Photopolymerization of hybrid monomer 3-(1-propenyl) oxypropyl acrylate

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Abstract

Hybrid monomer 3-(1-propenyl)oxypropyl acrylate, combining easy free radical and fast cationically polymerizable group, was synthesized by phase-transfer catalyzed substitution, isomerization and subsequently esterification. Its photopolymerization kinetics was monitored by Fourier transform real-time infrared spectroscopy (FTIR) with a horizontal sample holder. The results indicated that hybrid monomer showed inter-group interaction in photopolymerization process, which decreased moisture sensitivity to cationic photopolymerization process, and represented higher efficiency of photopolymerization when compared with blend system.
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1. Introduction

In the past decades, UV curing technique have been widely used for coatings, adhesives, solder masks, and experienced rapid growth all over the world [1–3]. Among the photoinitiating polymerization systems, acrylates and vinyl [4], 1-propenyl [5,6], 1-butenyl ethers [7], are the most widely used monomers for free radical and cationic photopolymerization process. But both of them had inherent shortcomings. The photoinitiating free radical polymerization of acrylates is inevitably inhibited by atmospheric oxygen. It has also been shown that some acrylate monomers are skin irritants. On the other side, vinyl, 1-propenyl and 1-butenyl ethers compounds, which are cationic polymerizable monomers, are not inhibited by atmospheric oxygen and are less irritating to the skin. However, water or other impurities may affect their cationic process [8].

Therefore, hybrid photopolymerization systems, which formed with a combination of different reactive groups or curing mechanisms, could be considered as a hopeful solution to overcome the drawbacks of pure systems [9]. A possible way to produce hybrid structure was by copolymerization of functionally different monomers, such as a mixture of acrylates and vinyl, 1-propenyl ethers. It has been reported that coatings produced from acrylate/vinyl ether hybrid systems involving the two mechanisms of UV-induced free radical and cationic polymerization exhibited better physical properties than those of acrylates alone [10]. Another way to produce hybrid structure was polymerization of monomers bearing two types of active group in one molecule. In the former blend system, free radical and cationic polymerization process might proceed independently to form an interpenetrating networks (IPN) composed of two kinds of network with hardly any crosslink via chemical bond [8]. The later hybrid system would be obviously better to form more uniform polymer networks and achieve a good balance between photopolymerization rate and mechanical properties of cured materials due to their unique chemical structures [11–16].

In this paper, 3-(1-propenyl)oxypropyl acrylate hybrid monomer was synthesized. Fourier transform infrared spectroscopy (FTIR) and ^{1}H nuclear magnetic resonance (NMR) were used to identify the monomer structure. Real time Fourier transform infrared (FTIR) with a horizontal sample holder system was used to investigate its photopolymerization kinetics.

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2. Experimental

2.1. Materials

The monomers ethyl propenyl ether (EPE, Acros Organics), *n*-butyl acrylate (BA, Beijing Chemical Reagent Company) and triethyleneglycol divinyl ether (DVE-3, ISP) were used as received. The photoinitiators triarylsulfonium salt (45 wt% solution in propylene carbonate, UVI-6976) and 2-hydroxy-2-methyl-1-phenyl-1-propanone (1173) were donated by Runtec Chemical Company (Changzhou, Jiangsu, China). 1.3-Propanediol, allyl bromide and other reagents were of analytical grade (Beijing Chemical Reagent Company) and were used without further purification. Acryloyl chloride was prepared as described in the literature [17].

2.2. Instrumentations

2.2.1. 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.

2.2.2. FTIR

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 5700 instrument (Nicolet Instrument, Thermo Company, USA). Real-time infrared spectroscopies (RTIR) were used to determine the conversions of double bond. The mixture of monomer and initiator was applied between two KBr crystals and irradiated with the UV radiation with UV spot light source (Rolence-100 UV, Taiwan, China) at room temperature. The light intensity on the surface of samples was 15–70 mW/cm^2, which was detected by radiometry (UV-A, Beijing Normal University, China).

2.3. Synthesis of 3-hydroxypropyl allyl ether

A 250 mL four-necked flask equipped with magnetic stirrer, thermometer, nitrogen inlet and dropping funnel were placed 22.8 g of 1.3-propanediol and 100 mL toluene. The reaction mixture was slowly heated to 40 °C under magnetic stirring. Then, 0.4 g of tetrabutyl ammonium bromide and 4 g of sodium hydroxide was added in turn, and solution of 12.1 g allyl bromide dissolved in 20 mL toluene was added dropwise. The reaction mixture was left at 65 °C for 8 h. Subsequently, the mixture was cooled to room temperature and the precipitate was filtered off and washed with toluene. The toluene was removed by rotary evaporation. Finally, 3-hydroxypropyl allyl ether was purified by vacuum distillation. Yield: 6.3 g (54%).

IR (cm^{-1}): 3383.7 (ν_{O-H}), 3080.6 ($\nu_{=C-H}$), 2939.8, 2865.0 (ν_{C-H_2}), 1646.8 ($\nu_{C=C}$), 1091.9 (ν_{C-O}).
^{1}H NMR: δ (ppm) 5.81 (m, 1H, –CH=CH$_2$), 5.19, 5.09 (d, 2H, –CH=CH$_2$), 3.89 (d, 2H, –OCH$_2$CH=CH$_2$), 3.66 (t, 2H, HOCH$_2$–), 3.52 (t, 2H, HOCH$_2$CH$_2$CH$_2$O–), 2.84 (s, 1H, HO–), 1.75 (m, 2H, HOCH$_2$CH$_2$–).

2.4. Synthesis of 3-hydroxypropyl 1-propenyl ether

A solution of 3-hydroxypropyl allyl ether (11.6 g) and potassium *tert*-butoxide (3.54 g) in 100 mL of dimethyl sulfoxide (DMSO) was heated to 100–110 °C for 2 h. The mixture was cooled to room temperature and poured into 50 mL of water. Extraction with diethyl ether/hexane (1/1, v/v) for three times, the organic layer was dried overnight by anhydrous magnesium sulfate. The solvent was removed by rotary evaporation. Then 3-hydroxypropyl 1-propenyl ether was obtained. Yield: 6.8 g (59%).

IR (cm^{-1}): 3355.8 (ν_{O-H}), 3041.0 ($\nu_{=C-H}$), 2928.2, 2878.7 (ν_{C-H_2}), 1668.1 ($\nu_{C=C}$), 1132.9 (ν_{C-O}).

2.5. Synthesis of 3-(1-propenyl)oxypropyl acrylate (POPA)

A mixture of 11.6 g of 3-hydroxypropyl 1-propenyl ether and 13 g of triethylamine in 100 mL of toluene was dissolved in a three-necked flask equipped with stirrer, thermometer, and dropping funnel. Under cooling (0–5 °C), 9.1 g of acryloyl chloride dissolved in 20 mL of toluene was dropped within 2 h. Then the precipitate was filtered off and washed twice with 20 mL of toluene. The organic layers were combined and washed with water, 1 mol/L hydrochloric acid, and saturated NaHCO$_3$ solution and dried over night with anhydrous sodium sulfate. Subsequently, the toluene was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (12/1, m/m) as eluent. Yield: 8.1 g (47.6%). The final product was identified by FTIR (Fig. 1) and ^{1}H NMR.

IR (cm^{-1}): 3041.2 ($\nu_{=C-H}$), 2963.0, 2921.2, 2876.3 ($\nu_{C-H_2, C-H_3}$), 1726.6 ($\nu_{C=O}$), 1668.2 ($\nu_{C=C}$), 1192.2 (ν_{C-O}), 810.6 ($\nu_{C=C}$).
^{1}H NMR: δ (ppm) 6.38, 5.80 (d, 2H, CH$_2$=), 6.09 (m, 1H, CH$_2$=CH–), 5.89 (d, 1H, –OCH=CH–), 4.36 (m, 1H, –OCH=CH–), 4.24 (t, 2H, –COOCH$_2$–), 3.78 (t, 2H, –CH$_2$OCH=), 1.96 (m, 2H, –CH$_2$CH$_2$CH$_2$–O–), 1.54 (d, 3H, –CH$_3$).

3. Results and discussion

Real-time infrared spectroscopy (RTIR) had become an important method for obtaining kinetics data of photopolymerization. Conversion data of free radical and cationic polymerization could be obtained by monitoring the decay of the acrylate double bond (ADB) 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} and the 1-propenyl ether double bond 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. The degree of conversion (DC) of the function groups could be calculated by measuring the peak area at each time of the reaction and determined using the following equation [18]. The rate
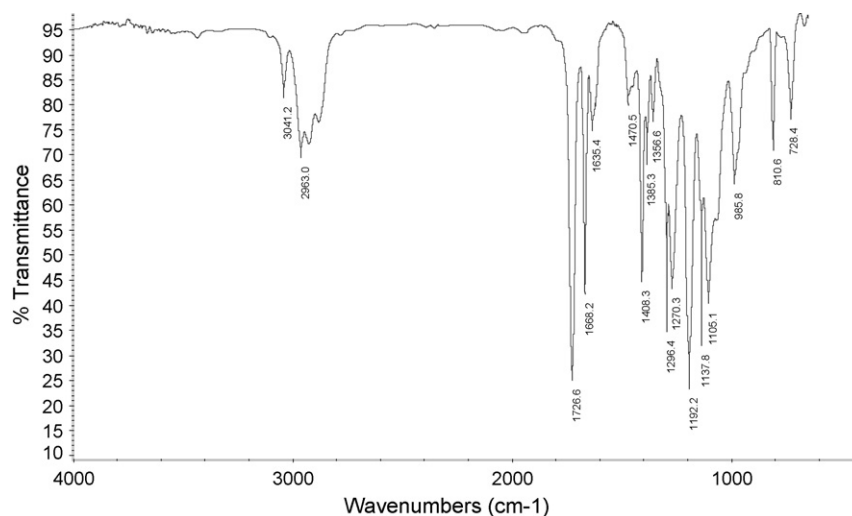
Fig. 1. FTIR spectrum of 3-(1-propenyl)oxypropyl acrylate.

of polymerization (R_p) could be determined from the differential of curve of conversion versus irradiation time [19]:

$$DC\,(\%) = \frac{A_0 - A_t}{A_0} \times 100 \qquad (1)$$

DC was the conversion at t time, A_0 and A_t were the peak area of function group before irradiation and at t time.

3.1. Photopolymerization of hybrid monomer POPA

Triarylsulfonium [20–22] salts were one of the most important representatives of onium salt cationic photoinitiators. They were also proved to produce the free radicals inducing the curing of acrylate monomers and prepolymers [23]. So triarylsulphonium salts were a kind of selection for initiating the hybrid system (Fig. 1).

The concentration of the photoinitiator was a key factor to affect the photopolymerization kinetics. Optimum cure rate was generally obtained at certain concentration of photoinitiator, whilst further increases in concentration did not produce corresponding increases in cure rate. The photopolymerization of POPA containing UVI-6976 with different concentrations (0.5, 1.0, 2.0, 3.0, 4.0 wt%) were monitored by RTIR in this research. It could be seen from Fig. 2(a) that with the increas-

ing of initiator UVI-6976 concentration, the conversions and the rate of polymerization of acrylate double bond increased until it reached 2.0 wt% and decreased slightly when initiator concentration over 2.0 wt%. But it was difference to cationic process of propenyl ether double bond (Fig. 2(b)). In the presence of 0.5 and 1.0 wt% of initiator, the final conversion of propenyl ether was very low (about 15 and 20%) after 15 min irradiation. When the concentrations of photoinitiator increased from 2.0 to 4.0 wt%, the rate of polymerization was very fast and the final double bond conversion increased from 65 to 99%. Especially when the concentration of UVI-6976 was 3.0 and 4.0 wt%, the conversion could reach about 90% within 1 min. The reason of this difference could be attributed to higher reactivity of free radical process than cationic process so that 2.0 wt% was enough initiator concentration to achieve adequate polymerization for free radical process. But for slower cationic process, increasing initiator concentration would improve both the final conversion and polymerize rate in range of 0.5–4.0 wt%. So the best initiator concentration for POPA must lie in between 2.0 and 3.0 wt% from view of both initiating ability and cost.

The effect of light intensity on photopolymerization could also not be ignored. In general, high light intensity resulted in higher active species concentration and consequently faster
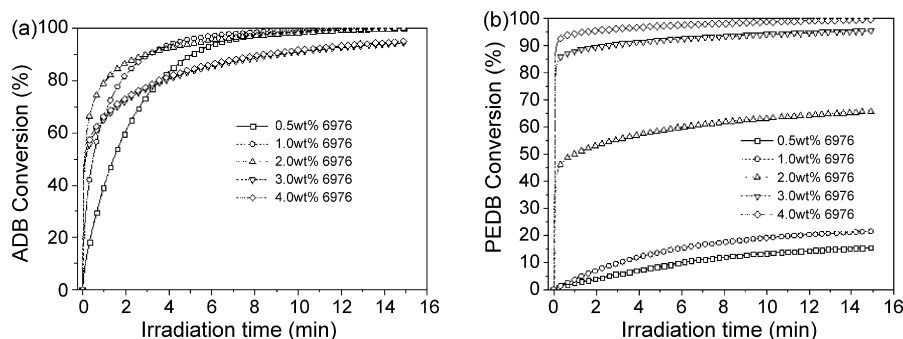

Fig. 2. Effect of photoinitiator concentration on photopolymerization of POPA ($I = 30$ mW/cm^2): (a) acrylate double bond (ADB); (b) propenyl ether double bond (PEDB).
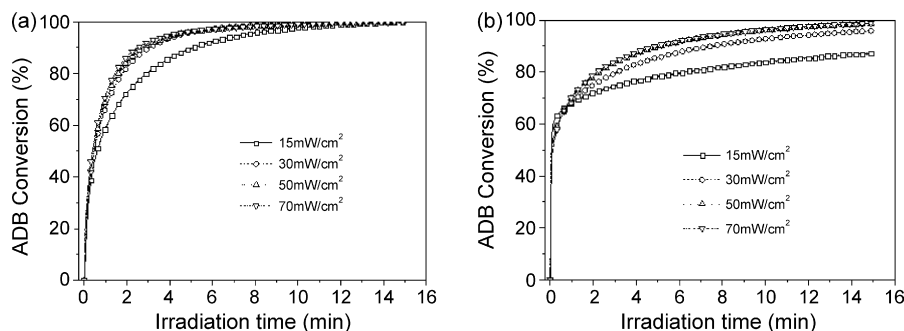
Fig. 3. Effect of light intensity on photopolymerization of acrylate double bond (ADB) of POPA. (a) [UVI-6976] = 1.0 wt%; (b) [UVI-6976] = 4.0 wt%.
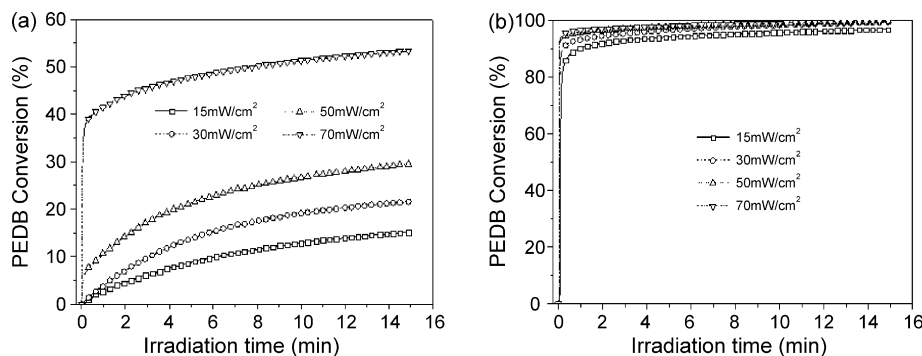

Fig. 4. Effect of light intensity on photopolymerization of propenyl ether double bond (PEDB) of POPA: (a) [UVI-6976] = 1.0 wt%; (b) [UVI-6976] = 4.0 wt%.

curing. The conversion versus time curves for the photopolymerization of POPA at different light intensity was shown in Figs. 3 and 4. It could be seen that the effect of light intensity was obvious when the concentration of initiator was low. As showed in Fig. 4(a), the final double bond conversion of propenyl ether increased from 15 to 53% when the light intensity varied from 15 to 70 mW/cm^2. However, light intensity had slight influence on photopolymerization of acrylate double bond (Fig. 3(a) and (b)) and propenyl ether containing 4.0 wt% of UVI-6976 (Fig. 4(b)). It was known that R_p was proportional to light intensity and initiator concentration, increasing light intensity would increase the reaction rate. But this influence was more obvious to low polymerize rate formulation because the change for very fast system would be too small to be detected. From the energy and cost saving point, reasonable high light intensity would be more suitable selection for higher price of photoinitiators. To POPA and UVI-6976 system, 50 mW/cm^2 was a proper value.

3.2. Effect of addition of free radical photoinitiator

Onium salts have poor spectral sensitivity at wavelengths where commercial mercury lamps emit light. Photosensitizers [24] and free-radical photoinitiators [25] have been successfully employed to extend their spectral response to longer wavelengths. Electron transfer from photogenerated electron donor radicals to the onium salts result in the formation of reactive species that were capable of initiating the cationic polymerization [26]. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (1173) was a class of free radical photoinitiator, which could participate in free radical promoted cationic polymerization. This mechanism was effective mainly for iodonium and some special

structure sulfonium but disabling for simple structure triarylsulfonium due to its unsatisfied redox potential [27]. As shown in Fig. 5, when 1173 was added to pure cationic system containing UVI-6976, no obvious improvement was observed both in final conversion and polymerization rate.

But when 1173 was introduced into hybrid system containing UVI-6976 (Fig. 6), the final conversion of propenyl ether double bond increased from 75 to 91% and polymerization rate increased about one third, and that of acrylate double bond were only slightly improved. This phenomenon could not be attributed to the free radical promoted cationic mechanism and it was also proved that there was very little trend for vinyl ether to copolymerize with acrylate through free radical mechanism [28]. So we
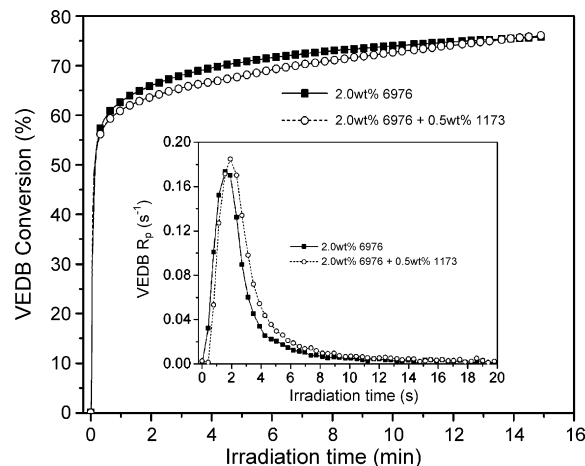

Fig. 5. Vinyl ether double bond (VEDB) conversion of DVE-3 photopolymerized by UVI-6976 and 1173 (I = 50 mW/cm^2, inner figure: reaction rate plots).
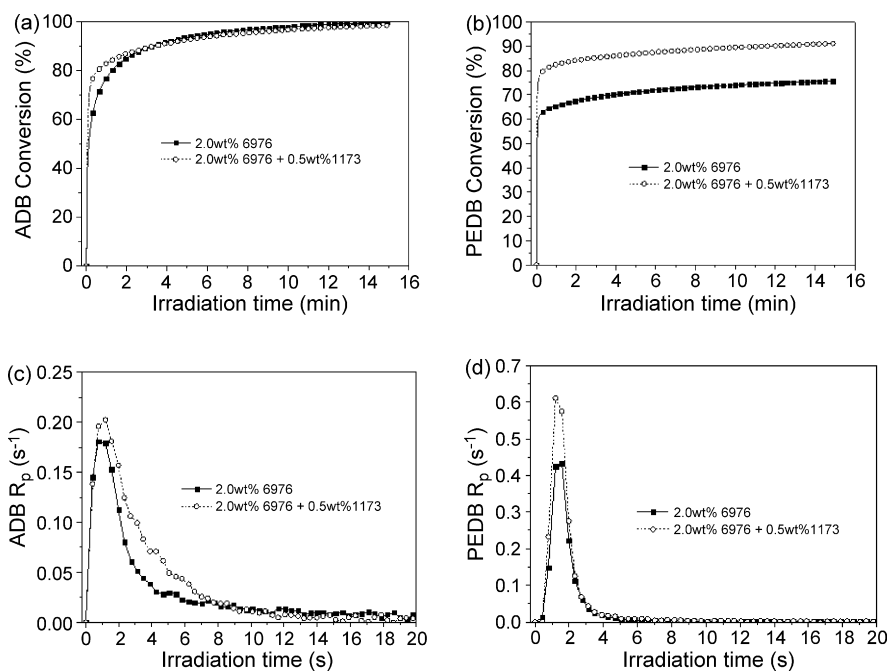
Fig. 6. Double bond conversion and rate of polymerization (R_p) of POPA, photopolymerized by UVI-6976 and 1173 ($I = 50\,\text{mW/cm}^2$): (a and c) acrylate double bond (ADB); (b and d) propenyl ether double bond (PEDB).

inferred that there must be some other mechanism to change the polymerization kinetics of propenyl ether, such as the interaction between two function groups in one molecule.

In order to demonstrate that there were some interactions between two function groups in one molecule, the comparison of photopolymerization kinetics between hybrid and blend system was investigated further. It was showed in Fig. 7 that the blend system showed much slower R_p than that of POPA,

either of acrylate double bond or propenyl ether double bond (Fig. 7(c) and (d)). However, the acrylate double bond conversion of both POPA and blend systems could reach close to 100% at the end of photopolymerization (Fig. 7(a)), and the propenyl ether double bond conversion of POPA was much higher than that of the blend system at the end (Fig. 7(b)). The phenomenon could be explained that photopolymerization of free radical sensitive acrylate double bond and cationic active propenyl ether
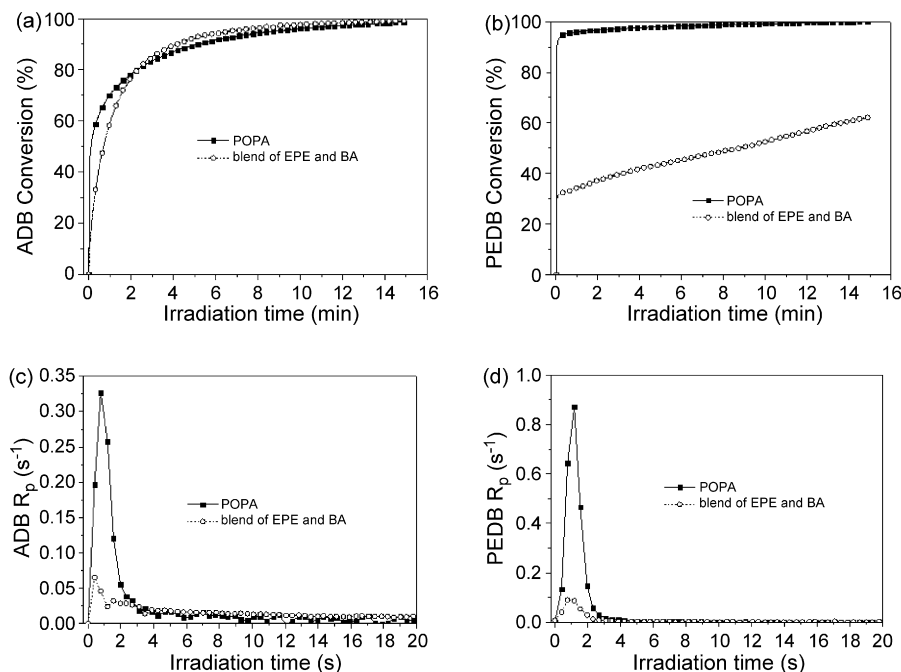

Fig. 7. Conversion and polymerization rate of POPA comparing with blend system. Blend system: $M_{EPE}/M_{BA} = 1/1$ ([UVI-6976] = 4.0 wt%, $I = 50\,\text{mW/cm}^2$). (a and c) acrylate double bond (ADB); (b and d) propenyl ether double bond (PEDB).
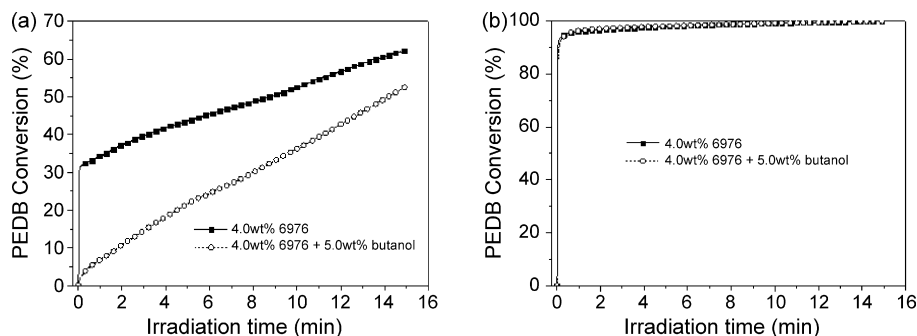
Fig. 8. Effect of butanol on cationic photopolymerization of blend system and POPA ($I = 50\,\mathrm{mW/cm^2}$). Propenyl ether double bond (PEDB). (a) Blend system: $M_{EPE}/M_{BA} = 1/1$; (b) POPA.

double bond locating in one hybrid monomer molecule could accelerate with each other. When faster polymerized free radical process proceeded, the propenyl ether double bond could exist as side group, arranging closer and more orderly, lead to faster polymerize rate due to decreasing of the hinder of viscosity. At the same time, the proceeding of cationic polymerization of POPA formed the crosslinking surface on liquid film faster than the blend system for its insensibility to oxygen; it decreased the oxygen inhibition effect for radical process of hybrid monomer because the oxygen penetration rate was decreased.

3.3. Effect of hydroxyl compound

Hydroxyl compound could inhibit cationic polymerization process and resulted in poor product, because hydroxyl compound could react easily with cationic species produced from the photolysis of photoinitiator, resulting the decreasing of active species [29]. However, Multifunctional acrylate, the component of the mixture system, usually has some OH-end groups, and this might affect the polymerization kinetics. For most of vinyl and propenyl ether, water and other alcohols influenced their cationic photopolymerization strongly. The effect of butanol on cationic photopolymerization of propenyl ether of blend system was explored in presence of 4.0 wt% UVI-6976 (Fig. 8). Herein, there was no effect on free radical polymerization of acrylate double bond both in blend system and in hybrid monomer with adding of butanol. For the blend system, it could be seen that the conversions and polymerization rates of propenyl ether double bond decreased greatly with the addition of butanol (Fig. 8(a)). But effect of butanol was different on hybrid system. For POPA with or without intentionally added butanol, it did not show different polymerization behaviors (Fig. 8(b)). It indicated that hybrid monomer could reduce hydroxyl compound sensitivity effectively. This could be attributed to different mechanism of polymerization of hybrid monomer. One hand the polymerize rate of cationic process could be improved by free radical process as mentioned above, on the other hand, the polymer net formed by acrylate double bond can further reduce encounter opportunity between propenyl ether double bond and hydroxyl compound, so could reduce its influence to cationic polymerization. Therefore, hydroxyl compound would not hinder the cationic polymerization process seriously.

4. Conclusions

A hybrid monomer 3-(1-propenyl)oxypropyl acrylate was prepared successfully by phase-transfer catalyzed substitution, isomerization and subsequently esterification with acryloyl chloride. The photopolymerzation kinetics results showed that it was very reactive while using triarylsulfonium salt as initiator. Compared with blend systems, the final conversion and reaction rate of free radical and cationic polymerization were improved obviously. Furthermore, hydroxyl compound sensitivity in cationic polymerization process was limited. This would be of great significance for exploring new vinyl ether monomer which is insensitive to moisture with the satisfied polymerization kinetics properties.

Acknowledgement

References

[1] C. Decker, Polym. Int. 45 (1998) 133–141.
[2] C. Decker, Macromol. Rapid Commun. 23 (2002) 1067–1093.
[3] E. Andrzejewska, Prog. Polym. Sci. 26 (2001) 605–665.
[4] J.V. Crivello, D.A. Colon, J. Polym. Sci. A: Pol. Chem. 21 (1983) 1785–1799.
[5] J.V. Crivello, K.D. Jo, J. Polym. Sci. A: Pol. Chem. 31 (1993) 2143–2152.
[6] J.V. Crivello, Y.L. Lai, J. Polym. Sci. A: Pol. Chem. 33 (1995) 653–663.
[7] C.M. Miller, E.D. Sudol, C.A. Silebi, M.S. El-Aasse, J. Polym. Sci. A: Pol. Chem. 33 (1995) 1381–1389.
[8] H. Itoh, A. Kameyama, T. Nishikubo, J. Polym. Sci. A: Pol. Chem. 34 (1996) 217–225.
[9] Y. Lin, J.W. Stansbury, Polymer 44 (2003) 4781–4789.
[10] J.D. Cho, J.W. Hong, J. Appl. Polym. Sci. 93 (2004) 1473–1483.
[11] J.V. Crivello, G. Lohden, Chem. Mater. 8 (1996) 209–218.
[12] J.V. Crivello, S.Y. Song, Chem. Mater. 12 (2000) 3674–3680.
[13] Y.J. Hua, F. Jiang, J.V. Crivello, Chem. Mater. 14 (2002) 2369–2377.
[14] S.K. Rajaraman, W.A. Mowers, J.V. Crivello, Macromolecules 32 (1999) 36–47.
[15] J.V. Crivello, R. Narayan, Chem. Mater. 4 (1992) 692–699.
[16] Y. Lin, J.W. Stansbury, J. Polym. Sci. A: Pol. Chem. 42 (2004) 1985–1998.
[17] G.Q. Wu, S.Q. Shi, P. Xiao, J. Nie, J. Appl. Polym. Sci. 102 (2006) 4589–4594.
[18] C. Decker, T. Nguyen, T. Viet, H.P. Thi, Polym. Int. 50 (2001) 986–997.
[19] C. Decker, K. Moussa, Macromolecules 22 (1989) 4455–4462.
[20] J.V. Crivello, J.L. Lee, Macromolecules 16 (1983) 864–870.

[21] J.V. Crivello, J.H.W. Lam, J. Polym. Sci. A: Pol. Chem. 17 (1979) 977–999.

[22] S.R. Akhtar, J.V. Crivello, J.L. Lee, M.L. Schmittt, Chem. Mater. 2 (1996) 732–737.

[23] J.V. Crivello, K. Dietllker,;1; Chemistry&Technology of UV&EB Formulation for Coatings, Inks&Paints. Vol III: Photoinitiators for Free Radical Cationic & Anionic Photopolymerization, SITA Technology, London, 1997, pp. 339-375.

[24] S.P. Pappas, B.C. Pappas, L.R. Gatechair, J.H. Jilek, W. Schanabel, Polym. Photochem. 5 (1984) 1.

[25] A. Ledwith, Polymer 19 (1978) 1217–1219.

[26] Y. Yagci, A. Ledwith, J. Polym. Sci. A: Pol. Chem. 26 (2006) 1911–1918.

[27] S. Denizligil, Y. Yagci, C.M. Ardle, Polymer 36 (1995) 3093–3098.

[28] H. Braun, Y. Yagci, O. Nuyken, Eur. Polym. J. 38 (2002) 151–156.

[29] H.R. Allcock, F.W. Lampe, J.E. Mark, Contemporary Polymer Chemistry, 3rd ed., Science, Beijing, 2003.