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SESAMIN AS A CO-INITIATOR FOR UV PHOTOPOLYMERIZATION[1]

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Abstract—Sesamin, a nature compound from sesame seed, which contains two cyclic acetal structures, was used as a co-initiator for UV polymerization initiator system, and 1,6-Hexanedioldiacrylate was used as the photopolymerization monomer. Photopolymerization kinetics was recorded by real-time infrared spectroscopy. For BP/Sesamin initiator system, the double bond conversion increased with the increase of Sesamin concentration and light intensity. Combination of p-chlorobenzophenone and Sesamin had the highest initiating reactivity. The polymerization rate and final double bond conversion of acrylate monomer were higher than that of methacrylate monomer.

INTRODUCTION

UV-curing of acrylate based formulations is a well established technique and has been subject of countless investigations and publications [1, 2]. Photopolymerization technique has been used in a lot of fields such as coatings, inks, adhesives, photolithography, and biomedical materials because of the advantages such as low energy consumption, environmental friendly and high efficiency [3–6].

It is well known that the photoinitiator is the key component of every UV-curable formulation. Briefly, free radical photoinitiators fall into two categories, namely, type I and II [7, 8]. Type I photoinitiators undergo an α-cleavage process to form two radical species (e.g., benzoin derivatives). Bimolecular photoinitiators, Type II, are based on compounds, whose triplet excited state abstract a hydrogen atom from suitable donors (co-initiator) producing an initiating radical. Among type II photoinitiators, benzophenone is the most important one because the use of amine makes possible the formulation of cost-effective UV inks and coatings. However there are many shortcomings such as bad odor, migration and evaporation for the use of amine co-initiator. Besides, amine co-initiator in formulations was prone to lead to yellowing, toxic and mutagenic [9, 10]. So investigations of new efficient co-initiators for BP are important undertakings.

Sesamin is a double cyclic acetal structure contained compound (Fig. 1), which is one of the lignans found in high concentrations in sesame seed and unroasted sesame oil [12]. It shows that sesamin causes a significant decrease in the activity and gene expression of hepatic fatty acid synthase and pyruvatekinase, the lipogenic enzymes [13], thus it may be biocompatible for the application of biomaterials. Since the active hydrogen between two alcohoxy groups in the cyclic acetals is abstractable, sesamin can be used as hydrogen donor to form a radical [11]. As a result, sesamin was chosen to substitute amine as a co-initiator for BP to initiate the photopolymerization of 1,6-hexanedioldiacrylate monomer in this study. The synergistic effect of sesamin on BP was investigated by near FTIR technique.

EXPERIMENTAL

Materials

1,6-Hexanedioldiacrylate (HDDA), tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA) (donated by Sartomer Chemical Co.), sesamin (Acros, New Jersey, USA), UV initiators (benzophenone derivatives) such as benzophenone (BP), p-chlorobenzophenone (CBP), and methyl-o-benzoylbenzoate (OMBB) were all donated by Runtech Chemical Co.

Instrumentation

FTIR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA). UV–Vis Absorption spectra were recorded in acetonitrile solution on a HitachiU-3010 UV–Vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). A cell path length of 1 cm

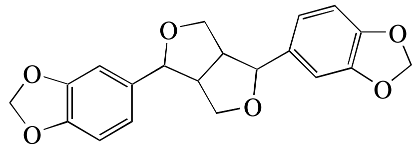

Fig. 1. Chemical structure of sesamin.

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[1] Статья печатается в представленном авторами виде.

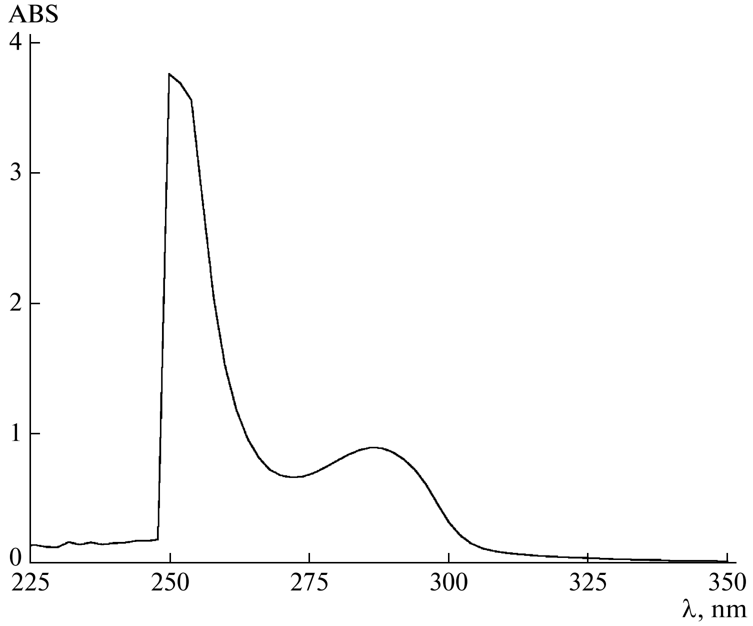

Fig. 2. UV-Vis absorption spectra of SA (1×10^{-4} mol/l) in DMSO.

was employed. UV spot source (EFOS Lite, 50 W miniature arc lamp, with 5-mm crystal optical fiber, Canada) was employed. Light intensity was recorded by the UV light radiometer (Photoelectric Instrument Factory, Beijing Normal University, Beijing, China).

Real-Time Infrared Spectroscopy

Fourier transform infrared spectra (FTIR) were obtained on a Nicolet 5700 instrument. Series real-time IR (RTIR) was used to determine the conversion of double bonds. The mixture of monomer, BP and co-initiator sesamin was placed in a mold made from glass slides and spacers with 15 ± 1 mm in diameter and 1.2 ± 0.1 mm in thickness. The samples were placed in the compartment of a Fourier transform infrared spectrometer and were simultaneously exposed to a UV-light source and an IR analyzing light beam. The absorbance change of the =C—H peak area from 6094.90 to 6174.50 cm^{-1} was correlated to the extent of polymerization. The degree of conversion, DC, can be expressed by the following relation:

$$\mathrm{DC\%} = (A_0 - A_t) \times 100/A_0,$$

where A_0 is the initial peak area before irradiation, and A_t is the peak area of the double bonds at t time.

RESULTS AND DISCUSSION

UV-Vis Absorption of Sesamin

UV-Vis absorption spectrum of sesamin in DMSO is shown in Fig. 2. It can be observed that sesamin possesses a maximum absorption peak at 250 nm, and another absorption peak at 315 nm which belongs to the absorption of benzodioxolane.

Kinetic Study of Photopolymerization Using Sesamin as a Co-Initiator

The kinetics of photopolymerization of various monomers using sesamin in different conditions was studied by real time infrared spectroscopy. The RTIR technology has been widely used to measure the double bond conversion of (meth)acrylate monomers under irradiation [14—16]. Upon irradiation, the extent of polymerization as a function of time was accurately reflected by measuring the decrease of the =C—H absorbance peak area. The rate of polymerization (R_p) could be calculated by the time derivative of the DC curve [17].

The photopolymerization of HDDA was performed with various BP/sesamin combinations. Figure 3 represents the kinetics of HDDA at the same BP concentration (2 wt %) and different sesamin concentrations. The obtained results indicated that in the absence of sesamin the limited conversion of the polymer (DC) was about 49% in 3 min. When the concentration of sesamin was 0.5 wt% the DC reached to 78% at the same period of time. Increasing the concentration of sesamin caused the increase of the conversion of mixture.

Similar to the BP-amine system, sesamin could be used instead of amine as a co-initiator. The concentration of sesamin had great influence on kinetics of HDDA. The higher the sesamin concentration, the more free radicals could be produced during irradiation resulting in the higher rate of polymerization.

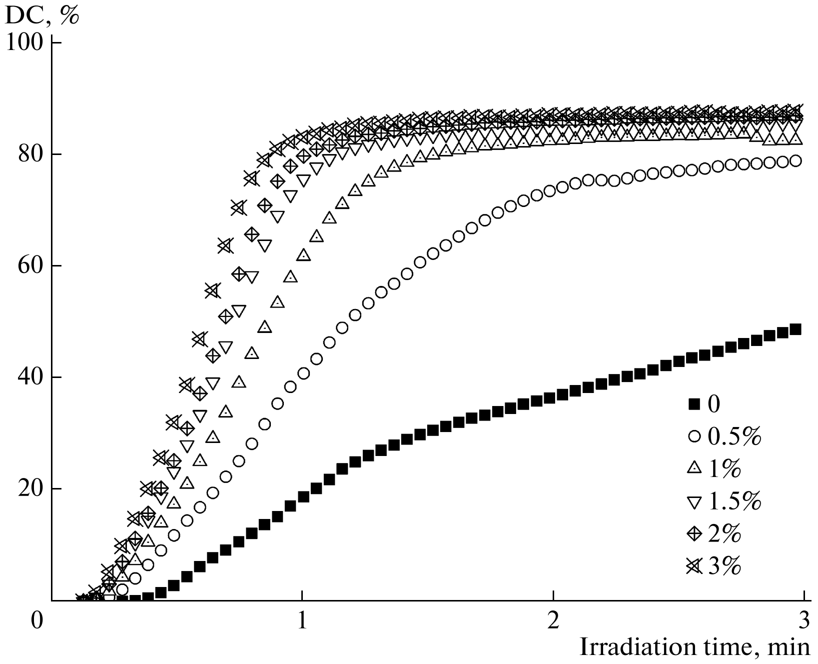

Fig. 3. The results of photopolymerization of HDDA with 2 wt % BP as initiator, using different concentration of sesamin as coinitiator. Light intensity = 30 mW/cm^2.

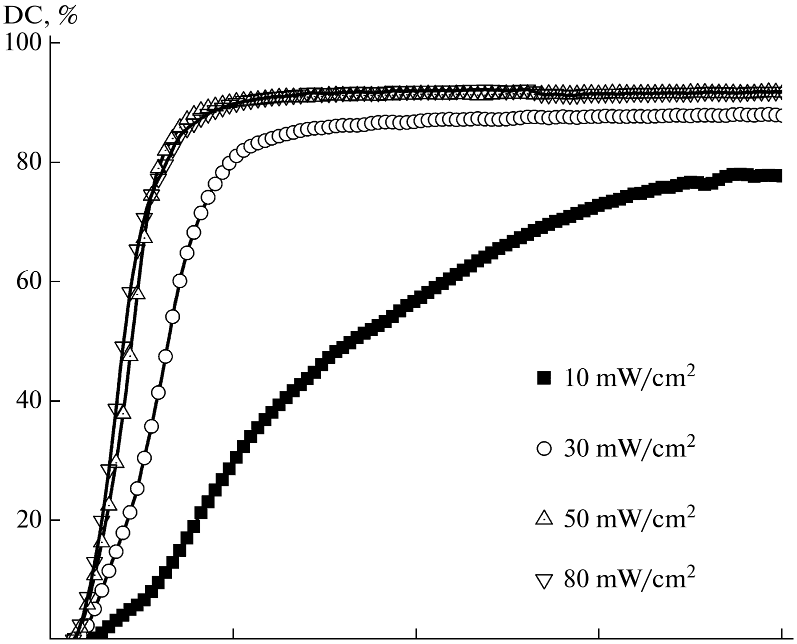

Fig. 4. The results of photopolymerization of HDDA with different light intensity. [BP] = [SA] = 2 wt %.

Figure 4 shows the conversion vs. time plots of HDDA initiated by 2 wt % BP in the presence of 2 wt % sesamin at different light intensity. When the light intensity increased from 10 to 80 mW/cm^2, the effect on the polymerization was similar to the influence of photoinitiator concentration. The polymerization rate and final conversion increased with the increase in light intensity. This was because the higher light intensity could yield more radicals, which led to the increase in polymerization rate and final conver-

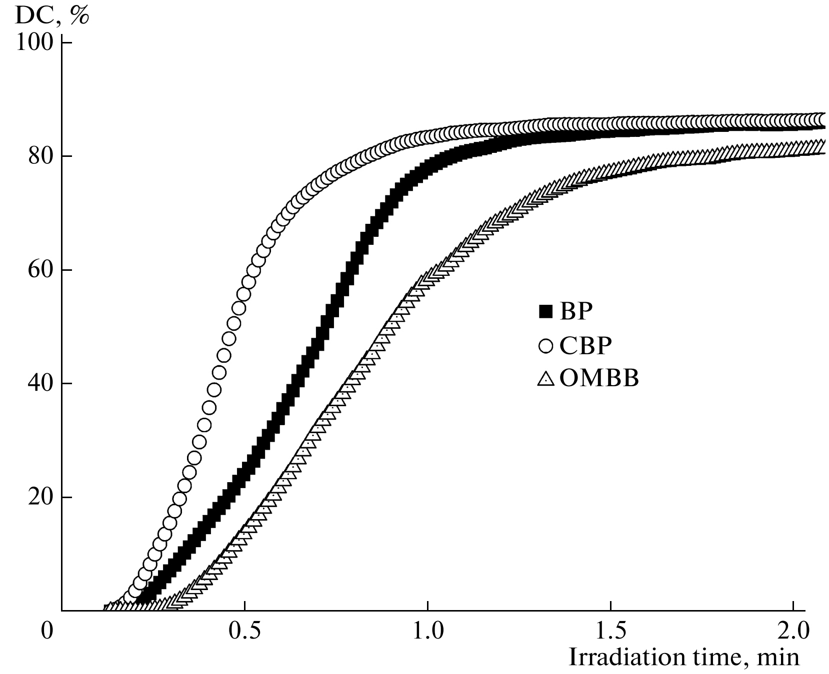

Fig. 5. The results of photopolymerization of HDDA with 2 wt% different BP as initiator. [sesamin] = 2 wt %.

sion. At the same time, the higher number of radicals yielded by the increase of light intensity could overcome oxygen inhibition more efficiently, resulting in the shortening of induction period.

Since the activity of most bimolecular photoinitiators for UV-curing relied on the well-known photoreduction of aromatic ketones, the chemical structures of BP derivatives played a great role in the kinetics of photopolymerization [18]. As shown in Fig. 5, among three BP derivatives, the limited conversion in the case of BP was slightly higher than in the case of OMBB, but was almost the same as for CBP. CBP provided the highest polymerization rate among the three BP derivatives systems. This is mainly because the different substation's BP derivatives can form different excited state under the light irradiation, resulting in different pairs of demonstrated ability to extract hydrogen. Cl-substituent is electron-withdrawing group while –COOMe is electron-donating group. As electron-donating groups with a fixed –COOMe, electron can be transferred to the carbonyl, making the excited state have a charge-transfer model. This will greatly reduce the electroaffinity of the carbonyl oxygen atom, as a result the ability of hydrogen abstraction is reduced and the initiator efficiency is decreased.

The efficiency of sesamin as co-initiator for the photopolymerization of various acrylates and methacrylates was also investigated by FTIR. Figure 6 shows the conversion versus time plots of different monomers. The results indicated that BP/sesamin was efficient photoinitiator for TPGDA, which showed the highest polymerization rate. The functionality of acrylates had a strong influence on the polymerization rate. Compared to the triacrylate TMPTA, HDDA is a diacrylate with lower initial concentration of acrylate groups, which leads to slower initial polymerization rate. As the functionality increased, the viscosity of the polymer increased, with the resulting gel effect and the higher cross-link density, which set a limit to the extent of conversion [19]. So poly(HDDA) has lower viscosity than poly(TMPTA), resulting in the higher final conversion. Besides, the polymerization rate and double bond conversion of TMPTA was significantly higher than that of TMPTMA, indicated that the rate of polymerization for acrylates was significantly higher than that of methacrylates with the same degree of functionality, because acrylates were more reactive than methacrylates.

CONCLUSIONS

It is clear that sesamin is an efficient co-initiator for BP to initiate the photopolymerization of HDDA. When BP was used alone as initiator, the final conversion was only 49% in 3 min, while adding 3 wt% of sesamin, the final double bond conversion reached to 87%. With increase in light intensity, the final double bond conversion increased. CBP showed the most effective initiate efficiency among the three BP derivatives systems. For BP/sesamin initiator system, the polymerization rate of TPGDA was the highest, and the polymerization rate and final double bond conversion of methacrylate monomer were lower than that of acrylate monomer.

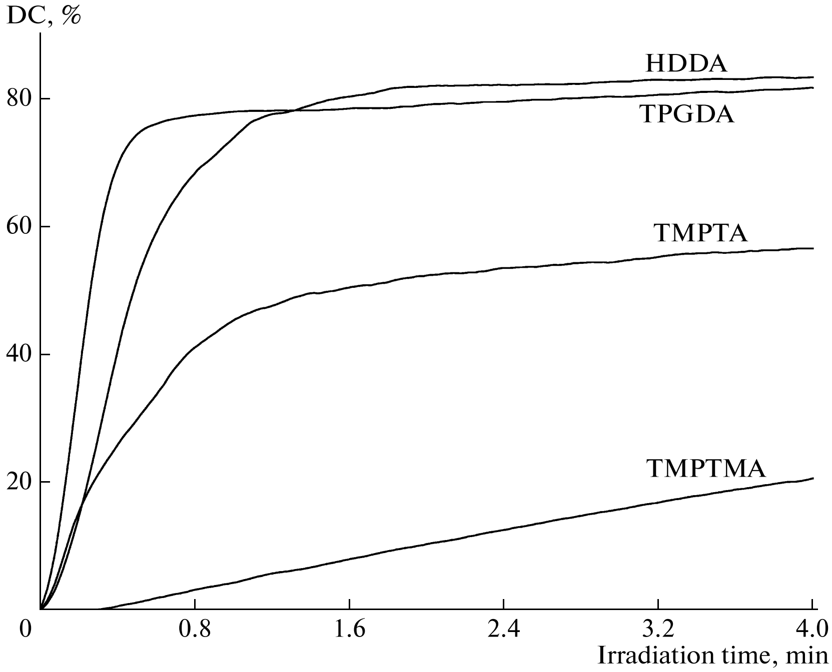

Fig. 6. Plots of double bond conversion of different monomers vs. irradiation time.

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