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PHOTOINITIATING BEHAVIOR OF MACROPHOTOINITIATOR CONTAINING AMINOALKYLPHENONE GROUP
Free-radical polymerization

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Photoinitiating behaviors of oligo(α-aminoketones) (OAK) macrophotoinitiator containing aminoalkylphenone group on free-radical photopolymerization had been investigated by differential photo-calorimetry (DPC). The macrophotoinitiator showed comparative performance with those commercial photoinitiators with lower molecular mass. The effect of photoinitiator concentrations and 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 OAK followed biradical termination mechanism. Photosensitizer isopropyl thioxanthone (ITX) and oxygen severely restricted the polymerization in these systems. Photoinitiators with lower molecular mass showed higher reactivity than those with higher molecular mass.

Keywords: *differential photo-calorimetry, photoinitiator, photopolymerization, UV-curing*

Introduction

The UV-induced cross-linking or polymerization of acrylates and other monomers has become a conventional and widely used curing technology. Generally, photoinitiator plays a crucial role in the UV-curing system. Good compatibility and high reactivity have always been major requirement for a photoinitiator, and properties such as low migration tendency are gaining increasing importance for certain application. However, as the conventional photoinitiators do not all participate in the actual photopolymerization, the residues and the degradation products formed during the photochemical reaction remain in the finished product, causing 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 [1]. One approach to overcome the problems is to synthesize photoinitiators with higher molecular mass, thereby lower migration tendency comparing with low molecular mass photoinitiators. A great effort was made in order to design and synthesise new macrophotoinitiators. Various polymeric photoinitiators based on the type I photoinitiators such as benzoin ethers or dialkoxyacetophenones derivatives, and type II photoinitiators such as benzophenone or thioxanthones derivatives, have been described [2–4].

Recently we have developed a new oligomeric photoinitiator (OAK) which was found to be very useful in UV formulations. It was synthesized from diphenyl ether, α-chloroisobutyryl chloride, and piperazine through the procedures of acylation, bromination, epoxidation and condensation polymerization. The illustrated diagram of synthesis is shown in Scheme 1, more details is reported elsewhere [5]. To the best of our knowledge, there has been very few studies on the UV-curing performance of macrophotoinitiator by DPC (also named photo-DSC). In this paper, the photoinitiating behaviors of the concerned macrophotoinitiator on free-radical polymerization have been investigated. And with the guidance of experiment, we will be able to making full use of its advantages for the desired application through designed selection of photopolymerization conditions. There are current and real potential applications.

Experimental

Materials

Oligo(α-aminoketones) (OAK) was synthesized by procedure described in another paper [5]. 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (MMMP), 2-hydroxy-2-methyl-1-phenyl-propanone (HMPP) were chosen as photoinitiators for compari-

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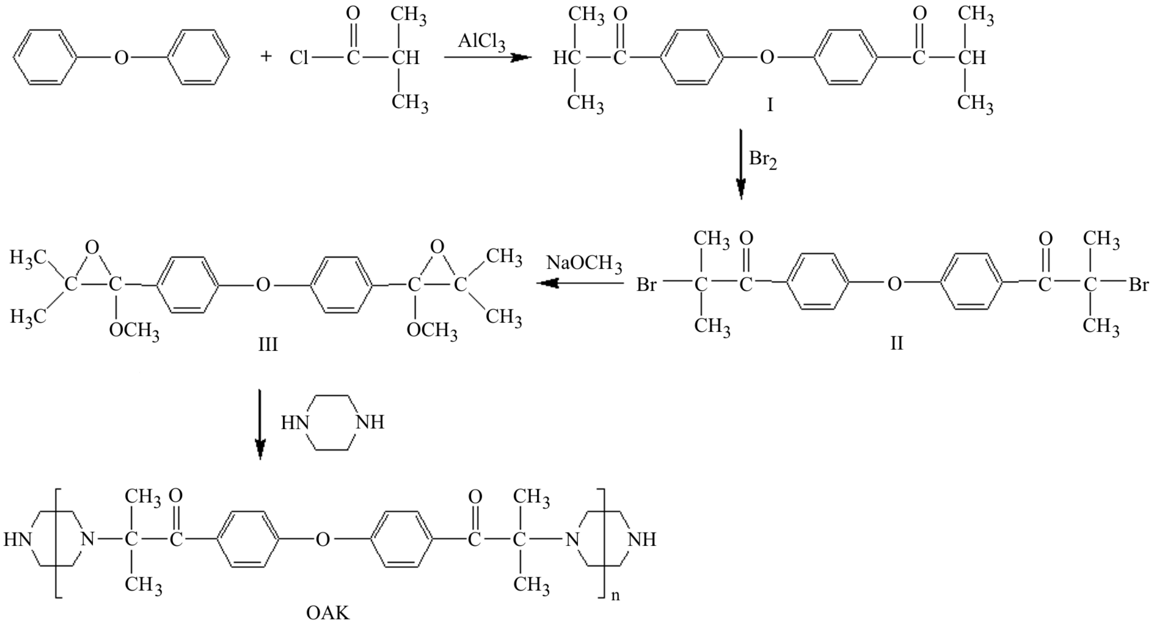


Scheme 1 Synthetic route to oligo(α-aminoketones) (OAK)

son and purchased from Ciba. 2-hydroxyethyl methacrylate (HEMA), 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA) were selected as monomers and provided by Cognis.

The chemical structures of photoinitiators and monomers used here are listed in Scheme 2.

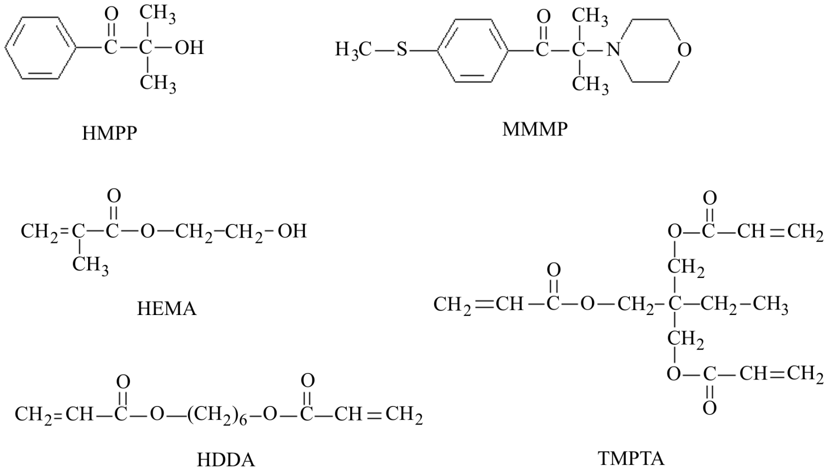
Measurements

UV-vis spectra were detected by a Varian CARY100 instrument. Differential photo-calorimetry (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 Photoelectric Instrument Factory, Beijing Normal University, China) which is sensitive in the wavelength range of 320–400 nm. The samples containing 1–5 mass% of the initiator were sonicated for 30 min to ensure complete dissolving, and then the sample weighed 2–4 mg was placed in aluminium sample pans. Each sample was held in isothermal conditions at 35°C in nitrogen prior to irradiation. The photopolymerization reaction was carried out until no heat was evolved. The data reported for each composition is an average of separate photopolymerizations. The baseline is subtracted in order to ensure the result is unaffected by the radiation enthalpy of background.

Results and discussion

Photo-initiation behavior of OAK

For the free-radical polymerization reaction is exothermic, the polymerization progress can be moni-



Scheme 2 Chemical structures of photoinitiators and monomers used

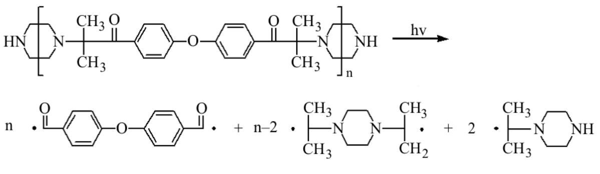
tored by means of DPC, by which the heat flow ($\mathrm{d}H/\mathrm{d}t$) from the sample during irradiation is measured as the function of reaction time (t). The reaction rate is calculated from the reaction enthalpy by the following equation:

$$R_\mathrm{p} = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}(H/H_\infty)}{\mathrm{d}t} = \frac{\mathrm{d}H/\mathrm{d}t}{H_0 m} \qquad (1)$$

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 [6]), and m the mole number of carbon double bond in the system. Conversion curve (α–t) can be obtained by integrating the polymerization rate curve ($\mathrm{d}\alpha/\mathrm{d}t$–$t$).

The conversion curve for photo-polymerization of HDDA initiated by OAK is shown in Fig. 1. In order to evaluate the initiation efficiency of OAK, two commercial photoinitiators with low molecular mass, HMPP and MMMP, were chosen for comparison, in which MMMP has similar chemical structure with OAK and can be regarded as the low molecular homolog. It is well established that the photo-decomposition of HMPP and MMMP follows Norrish type I mechanism. By comparing the three conversion curves, it can be found that OAK has the competitive performance with those low molecular photoinitiators. The induction period for HMPP is shorter than those for macrophotoinitiator OAK and MMMP, but the ultimate conversion is almost the same.

The photoactive oligomer in OAK has a weak C–C bond with dissociation energy lower than the 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 3.



Scheme 3 Proposed mechanism of photochemical decomposition of the macrophotoinitiator OAK

Because there are two weak C–C bonds within a repeat unit of the oligomer, the biradical intermediates will appear in the photo-decomposition outgrowth. It can increase the initiating efficiency or the probability of fragment bonded to the backbone of formed polymer chain. As photoinitiator is hard to reach complete photoscission in usual formulation, the photoinitiator left will keep its initial oligomeric state with low migration and low volatility. Even for the photolysis oligomeric molecule, the fragments might exhibit higher molecular mass enough to prevent volatilization.

Figure 2 shows the photo-initiation behavior for the polymerization of three types of monomers, HEMA, HDDA and TMPTA. These monomers exhibit similar polymerization profiles as those initiated

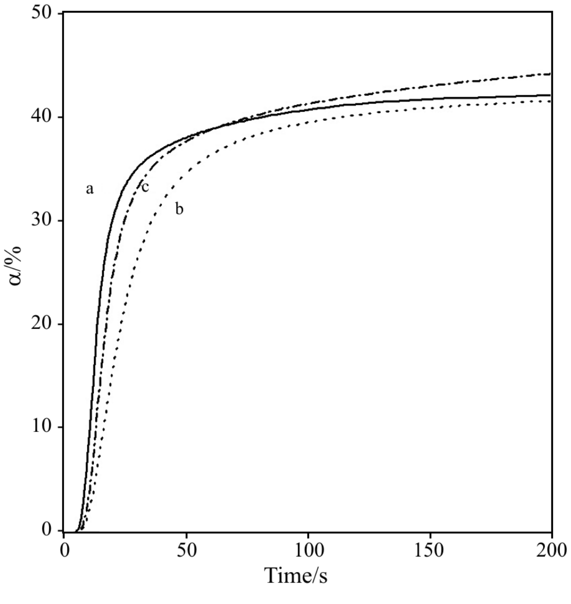


Fig. 1 Plots of α *vs.* t for HDDA initiated by a – 3.6 mass% HMPP (1173), b – 4.0 mass% OAK-1 (M_n=2030), c – 5.8 mass% MMMP (907), room temperature, nitrogen atmosphere, light intensity: 4 mW cm^{-2}

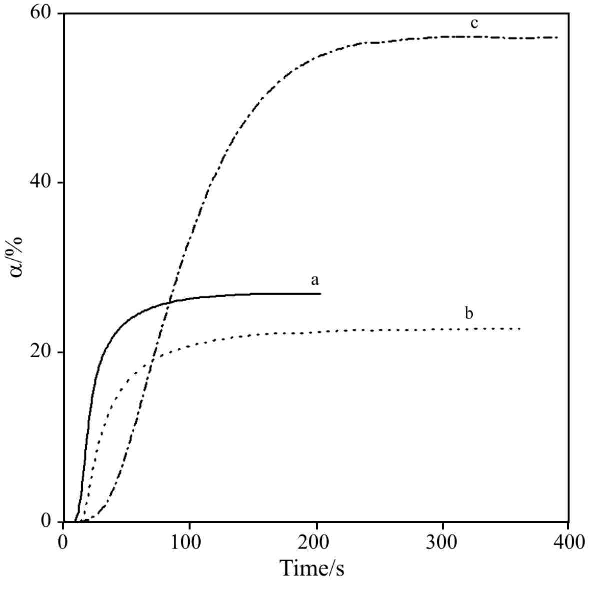


Fig. 2 Plots of α *vs.* t for different monomers, a – HDDA, b – TMPTA, c – HEMA, 2.0 mass% macrophotoinitiator OAK (M_n=4969)

with common low molecular photoinitiators. Difunctional monomer HDDA and trifunctional monomer TMPTA show much higher polymerization rate than mono-functional monomer HEMA in the early stage of polymerization.

Kinetics

The polymerization rate and conversion *vs*. exposure time for HDDA with various OAK (M_n=3913) concentration [*PI*] are shown in Fig. 3. It is found that the polymerization rate as well as the final monomer conversion increases with increasing the photoinitiator concentration. It is also found from Fig. 4 that increasing light intensity can increase the polymerization rate and the final monomer conversion.

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

$$R_p = -\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}}[M]R_i^{1/2} = = k_p\left(\frac{4\varepsilon\Phi}{k_t}\right)^{1/2}[M]I_0^{1/2}[\mathrm{PI}]^{1/2} \qquad (2)$$

where [*PI*] is the concentration of photoinitiator, [*M*] the concentration of monomer, ε the molar extinction coefficient of photoinitiator [7], 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 $3\cdot10^6$ M^{-1} s^{-1} for acrylate monomer [8], Φ the quantum yield of initiator (initiating efficiency), I_0 the incident light intensity. Figures 5 and 6 show the plots of R_p *vs*. $[PI]^{0.5}$ and R_p *vs*. $I_0^{1/2}$ at conversion between 5~12%. Linear relationships can be found for all the plots in these two figures, suggesting that the photo-polymerization initiated by OAK is in accordance with Eq. (2). Biradical termination mechanism is expected for this photo-polymerization system.

Effect of oxygen

Figure 7 clearly demonstrates the oxygen inhibition effect in the photopolymerization of HDDA initiated by OAK. In the presence of oxygen, the induction period of the reaction is longer than that in nitrogen atmosphere. This causes a lower degree of conversion of the reactive species in the presence of molecular oxygen due to its reaction with the free radicals generated from photoinitiator as well as with the polymeric radicals, forming peroxides which lead to inhibit or delay the free radical curing process [9].

Effect of sensitizer

2-methyl-l-I4(methylthio)phenyl-2-morpholinopropan-1-one (MMMP, Irgacure 907) is a good photoinitiator and widely used in white lacquer and blue printing ink. The reactivity of these systems can be further improved by the addition of sensitizers such as thioxanthones. An obvious increase in reactivity can be obtained using the combination of MMMP and isopropylthioxanthone (ITX) [10]. The triplet state ITX transfer energy to MMMP, the polymerization is initiated by the cleavage of MMMP, which possesses the lower triplet energy. Because MMMP is free radical photoinitiator, the polymerization is also initiated by the α-cleavage of MMMP under the irradiation. A synergistic effect exists in this case. As OAK may be considered as the oligomeric

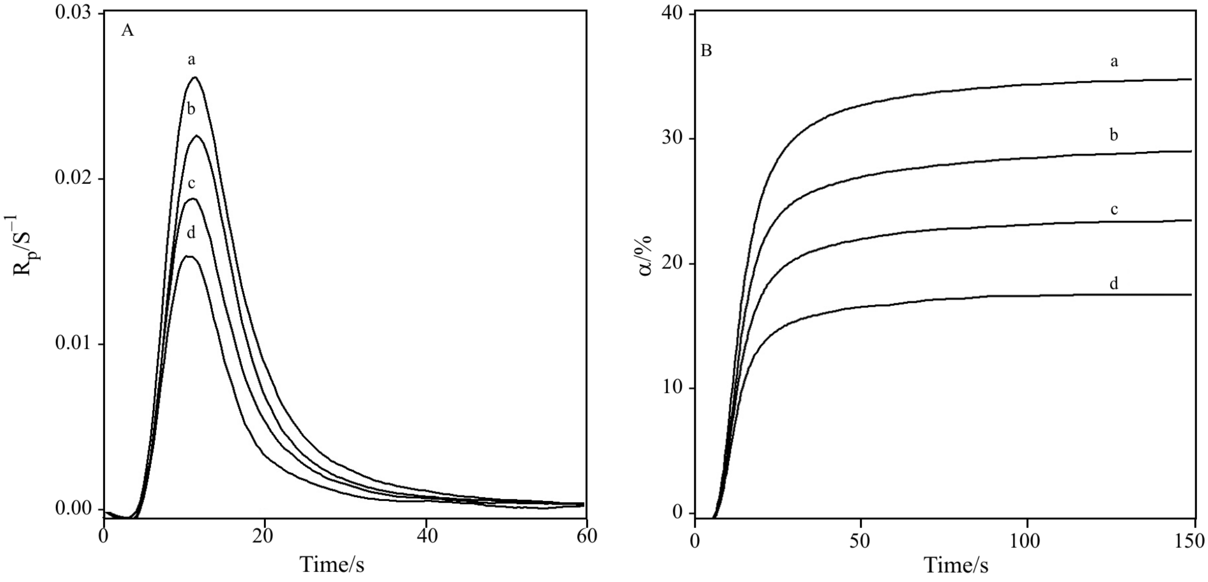


Fig. 3 Plots of A – R_p *vs*. *t* and B – α *vs*. *t* for HDDA with OAK (M_n=3913) concentration [*PI*] of a – 3.8, b – 3.0, c – 2.2 and d – 1.4 mass%, light intensity 4.0 mW cm^{-2}, nitrogen atmosphere, 35°C

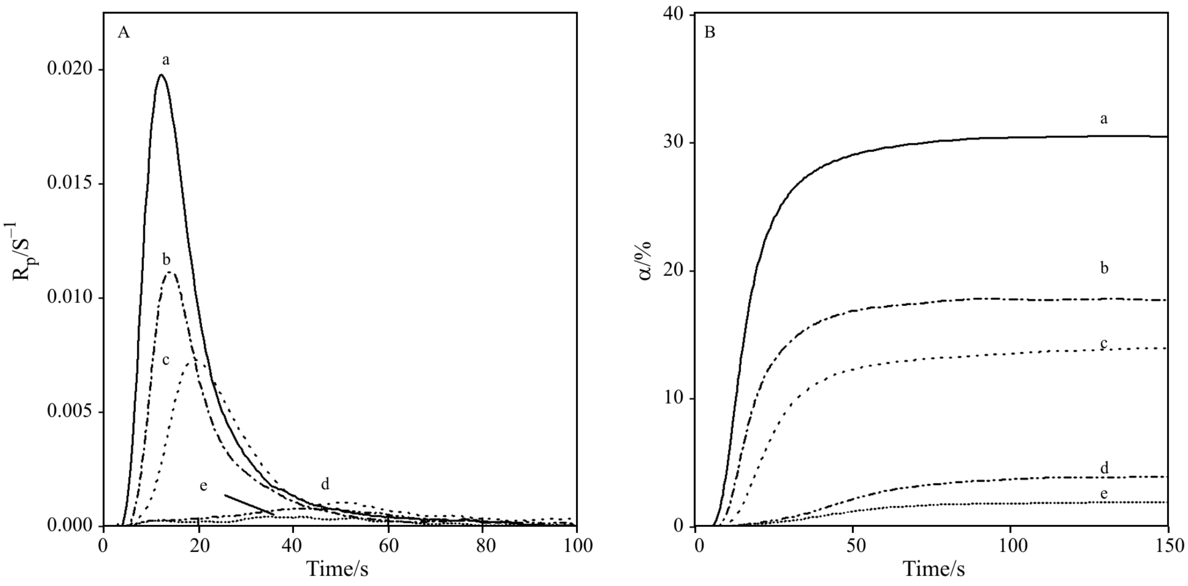


Fig. 4 Plots of A – R_p *vs.* *t* and B – α *vs.* *t* for HDDA with various light intensity. OAK (M_n=3913) concentration: 3.0 mass%, nitrogen atmosphere, 35°C, light intensity: a – 4.2, b – 3.0, c – 2.4, d – 1.3 and e – 0.84 mW cm^{-2}

MMMP, ITX was added to OAK initiated system for compassion. In contrast with expectation, a slower curing rate was observed, as shown in Fig. 8. This phenomenon can be illustrated by the UV-vis absorption characteristic of photoinitiator and ITX, as shown in Fig. 9. The macrophotoinitiator containing *tert*-amine structure exhibits absorption peaks at 228, 279 nm, and MMMP at 232, 307 nm, ITX at 235, 258 and 381 nm. The reactivity enhancement of MMMP is due to the fact that ITX is different form MMMP in the UV spectra profile, so ITX shares less incident light with the MMMP than OAK. ITX is excited to the triplet state by the long wave light (around 375 nm) and then an energy transfer from ITX to MMMP happens because ITX have triplet energies situated around 59–63 kcal mol^{-1}, which is higher than that of MMMP, and MMMP is subsequently activated by interacting with the excited state ITX. Because the main absorption band of OAK (279 nm) is nearer to that of ITX (258 nm) than to that of MMMP (307 nm), ITX added to the system will absorb competitively the incident light energy and affect the α-cleavage of OAK, leading to a lower initiation activity.

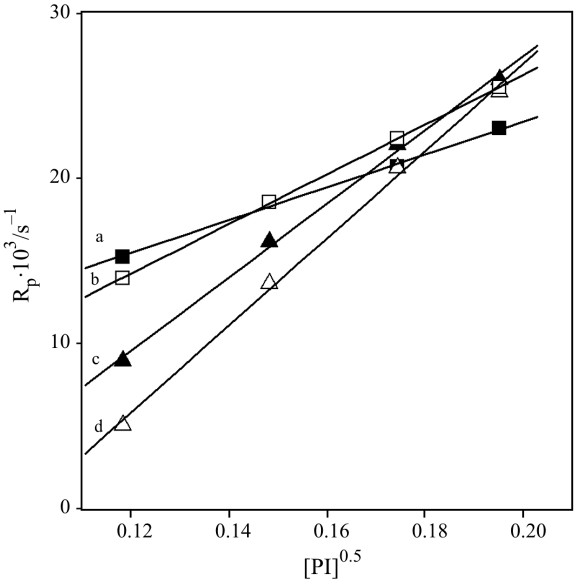


Fig. 5 Plots of R_p *vs.* $[PI]^{0.5}$ for OAK-initiated photo-polymerization of HDDA, at conversion of a – 5, b – 7, c –10 and d –12%

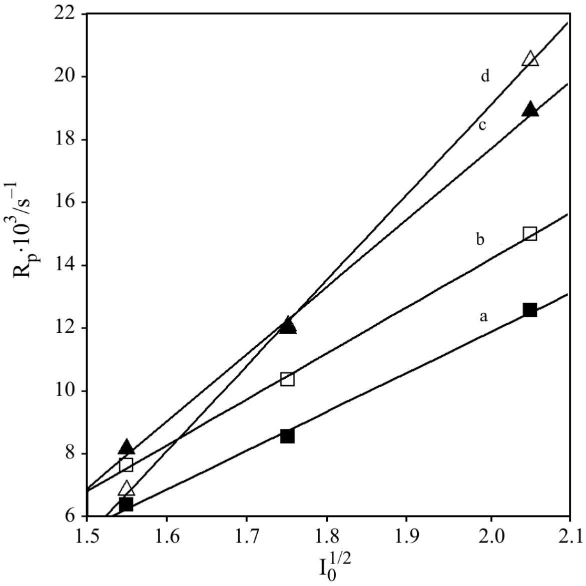


Fig. 6 Plots of R_p *vs.* $I_0^{1/2}$ for OAK-initiated photo-polymerization of HDDA, at conversion of a – 5, b – 7, c – 10 and d – 12%

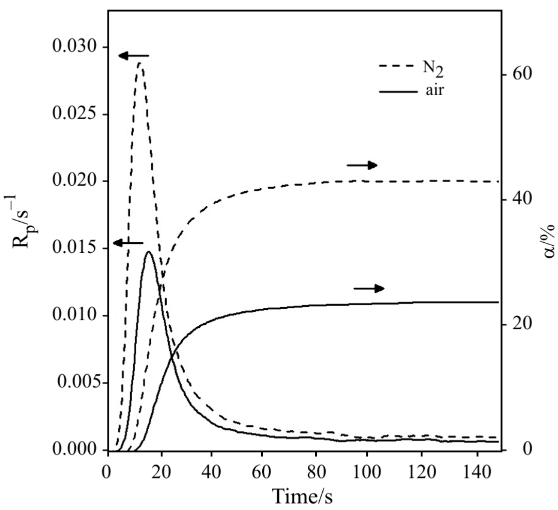


Fig. 7 Plots of R_p~*t* and α~*t* for HDDA with 4.0 mass% macrophotoinitiator OAK (M_n=2032) in various atmospheres, light intensity 4.0 mW cm^{-2}, 35°C

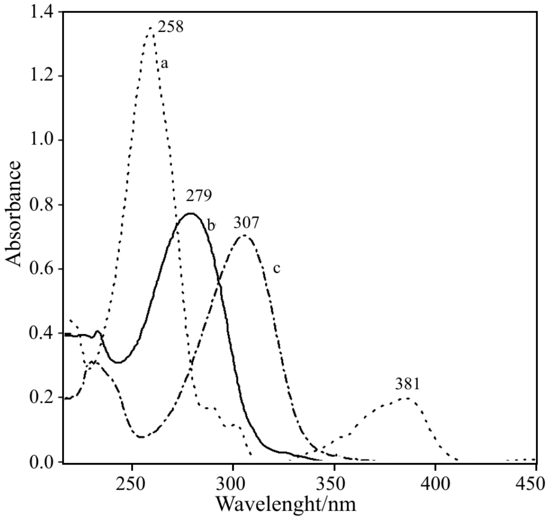


Fig. 9 The UV-vis spectra of a – ITX (3.3·10^{-5} M), b – OAK (3.8·10^{-5} M by repeat unit, M_n=2691) and c – MMMP (3.8·10^{-5} M) in CH_2Cl_2

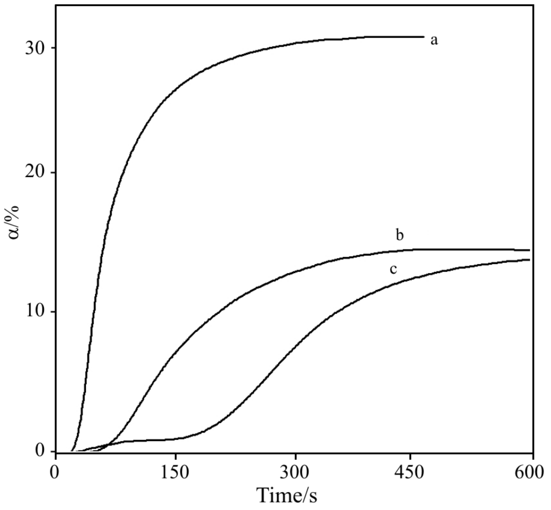


Fig. 8 Conversion *vs*. exposure time for HDDA with 2.0 mass% macrophotoinitiator (M_n=3913), light intensity 3.6 mW cm^{-2}, nitrogen atmosphere, 35°C, a – without ITX, b – 0.29% ITX and c – 0.80% ITX

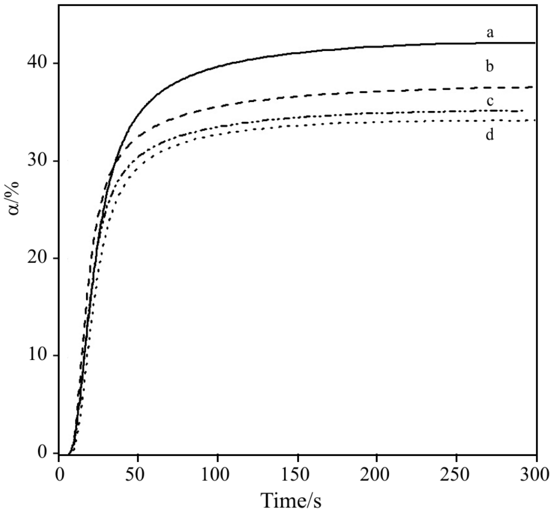


Fig. 10 Conversion *vs*. exposure time for HDDA photopolymerization with 4 mass% various molecular mass macrophotoinitiator, light intensity 4.0 mW cm^{-2}, nitrogen atmosphere, 35°C, a – M_n=2032, b – M_n=2581, c – M_n=3011, d – M_n=3144

Effect of molecular mass

In some cases, the macrophotoinitiator shows higher reactivity than low molecular mass analogues due to energy migration effect or efficient intramolecular reaction within a polymer, which is so-called 'polymer effect'. Thus, high molecular mass polymers should show high reactivity. However the result obtained here revealed an inverse behavior. For the macrophotoinitiators with $\overline{M}_n$ in the range of 2000–3000, increase in molecular mass reduced the initiation efficiency, as shown in Fig. 10. An energy transfer process predicted is not observed in the result. Because there are weak bands in the polymeric backbone, the polymeric chain is divided into several fragments by α-cleavage under the irradiation of UV light, as a result the energy transfer is broken. Under the consideration of migration aptitude, initiation efficiency and compatibility with monomer and resin, initiator with adequate molecule mass is preferable.

Conclusions

Investigation of the photopolymerization process by DPC revealed that conversion and rate profiles were changed as a function of the macrophototoinitiator concentration and light intensity. Biradical termination occurred at low conversion region of the polymerization, in accordance to the theoretical presumption. The conversion and polymerization ratio decreased with increasing molecular mass of macrophotoinitiator, and energy transfer effect was not observed in this system. Different from 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (MMMP), the initiation reactivity of the macroptotoinitiator decreased with the addition of sensitizers ITX. Oxygen can delay the free radical curing process initiated by the macrophotoinitiator.

Acknowledgements

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