Polymer 53 (2012) 3172-3177

Contents lists available at SciVerse ScienceDirect

Polymer



Photoinduced redox initiation for fast polymerization of acrylaytes based on latent superbase and peroxides

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A R T I C L E I N F O

Article history: Received 10 February 2012 Received in revised form 6 April 2012 Accepted 16 May 2012 Available online 23 May 2012

Keywords: Photolatent superbase Peroxides Photoinduced redox

ABSTRACT

The article presents a highly effective strategy for photopolymerization of acrylates *via* photolatent redox-accelerated reaction based on the synergistic photoinitiating systems containing photolatent superbase and readily available peroxides. Polymerization of acrylates could be instantly initiated with the effective interaction between the photogenerated amine and peroxides. Due to the persistent interaction of produced longeval amine with peroxides, remarkable post conversion after irradiation, which is significant for radiation crosslinking of photo-screened materials, was thus initially achieved in photoinitiated free radical polymerization. To explore the synergistic interactions of the photoinitiating systems, the effect of peroxide structures and QA-DBU:BPO ratios had been examined by RTIR, showing that all peroxides are applicable as the final conversion rate of acrylates is concerned. Further, BPO and CHP significantly accelerated the photopolymerization rate in air atmosphere. The synergistic efficiency of QA-DBU and BPO as a photopolymerization initiatiation system was close to that of the conventional D-1173 photoinitiator.

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1. Introduction

Photochemical generation of bases, utilized to catalyze versatile types of organic reactions in order to offer new polymers with special and outstanding properties [1-4], have been investigated for a wide range of applications [5–7]. To date, photocatalytic ringopening polymerization (ROP) of epoxide resin by photolatent base is one of the most common strategies [8,9]. However, the present traditional photolatent base may have limited applications in photosensitive materials due to the weaker basicity, lower catalytic activity and quantum yields [10,11]. Photolatent superbasecatalyzed polymerization, which has been recently explored, provides an attractive alternative to conventional base-catalyzed polymerization [12-14]. Thanks to these effective organocatalysts [15], several kinds of polymers are now accessible by employing suitable reactions such as thiol-click reactions [16], transesterification reaction [17], living anionic ring-opening polymerization of cyclic esters [18], and the Michael addition of acrylates

* Corresponding author. Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China. Tel./fax: +86 20 8411138. *E-mail addresses*: cesyjw@mail.sysu.edu.cn, cedc30@zsu.edu.cn (J. Yang). with acetoacetates [19], *etc.* Nevertheless, these advances are not satisfactory as a highly effective catalyst in many applications, because organocatalyst availability is still limited to subsequent high temperature treatment for a long time and lower conversion efficiency [14]. Indeed, there is no clear path for photolatent base to initiate ambient radical photopolymerization with higher conversion and polymerization rate. So further development in molecular design and new concept of base-catalyzed polymerization is desired [20].

In this paper, a highly effective method has been proposed to eliminate the aforementioned difficulties under ambient conditions *via* photolatent redox-accelerated reaction based on the synergistic photoinitiating systems containing photolatent superbase and readily available peroxides. Although not directed to the photopolymerization area, a lot of studies on redox polymerization have already demonstrated (i) the lower polymerization temperature and (ii) a quite high reactivity of the redox system to initiate the polymerization of acrylates [21,22], thus it is of great interest to apply this latent approach to light induced polymerization reactions.

As part of our continuous interest in developing highly effective photolatent base systems to prevail over the existing problems or enhance the efficiency of UV-curable formulations, herein we report the quaternary ammonium salt (QA-DBU) possessing two





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photosensitive groups, 4-methylbenzophenone (MBP) and tetraphenylborate, in the structure. The covalent binding of MBP and 1,8-diazabicyclo[5.4.0]unde-7-ene (DBU) was done to improve the photoreactivity of the photolatent base compared to the physical mixture. Our work has focused on the redox-induced propagating behavior due to the self-enrichment effect of superbase toward the unreacted areas during polymerization [23], providing a highly effective technology platform based on photolatent superbase in the fields of not only thin materials, but also thick samples that the current photopolymerization fails to cure. Then, the synergistic interactions of combining BPO with QA-DBU were further explored in order to design a novel photoinitiator system that can undergo efficient free radical photopolymerization. Interestingly, the photolatent redox couple on exposure can induce a remarkable acceleration of free radical polymerization of acrylates compared to the immediate initiation by guaternary ammonium salt reported in the literature [24-27], and also exhibit enhanced or specific properties such as the self-propagating polymerization.

2. Experimental

2.1. Materials

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), sodium tetraphenylborate, dibenzoyl peroxide (BPO), dicumyl peroxide (DCP), *tert*butyl peroxybenzoate (TBPB) and cumene hydroperoxide (CHP) were purchased from Aladdin-reagent (China). BPO was purified by dissolving in CHCl₃ at room temperature and precipitated into MeOH. DCP was recrystallized from 95% ethanol before use. 2-Hydroxy-2, 2-dimethylacetophenone (Darocur 1173, abbreviated as D-1173, Ciba company), triphenylboron (BPh₃, Alfa Aesar) and trimethylol propane triacrylate (TMPTA, Sartomer Company) were used as received. 4-(Bromomethyl)benzophenone was synthesized according to the literature procedure [28]. All solvents were dried over 4 A molecular sieves before use. Other chemicals were used as received unless otherwise noted. The chemical structures of QA-DBU, TMPTA, BPO, DCP, TBPB and CHP are shown in Scheme 1.

2.2. Photodecomposition dynamics of QA-DBU

First, QA-DBU in acetonitrile (1×10^{-5} mol/L) was put into a quartz cell. Next, the photodecomposition was carried out by optical cable-directed UV lamp (RW-UVA- Φ 200U, Runwing Co. China) over time (0 min, 1 min, 2 min, 5 min, 10 min), then UV–Vis Spectroscopy were measured. In these experiments, the optical cable was placed at about 1 cm from the surface of the solution and the light intensity was 20 mW/cm² measured by a UV-radiometer (type UV-A, Photoelectric Instrument Factory, Beijing Normal University).

2.3. Quantum yield of photogenerated DBU

QA-DBU (1.96 \times 10⁻⁵ mol) in DMSO-d₆ (0.7 mL) was put into a quartz tube, after irradiation in air, then ¹H NMR spectra were measured. The light intensity was measured as 4.16 \times 10⁻⁹ E cm⁻² s⁻¹ at 365 nm.

2.4. Thermal stability studies of peroxides

A portion of peroxide in TMPTA ($2.2 \times 10^{-5} \text{ mol/g}$) was placed in an aluminum pan and completely sealed. The polymerization profile was monitored by DSC under a nitrogen atmosphere, where the temperature of the sample was raised rapidly from 40 °C to 200 °C at a heating rate of 10 °C/min.

2.5. Photopolymerization

Photopolymerization behavior of the QA-DBU under different conditions was studied by real-time infrared spectroscopy (RTIR). Typical procedure: QA-DBU (0.0146 g, 2.2×10^{-5} mol) and peroxide

O CH_2N $\bar{B}Ph_4$

photolatent superbase: QA-DBU



trimethylolpropane triacrylate (TMPTA)



cumene hydroperoxide (CHP)



benzoyl peroxide (BPO)



tert-butyl peroxybenzoate (TBPB)



dicumyl peroxide (DCP)

Scheme 1. Chemical structures of QA-DBU, TMPTA, CHP, BPO, TBPB, DCP.

 $(2.2\times10^{-5}$ mol) were dissolved in acetone (0.5 mL) under ultrasonication, then TMPTA (1 g) was added to this solution. At last, the mixture was injected into a mold.

2.6. Preparation of 4-(bromomethyl)benzophenone-(1,8diazabicyclo[5.4.0]undec-7-ene)ammonium bromide

A solution of 4-(bromomethyl)benzophenone (2.75 g, 10 mmol) in toluene (200 mL) was added dropwise into a solution of DBU (1.67 g, 11 mmol) in toluene (30 mL). After the mixture was stirred at room temperature for 12 h, the precipitated bromide was filtered, and dried in vacuo to give white solid (yield: 94.8%). ¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.83 (d, 2H), 7.76 (m, 2H), 7.58 (t, 1H), 7.47 (t, 2H), 7.38 (d, 2H), 5.00 (s, 1H), 3.8 (m, 6H), 2.96 (m, 2H), 2.26 (m, 2H), 1.77 (s, 6H). ¹³C NMR (300 MHz, CDCl₃, δ , ppm): 195.89, 167.90, 138.97, 137.75, 137.27, 132.88, 131.10, 130.08, 128.58, 126.62, 57.27, 56.37, 50.09, 48.38, 30.06, 28.82, 26.36, 23.00, 20.68.

2.7. Preparation of 4-methylbenzophenone-(1,8-diazabicyclo[5.4.0] undec-7-ene)ammonium tetraphenylborate (QA-DBU)

To a solution of ammonium bromide salt (4.27 g, 10 mmol) in water (500 mL) was added slowly a slight stoichiometric excess of sodium tetraphenylborate (3.76 g, 11 mmol) solution in water (40 mL) with stirring at room temperature. Precipitate of the salt was filtered, washed several times with water, and dried in vacuo. Recrystallized from a mixture of ethanol and acetone to give white crystals (yield: 85%). ¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.75 (m, 4H), 7.60 (m, 1H), 7.48 (m, 2H), 7.42 (m, 8H), 7.02 (t, 8H), 6.87 (t, 6H), 3.90 (s, 2H), 2.98 (s, 2H), 2.69 (d, 4H), 2.10 (s, 2H), 1.35 (d, 8H). ¹³C NMR (300 MHz, CDCl₃, δ , ppm): 195.79, 167.47, 164.97, 164.31, 163.66, 163.01, 140.94, 137.56, 137.17, 136.22, 133.43, 130.81, 130.19, 129.26, 127.33, 125.97, 122.19, 56.36, 55.13, 49.48, 48.14, 28.63, 28.52, 26.14, 23.13, 20.27.

2.8. Characterization

The NMR spectra were obtained on a Varian 300 MHz spectrometer with CD₃Cl or DMSO- d_6 and TMS as the solvent and internal standard, respectively. UV–S absorption spectra were obtained on a Perkin Elmer Lambda 750 UV–Visible spectrophotometer. Differential scanning calorimetry (DSC) measurements were recorded on a TA instrument (DSC 2910) at a heating rate of 10 °C/min. Electrospray ionization mass spectra (ESI-MS) were acquired on a Thermo Finnigan LCQ DECA XP ion trap mass spectrometer, equipped with an ESI source.

Real-time infrared spectra (RTIR) was conducted with a modified Nicolet 5700 instrument with a horizontal sample holder. Changes in the peak area from 6104 to 6222 cm⁻¹ attributed to the stretching vibration of the acrylate carbon–carbon double bond, were widely used to monitor acrylate polymerization kinetics for thick films [29]. The compounds were injected into a mold from two glass plates and spacers with 15 ± 1 mm in diameter and 1.2 ± 0.1 mm in thickness, then irradiated with a UV-light source (Rolence-100 UV, Taiwan, China) by a light guide attached to the RTIR unit in air at 22 °C. The light intensity at the surface level of the cured samples was measured to be 20 mW/cm².

3. Results and discussion

3.1. Photodecomposition dynamics and detection of DBU from QA-DBU

Photodecomposition of QA-DBU in acetonitrile (1×10^{-5} mol/L) was investigated by UV–Vis Spectroscopy. As shown in Fig. 1,



Fig. 1. UV–Vis spectral changes of QA-DBU in AN (1 \times 10⁻⁵ mol/L) being irradiated over time: 0 min, 1 min, 2 min, 5 min, 10 min.

a distinct decrease in absorption bands at 196 nm and 224 nm was observed with irradiation time, respectively, whereas the latter exhibited red-shifted absorption maxima after irradiation and a new absorption band appeared at 252 nm. These facts suggested that photodecomposition reaction of QA-DBU proceeded in acetonitrile.

ESI-MS was employed to detect the photogenerated bases. Fig. 2 shows that the detection of protonated DBU (m/z = 153.3) after 30 min irradiation (Fig. 2a) was the direct evidence for the formation of DBU from irradiated QA-DBU. In comparison, the signal intensity of MBP-DBU (m/z = 347.4) was apparently smaller after irradiation than before irradiation.

3.2. Quantum yield of photogenerated DBU

In order to further confirm the liberation of DBU from irradiated QA-DBU, a series of ¹H NMR spectra were measured (Fig. 3). The protons H_a (2.87–2.85 ppm) and H_b (2.05 ppm, Fig. 3a) in QA-DBU were disappearing after irradiation, meanwhile new protons H_c (2.61–2.58 ppm) and H_d (1.88 ppm, Fig. 3b), corresponding to the same peak (2.50 ppm, 2.26–2.22 ppm) in DBU (Fig. 3d) appeared. This fact shows that DBU was generated in the photolysis.

Quantum yield and conversion rate for amine formation in the photolysis were calculated by integrating the area of the new peak at 2.40 ppm, normalized by an internal standard peak at 2.50 ppm due to the solvent residual methyl proton of DMSO- d_6 . As shown in Fig. 4, the quantum yield of photodecomposition (Φ_d) of QA-DBU in DMSO- d_6 is 0.435, and the efficiency of photogenerated DBU proved to be high, ~90% conversions, was obtained after just 30 min irradiation.



Fig. 2. Positive ion ESI-MS spectra of QA-DBU in DMSO (0.01 mM) (a) after and (b) before irradiation.



Fig. 3. ¹H NMR spectral changes of QA-DBU (a) before and (b) after 30 min irradiation at 365 nm, and as well of (c) a mixture of Ph_3B and DBU and (d) DBU.

3.3. Thermal stability studies of peroxides

In Table 1, DSC data (T_{onset} , T_p) in TMPTA, as well as activation energy (E_a), and half-life ($t_{1/2} = 1$ h) concerning all four peroxides together with the definition of specific temperature parameters that will be used hereinafter, are listed. As can be noticed, to our surprise CHP started decomposition at temperature that was much lower than the others. Actually, BPO and TBPB had no significant differences both in T_{onset} and T_p , while DCP turned out to be more stable (T_{onset} equal to 130 °C). In comparison, the exothermic peak of TMPTA in the absence of initiator shifted to higher temperature at 187 °C. This trend is confirmed by the corresponding E_a values and half-life, which are equal to 108 kJ/mol and 254 °C for CHP, while they are 125 kJ/mol and 130 °C for BPO, 144 kJ/mol and 167 °C for TBPB, 167 kJ/mol and 175 °C for DCP, respectively. These results indicate that peroxides are usable for acrylates at room temperature.

3.4. Photopolymerization initiated by QA-DBU coupling with different peroxides

To investigate the effect of peroxide structures (BPO, DCP, TBPB and CHP), the photopolymerizations initiated by QA-DBU coupling with different peroxides were carried out by RTIR under constant illumination (Fig. 5), showing that all peroxides are applicable as the final conversion rate of acrylates is concerned. Further, BPO and CHP (Fig. 5a and b) significantly accelerated the photopolymerization. Taking BPO as an example (Fig. 5a), within 20 s, almost 90% of the acrylate double bonds were converted to polymer while just about 50% irradiated by QA-DBU alone under the same conditions,



Fig. 4. Quantum yield and conversion rate of photogenerated DBU.

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Thermal data and kinetic data of the radical initiators studied in this work.

| Initiator | Tonset | T_p | E_a (kJ/mol) | $t_{1/2} = 1 \min (^{\circ}C)$ |
|------------|--------|--------|----------------|--------------------------------|
| CHP | 65 | 73 | 108 | 254 |
| BPO | 87 | 96,133 | 125 | 130 |
| TBPB | 87 | 95,114 | 144 | 167 |
| DCP | 130 | 149 | 167 | 175 |
| Only TMPTA | 175 | 187 | - | - |

 T_{onset} is temperature at which the heat flow begins. T_p is the peak temperature which the sample releases the maximum heat flux in TMPTA ($2.2 \times 10^{-5} \text{ mol/g}$) at a heating rate of 10 °C/min under N₂ atmosphere. The activation energy (E_a) and half-life ($t_{1/2} = 1 \text{ min}$) are available from literature [30–33].

assigned to the high activity with DBU. The efficiency of QA-DBU and BPO as a novel photopolymerization initiatiation system was close to that of the conventional D-1173 photoinitiator (Fig. 6). Due to the relatively lower decomposition activity and the higher absorption of ultraviolet light, photopolymerization with TBPB or DCP (Fig. 5c or d) occurred with a relatively long induction period approximately 10 s. Furthermore, the bimolecular radical generation process were generally slower than free radical photoinitiators (QA-DBU) which formed radicals unimolecularly. However, a higher final conversion rate about 85% was achieved (Fig. 5c).

3.5. The synergistic efficiency of QA-DBU and BPO

We further evaluated the effect of QA-DBU:BPO ratios on the photopolymerization of TMPTA (Fig. 7). Fig. 7b–f illustrated that as the QA-DBU:BPO ratios decreased, the time to reach the maximum polymerization rate (R_p^{max}) was shortened, but all the final conversion increased to above 85%. It is well known that either quaternary ammonium salt or BPO can be separately used as a free radical photoinitiator. In comparison, QA-DBU alone had a lower R_p^{max} and final conversion of ~75% (Fig. 7a). Likewise, BPO alone didn't have a remarkable effect on the final photopolymerization of



Fig. 5. Photopolymerization kinetics of TMPTA initiated by QA-DBU coupling with different peroxides in air: (a) BPO (\blacksquare), (b) CHP (\bigstar), (c) TBPB (\bullet), (d) DCP (\blacktriangle), and (e) only QA-DBU (\bigcirc).



Fig. 6. Photopolymerization kinetics of TMPTA initiated by: (a) QA-DBU and BPO (□), (b) D-1173 (●).

TMPTA (Fig. 7g). For the ratio of 1.5:0.5 (Fig. 7b), the initial polymerization rate of the acrylates was roughly twice that of the system initiated only by QA-DBU, indicating that redox reaction significantly accelerate the photopolymerization in air atmosphere, which can be explained below. The photolatent superbase system on exposure could first undergo the immediate initiation by quaternary ammonium salt which formed radicals unimolecularly, accompanied with the liberation of DBU. Due to the physical diffusion toward the unreacted areas during polymerization, longeval superbase would persistingly interact with peroxides, and thus actuate highly effective redox reaction, exhibiting a remarkable accelerating effect compared to QA-DBU system, therefore improve the rate and conversion.

3.6. Self-propagating polymerization initiated by QA-DBU coupling with BPO

The major challenge in photopolymerizing thick bulk materials arises from the fact that the light is unable to penetrate into deeper



Fig. 7. Polymerization kinetics of TMPTA irradiated at 20 mW/cm² in air for different QA-DBU:BPO ratios: (a) 2:0 (\bigcirc), (b) 1.5:0.5 (\blacksquare), (c) 1.34:0.66 (\bullet), (d) 1:1 (\blacktriangle), (e) 0.66:1.34 (\star), (f) 0.5:1.5 (\bullet) and (g) 0:2 (\Box).



Fig. 8. Kinetics of polymerization of TMPTA initiated by the corresponding initiator in the presence of cyan pigment (0.8 wt%). During first \sim 15 s, terminated the photo-initiation, then monitored the self-propagating characteristic: (a) QA-DBU and BPO, (b) BPO and as well of (c) BPO without UV exposure.



Fig. 9. Changes in the stretching vibration of the acrylate carbon–carbon double bond at 6163 cm⁻¹ over time: 0 min, 10 min, 1 h, 3 h, 5 h.

layers due to the absorption of the upper layer, which prevents its use in a variety of applications. Fig. 8a demonstrates the kinetic curve of photopolymerization of TMPTA initiated by QA-DBU and BPO, in the presence of cyan pigment (0.8 wt%) in order to get a lower initial conversion. Remarkably, the two-component initiator system didn't exhibit rapid termination of TMPTA polymerization when the irradiation source was turned off. Specifically, a threshold value of conversion with first 15 s illumination was about 13%. However, polymerization efficiently carried on in the dark and the final conversion value attained was $\sim 40\%$ at 5 h. The decrease of C=C stretching vibration at 6163 cm⁻¹ is observed in Fig. 9. In comparison, BPO alone with UV exposure or not wouldn't have a remarkable effect on the final conversion of photopolymerization initiated by QA-DBU and BPO (Fig. 8b and c), which further confirms the persistent interaction of produced longeval amine with peroxides via the self-propagation of superbase toward the unreacted areas. These desirable results for self-propagation polymerization provide a promising future for their application to high pigmented photopolymerizable compositions.

4. Conclusion

A highly effective strategy for photopolymerization of acrylates *via* photolatent redox-accelerated reaction based on the synergistic photoinitiating systems containing photolatent superbase (QA-DBU) and readily available peroxides was presented. The results show significant advantages over conventional photolatent base-catalyzed ring-opening polymerization of epoxide resin as they exhibit: lower temperature photopolymerization, higher polymerization rates and

self-propagating polymerization. This provides a highly effective technology platform for photolatent base in the fields of not only thin materials, but also thick samples that the current photopolymerization fails to cure. Using this method, all peroxides are applicable as the final conversion rate of acrylates is concerned. Typically the accelerated polymerization induced by superbase-catalyzed decomposition of BPO or CHP at ambient conditions was demonstrated. Remarkably, the final conversion of the photolatent redox initiator system reached ~40% at 5 h even when the light source was extinguished, more than twice as high as the threshold value of conversion at ~13%. Due to the self-propagating effect of the living composition, photolatent superbase-catalyzed decomposition of peroxides induced polymerization can be used for the photocrosslinking of thick material or highly pigmented systems where the light penetration is one of the main challenging problems.

Acknowledgments

This research was financially supported by National Natural Science Foundation of China (Grant No. 20974127). Special thanks are dedicated to Prof. Nie Jun of Beijing University of Chemical Technology, who provided significant help in the RTIR measurement.

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