Photoinitiating Behavior of Bifunctional Photoinitiator Containing α-Hydroxyalkylphenone Group on Free-Radical Polymerization

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ABSTRACT: Photoinitiating behaviors of bis[4-(2-hydroxy-isopropionyl)]ether photoinitiator on free-radical polymerization have been investigated. The kinetics of photopolymerization initiated by the photoinitiator was studied by means of differential photocalorimetry. The bifunctional photoinitiator showed comparative performance with those commercial photoinitiators with monofunctional chromophoric group. The effect of UV intensity on the polymerization rate was investigated, and the value of exponential factor was found to be 0.5 at the beginning of polymerization, suggesting that the photopolymerization initiated by bis[4-(2-hydroxy-isopropionyl)] ether followed biradical termination mechanism. Photosensitizer triethylamine improves the initiating efficiency while oxygen is shown to restrict polymerization in this system. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5297–5302, 2006

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INTRODUCTION

The UV-induced crosslinking or polymerization of acrylates and other monomers has become a widely used curing technology. Generally, photoinitiator plays a crucial role in the UV-curing system.[1–3] It absorbs UV radiation and then generates free radicals, which initiate polymerization reaction. Good compatibility and high reactivity have always been major requirement for a photoinitiator. Properties such as low migration tendency are gaining increasing importance for certain applications. However, as the conventional photoinitiators do not all participate in the actual photopolymerization, their excess, unreacted residues, as well as their degradation products formed during the photochemical reaction remain in the finished product. Initiator residues and/or degradation products may cause unpleasant odor, which should be avoided in some applications such as food packaging and cosmetic bottle. Their diffusion out of the coating and into surrounding media may also create problems.[4] Conventional monofunctional photoinitiators suffer from VOC problem due to their low molecular weight. One approach to overcome the problem is to synthesize photoinitiators with higher molecular weight, thereby lowering migration tendency comparing with low molecular weight photoinitiators. A great effort has been made.[5] One successful example is Esacure KIP 150, which was developed and commercialized by Lamberti, but the cured film based on it is often rigid and brickle because of the α-methyl styrene backbone in KIP 150. Another disadvantage of this approach is that for most of photoinitiators the photoinitiating activity will descend in some degree as they are immobilized to the macromolecular backbone.

Recently, we have developed a novel bifunctional photoinitiator bis[4-(2-hydroxy-isopropionyl)]ether (BHPE), which contains two α-hydroxyalkylphenone chromophoric groups. Very low migration tendency was found for this photoinitiator.[6] It was synthesized from diphenyl ether and α-chloroisobutyryl chloride through the procedures of acylation, bromination, and hydrolyzation. The illustrated diagram of synthesis is shown in Scheme 1, and more details are reported elsewhere.[6] In this article, the photoinitiating behaviors of the concerned bifunctional photoinitiator on free-radical polymerization have been investigated by differential photocalorimetry (DPC; also named photo-DSC).
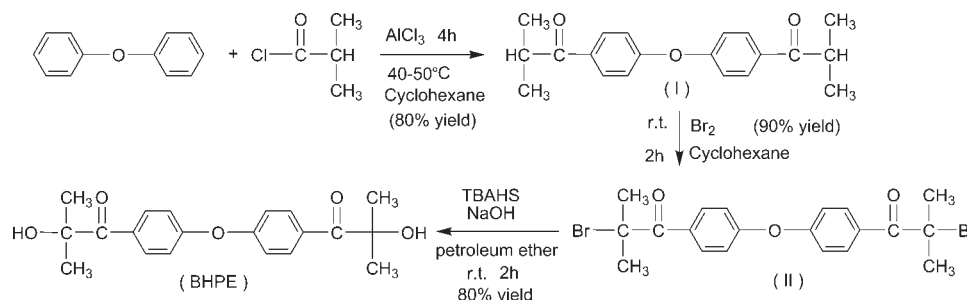
EXPERIMENTAL

Materials

BHPE was synthesized by procedure described in another paper.[6] 1-Hydroxycyclohexylphenyl ketone

Scheme 1 Synthetic route of BHPE.

(HCPK, Irgacure 184), 2-hydroxy-2-methyl-1- phenyl-propanone (HMPP, Irgacure 1173) were chosen as photoinitiators for comparison and purchased from Ciba (Shanghai, China). Hydroxyethyl methyacrylate (HEMA) and trimethyolpropane triacrylate (TMPTA) were selected as monomers and provided by Cognis.

Measurements

UV/vis spectra were detected by a VARIAN CARY100 instrument. DPC tests were carried out on a modified CDR-4 DSC (from Shanghai Balance Instrument Plant) with a middle pressure mercury lamp as radiation source. The light intensity was measured by a UV-radiometer (type UV-A, from Photoeletric Instrument Factory, Beijing Normal University, China) that is sensitive in the wavelength range of 320–400 nm. The samples containing 1–5 wt % of the initiator were sonicated for 30 min to ensure complete dissolving, and then the sample weighed 2–4 mg was placed in an open clear aluminum sample pan. Each sample was held in isothermal conditions at 35°C in nitrogen prior to irradiation. The photopolymerization reaction as carried out until no heat was evolved. Data reported for each composition are an average of separate photopolymerizations. The baseline is subtracted to ensure the result is unaffected by the radiation enthalpy of background.

RESULTS AND DISCUSSION

Photoinitiation behavior of BHPE

For the free-radical polymerization reaction is exothermic, the polymerization progress can be monitored by means of DPC, by which the heat flow (dH/dt) from the sample during irradiation is measured as the function of reaction time (t). The reaction rate is calculated from the reaction enthalpy by the following equation:

$$R_p = \frac{d\alpha}{dt} = \frac{d(H/H_\infty)}{dt} = \frac{dH/dt}{H_0 \times m} \quad (1)$$

where R_p is the polymerization rate, $H_\infty(=H_0 m)$ the total enthalpy, H_0 the molar enthalpy of C=C bonds in polymerization (80.0 kJ mol^{-1} for the acrylate ester double bond calculation, 57 kJ mol^{-1} for methylacrylate ester double bond calculation[7]), and m the mole number of carbon double bond in the system. Conversion curve ($\alpha \sim t$) can be obtained by integrating the polymerization rate curve ($d\alpha/dt \sim t$).

The conversion curve for photopolymerization of TMPTA initiated by BHPE is shown in Figure 1. To evaluate the initiation efficiency of BHPE, two commercial photoinitiators with low molecular weight, HMPP and HCPK, which can be regarded as the monofunctional photoinitiator homologue, were chosen for the comparison. It is well established that the photodecompositions of HMPP and HCPK follow Norrish type I mechanism. By comparing the three conversion curves, it can be found that the BHPE has the competitive performance with those monofunctional photoinitiators. The induction period for BHPE is similar to those for monofunctional photoinitiator HMPP and HCPK, and the final conversion is almost the same.

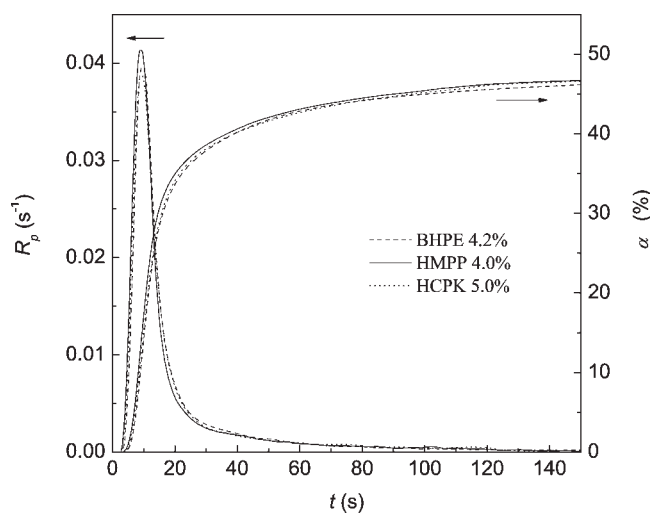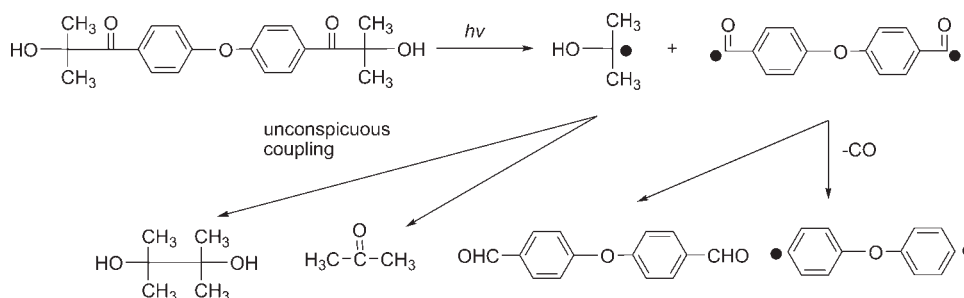The photoactive chromophore in BHPE has a weak C—C bond, with dissociation energy lower than the

Figure 1 Polymerization rate and conversion versus reaction time for the photopolymerization of TMPTA initiated by various photoinitiators at room temperature, nitrogen atmosphere, light intensity: 2.0 mW cm^{-2}.

Scheme 2 Proposed mechanism of photochemical decomposition of the bifunctional photoinitiator BHPE.

excitation energy of its reactive excited state. α-cleavage will take place when the sample is irradiated by UV light. The proposed photodecomposition process is shown in Scheme 2.

Because there are two weak C—C bonds within a molecule, the biradical intermediates will appear in the photodecomposition fragments. It can increase the initiating efficiency or the probability of fragment bonded to the backbone of formed polymer chain.

Figure 2 shows the photoinitiation behavior of BHPE in initiating the polymerization of two types of monomers, HEMA and TMPTA. These monomers exhibit similar polymerization profiles to those initiated with monofunctional photoinitiators. The sharp rise at the beginning of polymerization indicates autoacceleration of the bulk polymerization reaction. After reaching the maximum polymerization rate, the reaction slows down as the polymer gels. Trifunctional monomer TMPTA shows much higher polymerization rate

and shorter induction period than does monofunctional monomer HEMA in the early stage of polymerization. In the case of multifunctional monomer, the chain radicals are embedded by more rapid onset of gelation and vitrification caused by higher density of crosslinks, and the chain radical was diffusion controlled even at early stage of the curing reaction.[8] As a result of higher reaction rates due to higher concentrations of functional groups, more dense networks reduce the extent of double bond conversion, leaving a large portion of them unreacted (40–50% for TMPTA).

Kinetics

The plots of conversion versus exposure time for TMPTA with various light intensity are shown in Figure 3. It is found that increasing light intensity can increase the polymerization rate and the final monomer conversion.
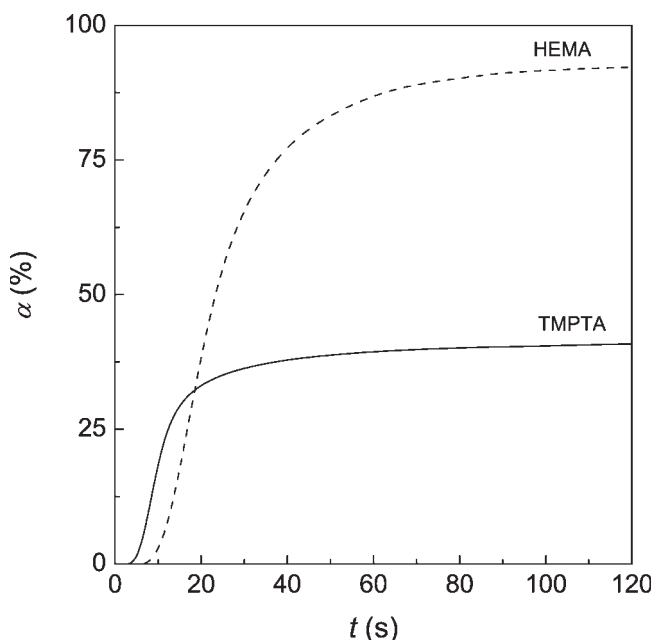

Figure 2 Conversion versus reaction time for the photopolymerization of different monomers initiated by 4.0 wt % of BHPE, nitrogen atmosphere, light intensity: 2.0 mW cm^{-2}.
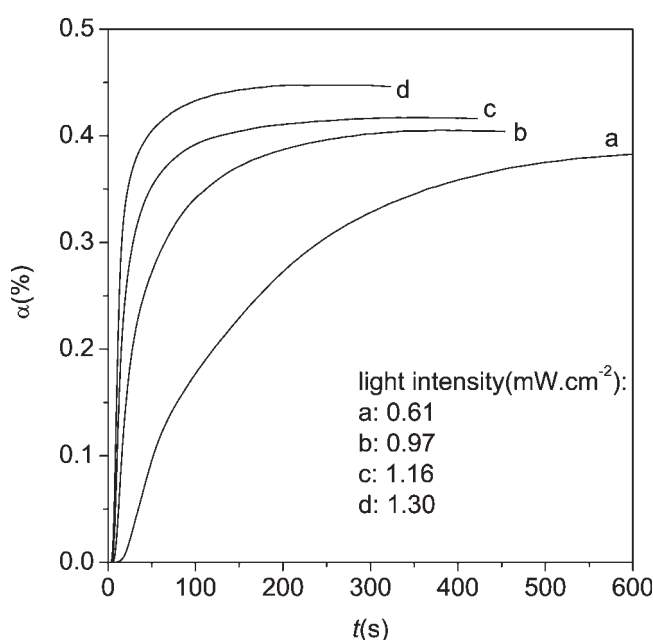

Figure 3 Conversion versus reaction time for the photopolymerization of TMPTA initiated by BHPE (3.0 wt %) at different light intensity, nitrogen atmosphere, 35°C.
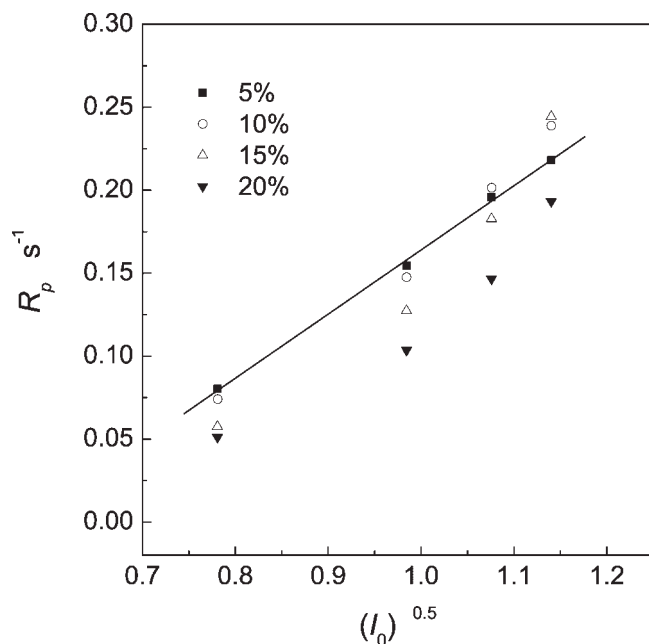
Figure 4 R_p versus $(I_0)^{0.5}$ for the photopolymerization of TMPTA initiated by BHPE at different conversion.

For free radical polymerization with biradical termination mechanism, the rate of polymerization is generally given by

$$R_p = -\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}} [M] R_i^{1/2}$$

$$= k_p \left(\frac{4\Phi\varepsilon\mathring{A}}{k_t}\right)^{1/2} [M] I_o^{1/2} [PI]^{1/2} \quad (2)$$

where PI is the concentration of photoinitiator, $[M]$ the concentration of monomer, ε the molar extinction coefficient of the photoinitiator,[9] k_p the rate constant of propagation (around 10^3 M^{-1} s^{-1} for acrylate monomer), k_t the rate constant of termination (typically of the order of 3×10^6 M^{-1} s^{-1} for acrylate monomer,[10] Φ the quantum yield for the initiator (initiating efficiency), and I_0 the incident light intensity. The application of eq. (2), which was derived on assumptions of steady-state and bimolecular termination, is limited for describing the photopolymerization of multifunctional monomers. However, if the gel effect is not significant, this equation was also applied to describe the crosslinking polymerization in the initial stage of the reaction. Figure 4 shows good linear relationship between R_p and $(I_0)^{1/2}$ at conversions of 5%, suggesting that the photopolymerization initiated by BHPE is in accordance with eq. (2) at low conversion. Biradical termination mechanism is expected for this photopolymerization system at low conversion region. But at conversion higher than 5%, nonlinear relationship between R_p and $(I_0)^{1/2}$ was found. This was explained by strongly limited diffusion of the polymer radicals in

the matrix that led to the dominance of primary termination with small and mobile initiator-derived radicals. At higher conversions, the termination mechanism of combined second-order and primary radical termination (reaction of macroradicals with initiator-derived radicals) dominated.

Effect of oxygen

Figure 5 demonstrates the oxygen inhibition effect in BHPE-initiated photopolymerization of TMPTA. In the presence of oxygen, the induction period of the reaction is longer than in a nitrogen atmosphere. This causes a lower degree of conversion of the reactive species in the presence of molecular oxygen because of its reaction with the free radicals generated from photoinitiator as well as with the polymeric radicals, forming peroxy radicals, leading to significant retardation (or even inhibition) of the free radical curing process.[11] Oxygen inhibition may result in the use of a far greater dose of radiant energy than expected to obtain a cure. This would be especially true if the "nitrogen blanket" was not used.

Effect of sensitizer

The reactivity of these systems can be further improved by the addition of sensitizers/coinitiator. An obvious increase in reactivity can be obtained using the combination of HMPP and 2-methyl-1-[4-(methylthio)-phenyl]-2-morpholinopropan-1-one(MMMP).[12] Other examples include HMPP (sensitized by triethylamine)
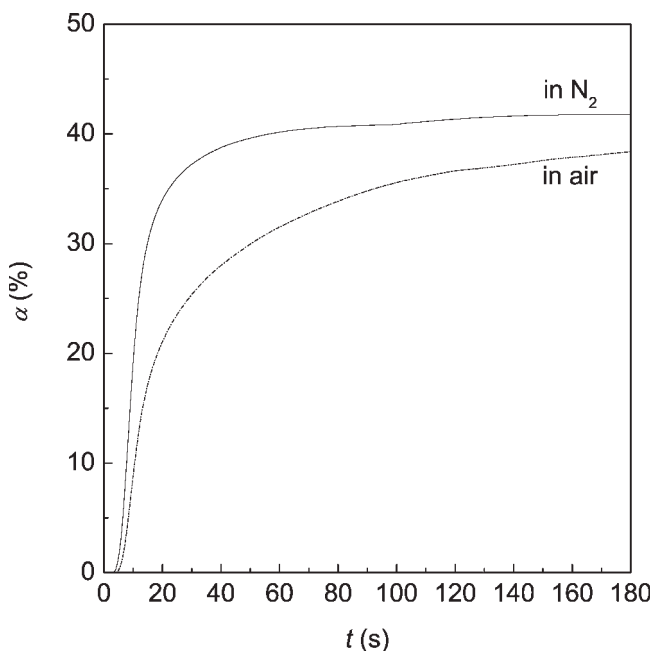

Figure 5 Conversion versus reaction time for the photopolymerization of TMPTA initiated by 4.0 wt % of BHPE in various atmospheres, light intensity 2.0 mW cm^{-2}, 35°C.

and MMMP (sensitized by isopropylthioxanthone).[13] A synergistic effect exists in this case. As BHPE may be considered as the HMPP analogue, amine derivatives were added to BHPE initiated system for compassion. The result of sensitivity is shown in Figure 6. The phenomenon can be illustrated by formulation, as shown below:

$$ArCO \bullet + RH \text{ (triethylamine) } \rightarrow ArCHO + R \bullet$$

After the α-cleavage of BHPE, H-abstraction reaction occurs between the benzoyl radical formed and amine molecule, which led to the formation of α-aminoalkyl radical. The α-aminoalkyl radical has been proved to be very efficient in initiating free radical polymerization.[14]

Effect of Temperature

The peak polymerization rates and other parameters at various UV-curing temperatures are listed in Table I. The data of peak reaction rate (R_p^{max}) as well as the final conversion (α_∞) show an increase in the lower temperature region followed by a decrease or a plateau at higher temperatures. At the beginning of the temperature rise period, the increases in R_p^{max} with temperature is corresponding to an Arrhenius-like behavior. Propagation dominates at this stage. The temperature rise improves the segmental mobility of the polymer chain and makes more residual unsaturation sites accessible for polymerization. However, at temperature
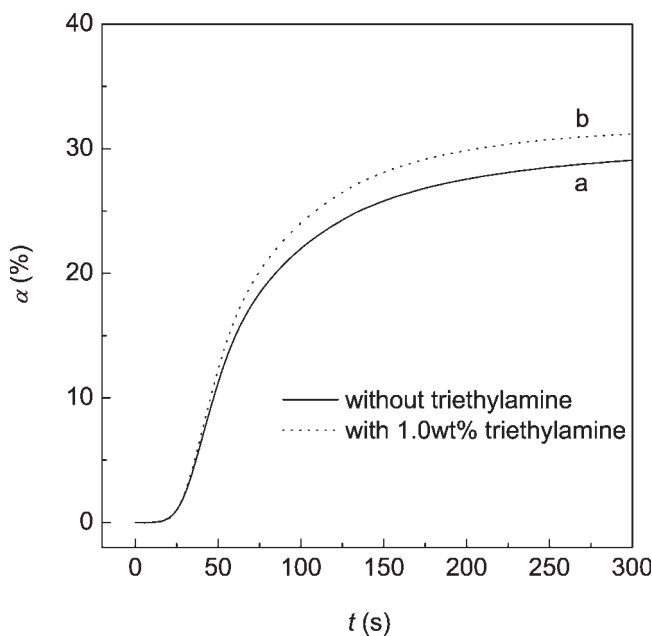
TABLE I
Summarized Results of Several Kinetics Variables of Photopolymerization at Different Temperatures (Light Intensity: 1.8 mW cm^{-2})

Temp. (°C)	$t_{induction}$ (s)	t_{peak} (s)	R_p^{max} (s^{-1})	α_∞ (%)
28	8.4	17.6	0.0084	26.5
40	7.0	15.5	0.0085	29.6
55	5.6	13.6	0.012	39.3
64	6.7	15.1	0.010	35.2
74	7.8	16.8	0.0076	34.6

higher than 55°C, the polymerization rate decreases with increasing temperature. This can be explained in terms of depropagation or chain transfer. At higher polymerization temperatures, termination becomes more prominent, which affects the polymerization rate. The increase in termination rate may be associated with chain transfer, which is energetically favored at elevated temperatures because the activation energy of the chain-transfer reaction is higher than that of the propagation process by 20–40 kJ mol^{-1} with active transfer agents. The occurrence of chain transfer always leads to a drop in the polymerization rate. Lecamp et al.[15] believed that this slowing down effect was also due to the thermal polymerization. The existence of thermal polymerization before irradiation interferes with the system consumes acrylate monomer, which decreases polymerization rate and therefore results in low conversion.

When the polymerization rates were plotted against the inverse of the curing temperatures, an Arrhenius relationship was found (not shown here), and the activation energy calculated from the slopes of each data pairs in the curve was 19.6 kJ mol^{-1} following Arrhenius theory:

$$k = A \exp^{-E_a/RT}$$

where A is the pre-exponential factor. This value is smaller than the obtained value of the epoxy and vinyl ether systems. This is one of the reasons why acrylate-based resins are the most widely used light-curable systems, for they are of lower reaction barrier and more reactive and, therefore, require less energy to cure. In addition, they are used to achieve desired properties and crosslinking between polymer chains.

CONCLUSIONS

Investigation of the photopolymerization process by DPC revealed that BHPE has the competitive performance with those commercial monofunctional photoinitiators. Conversion and rate profiles were changed as a function of light intensity. The biradical termination occurs at the beginning of the polymerization, in accordance with the theoretical presumption. With the

Figure 6 Conversion versus reaction time for the photopolymerization of TMPTA initiated by 2.0 wt % of BHPE with and without triethylamine, light intensity: 3.6 mW cm^{-2}, nitrogen atmosphere, 35°C.

increase in temperature, the final conversion and polymerization ratio increase at lower temperature, while decrease at higher temperature. Similar to Irgacure HMPP, the initiation reactivity of the bifunctional photoinitiator will increase with the addition of sensitizers triethylamine. Oxygen can delay the free radical curing process initiated by BHPE.

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