1([UVI-6976] = 4.0$ wt %, $I = 50$ mW/cm^2), (a,b): Acrylate Double Bond (ADB); (c,d): Propenyl Ether Double Bond (PEDB).

to its unsatisfied redox potential.[23] As shown in Figure 8, when 2-hydroxy-2-methyl-1-phenyl-1-propanone (1173) was added to pure cationic system containing UVI-6976, no obvious improvement was observed both in final conversion and polymerization rate. It means that there was almost no improvement with the addition of free radical photoinitiator (1173) to triarylsulfonium (UVI-6976) for pure cationic system.

But effect of the addition of free radical photoinitiator 1173 on hybrid monomer system was different (Fig. 9). For the cationic polymerizable propenyl ether double bond, adding of 1173 increased the double bond conversion from 85 to 99% at light intensity of 30 mW/cm^2, and from 87 to 99% at light intensity of 50 mW/cm^2, and the polymerization rate also increased [Fig. 9(c, d)]. But for the free radical polymerizable acrylate double bond, adding of 1173 demonstrated just a little effect both on the polymerization rate and conversion [Fig. 9(a, b)]. Since this phenomenon could not be attributed to the free radical promoted cationic mechanism. And it is also proved that there is very little trend for vinyl ether to copolymerize with acrylate through free radical mechanism.[11] So there might be some other mechanism to change the polymerization kinetics of propenyl ether group, such as the interaction between two function groups in one molecular.

Comparison of hybrid and blend system

Hybrid monomer was defined as a comonomer which contains different reactive groups, in this study it contained acrylate group and propenyl ether group. The blend system in this work was blend monomer of butyl acrylate and ethyl propenyl ether with equal molar ratio. The results in Figure 10(a,b) showed that acrylate double bond conversion for hybrid and blend system had only slight difference, but the polymerization rate of hybrid system was higher than that of blend system obviously. Furthermore, for the propenyl ether double bond polymerization [Fig. 10(c,d)], the blend system showed a very low rate of polymerization and double bond conversion (62%), the hybrid system showed fast polymerization rate and high double bond conversion (99%), which indicated that in hybrid monomer the polymerization of acrylate double bond and propenyl ether double bond impacted each other causing the increase of both double bond conversion. This result had been observed in our lab for the other hybrid monomers,[24] but the mechanism is still unknown.

CONCLUSIONS

The synthesized hybrid monomer could photopolymerize by the triarylsulfonium (UVI-9676), and the

concentration of triarylsulfonium, light intensity has great effect on polymerization kinetics. Adding free radical photoinitiator (1173) could promote the cationic polymerization of propenyl ether double bond. The hybrid monomer had higher rate of polymerization and double bond conversion than that of the similar blend system.

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