

PERFORMANCE AND INITIATION MECHANISM OF ISOPROPYLTHIOXANTHONE IN SURFACE PHOTOGRAFTING

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Abstract In a polymerization model with low density polyethylene (LDPE) as the substrate and acrylic acid (AA) as the monomer, the performance of isopropylthioxanthone (ITX) in initiating surface photografting polymerization was evaluated. The results show that the reactivity of photopolymerization and photografting of ITX locate between benzophenone (BP) and benzildimethylketal (BDK) for polymerization, $\text{BDK} > \text{ITX} > \text{BP}$; for surface grafting polymerization, $\text{BP} > \text{ITX} > \text{BDK}$. These results can be explained by a reaction mechanism of the inter-molecular or intra-molecular hydrogen abstraction reaction of ITX.

Keywords Photografting polymerization, Photopolymerization, Hydrogen abstraction reaction

INTRODUCTION

The fragmentation and the hydrogen abstraction from an H-donor of carbonyl compounds under UV irradiation form the chemical basis of photopolymerization^[1]. BDK is a typical cleavable photoinitiator, therefore, it has been widely used in photocuring industry. BP is a typical hydrogen abstractable photoinitiator so that BP and its derivatives play a main part in photografting^[2] and photocross-linking processes^[3]. ITX is a commercial photoinitiator for photocuring applications. Because of its strong absorption both at short UV (200~300 nm) and at long UV (300~400 nm) wavelengths, ITX is used as a highly efficient photoinitiator in UV-cured ink, adhesive, coating, photo resist and so on. But its performance and application in surface photografting have not been reported in a publication.

Some groups have reported the vapor and liquid phase photografting processes with^[4, 5] or without photoinitiators^[6]. In previous publications, we not only developed a bulk surface photografting process^[7], but also studied in details the photografting reactivity of four kinds of carbonyl compounds^[8]. The present study will deal with the performance of ITX in initiating surface photografting on a experiment model with low density polyethylene (LDPE) as the substrate and acrylic acid (AA) as the monomer.

EXPERIMENTS

Materials

Commercial LDPE film (Boading corporation of plastic) of 60 μm thickness was used as the polymer substrate. Acrylic acid (No. 6 Chemistry Reagent Factory of Tianjin), BP (No. 1 Reagent Factory of Shanghai), BDK (Ciba Company), ITX (No. 1 Chemistry Company of USA) and ethyl 4-(dimethylamino)benzoate (EDAB) (No. 1 Chemistry Company of USA) were used as received.

Experimental Procedure

The setup for photopolymerization experiments described in a previous paper^[9]. A drop of solution containing

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monomer and photoinitiator was deposited on the surface of the bottom LDPE film with a micro-syringe. A top film was placed on top and the drop of solution was spread into an even and very thin (about 4 μm) liquid layer using suitable pressure with a quartz plate. The assembled unit was irradiated by UV radiation from the top and the extent of polymerization is controlled by varied the irradiation time.

The percentage conversion (C_p) of monomer into polymer and the percentage grafting conversion (C_g) are obtained by a gravimetric method according to the following equations:

$$C_p = 100 \cdot (W_p/W_o)$$

$$C_g = 100 \cdot (W_g/W_o)$$

where W_o is the weight of monomer between the two films, and W_p is the weight of polymer formed, including homopolymer and grafting polymer, obtained by weighing after vaporization of the residual monomer at 35°C for 24 h in a vacuum oven. W_g is the weight of the grafted polymer in the top and bottom films, obtained by weighing after extraction of the homopolymer with water. The percentage grafting efficiency G_E is the ratio of W_g and W_p ($G_E = W_g/W_p$), which could be increased by increasing grafting polymer and decreasing homopolymer.

RESULTS AND DISCUSSION

Photografting Reactivity

Figures 1 and 2 show the polymerization reactivity and the grafting reactivity of AA on LDPE films photoinitiated by ITX, BDK and BP. It can be seen that for polymerization, the photoinitiation reactivity of ITX is lower than that of BDK, but higher than that of BP, and for grafting polymerization, the reactivity of ITX is lower than that of BP, but higher than that of BDK; the average grafting efficiency G_E of these three photoinitiators is 86% (BP), 65.2% (ITX) and 12.8% (BDK), respectively. These results demonstrate that under the present reaction system, ITX is an efficient surface photografting initiator.

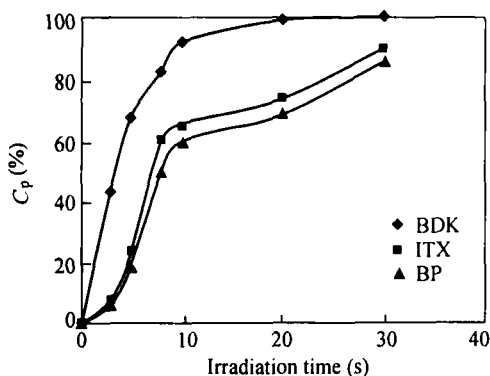


Fig. 1 The polymerization conversion of acrylic acid initiated by BDK, ITX and BP (0.1 mol/L) versus irradiation time at 55°C

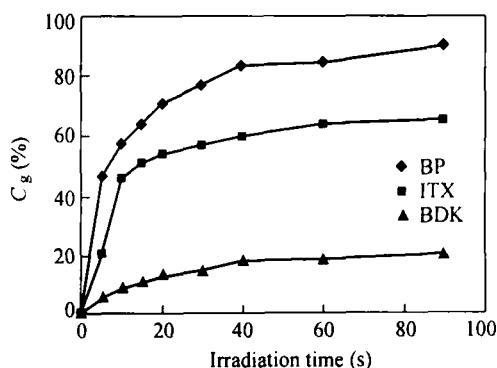


Fig. 2 The grafting conversion of acrylic acid initiated by three different photoinitiator (0.1 mol/L) versus irradiation time at 55°C

Photografting Reactivity of ITX-EDAB

In practical formulations, ITX is usually used along with the activated agent EDAB. The performance of the initiation system is shown in Figs. 3 and 4.

The results spell out that the addition of EDAB could really increase the initiation reactivity of ITX, but greatly reduces its grafting ability. The reason for this could be attributed to the suppression of hydrogen abstraction of ITX-EDAB compared to that of ITX-LDPE.

Concentration and Temperature

As shown in Fig. 5, both polymerization and grafting conversions increase with the increase of ITX concentration

within the range of 0.005–0.05 mol/L, but the polymerization conversion increases slowly. The reason may be that the more ITX molecules present the greater is the number of reaction sites.

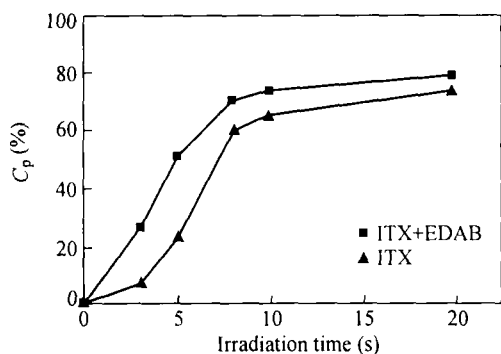


Fig. 3 The polymerization conversion of acrylic acid initiated by ITX (0.02 mol/L) and ITX (0.02 mol/L) plus EDAB (1.4 wt%) versus irradiation time at 55°C

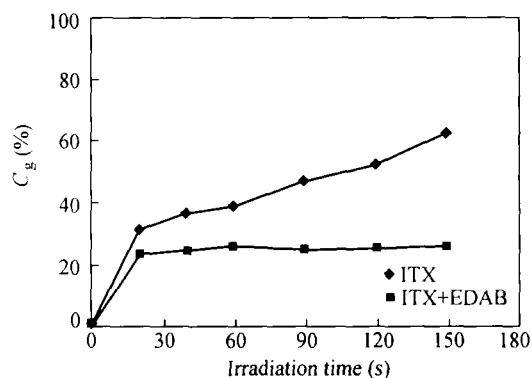


Fig. 4 The grafting conversion of acrylic acid initiated by ITX, ITX (0.02 mol/L) plus EDAB (1.4 wt%) at 55°C

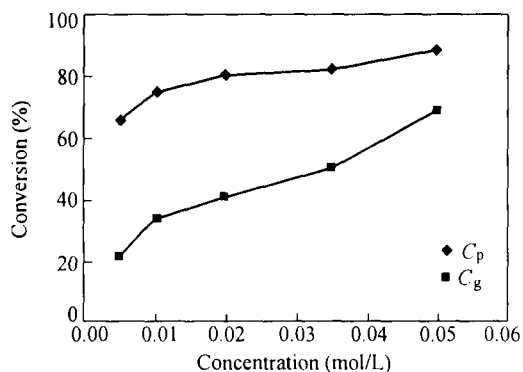


Fig. 5 The conversion of acrylic acid versus the concentration of ITX irradiated for 20 s at 55°C

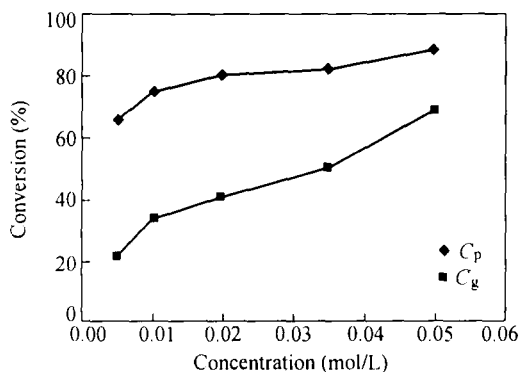


Fig. 6 The conversion of acrylic acid versus the reaction temperature initiated by ITX (0.02 mol/L) for 20 s

The effect of reaction temperature on polymerization is shown in Fig. 6.

It could be seen from Fig. 6 that with increasing reaction temperature, the grafting conversion is significantly increased but total polymerization conversion keeps constant and then decreases. The reason for this lies in the fact that along with the temperature increase, the hydrogen atom activity of the LDPE film rises, and the surface grafting sites increase, resulting in an increase in C_g ; along with the temperature increases, AA monomer and photosensitive molecules penetrate easier into the inside of LDPE film and the interface of LDPE and monomer is broadened, the curve of C_g significantly ascends. But when the temperature increases further, e.g. higher than 55°C, AA monomer penetrates more rapidly into the inside of LDPE film, some passes through LDPE film and vaporizes in air. Since the amount of AA monomer is reduced, it is not surprising that the overall polymerization conversion exhibits the above tendency.

UV Wavelength

The approach of using polyethylene PET as filter to cut off the far UV light of short wave-length (200–300 nm) was adopted in the previous publication^[9]. With the same experimental method and polymerization conditions, ITX shows a big difference between BDK and BP, as seen in Fig. 7, i.e. for BDK and BP initiation system after filtering out the short wave length UV light, almost no surface grafted polymer was detected. In contrast, for the

ITX and ITX-EDAB system, about 20% surface grafted polymer could be obtained. The character of ITX proves to be an advantage over BP and its derivatives.

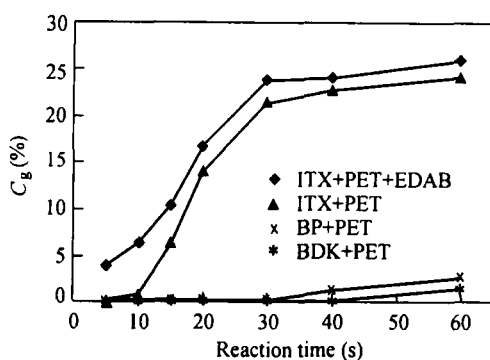
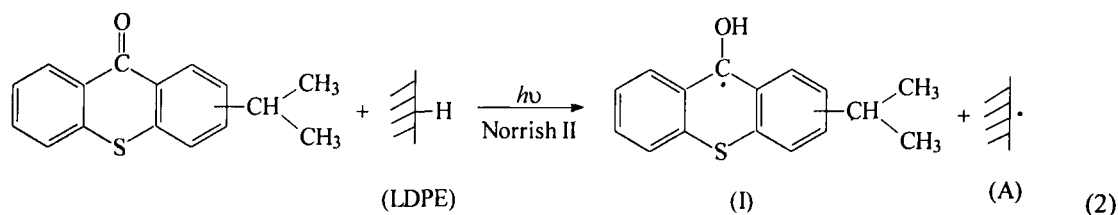
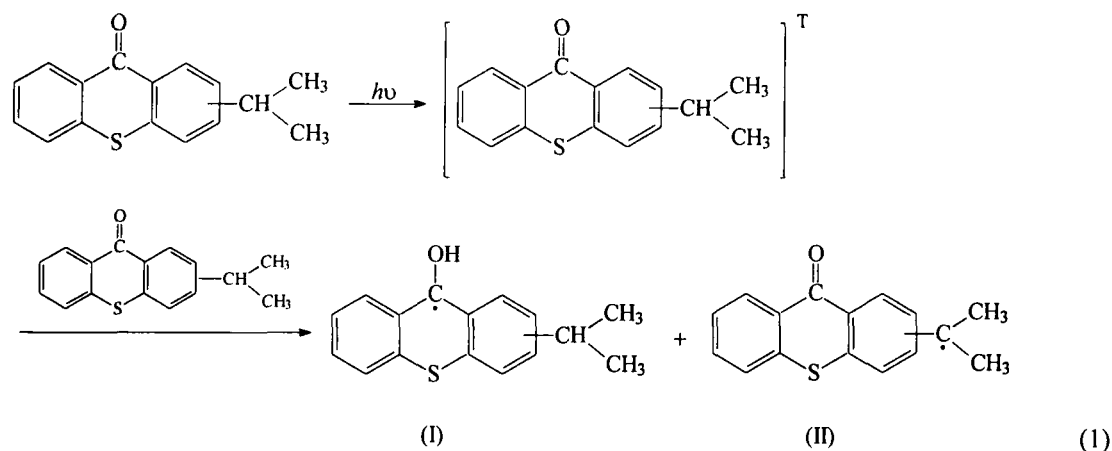


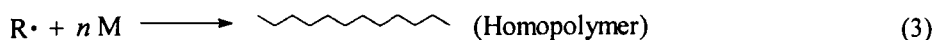
Fig. 7 The grafting conversion of acrylic acid versus irradiation time for ITX, ITX plus EDAB, BP and BDK (0.1 mol/L) deposited on 50 μm PET film at 55 $^{\circ}\text{C}$

Photoinitiation Mechanism

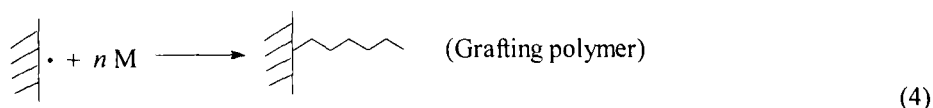
Based on the above experimental results, the following initiation mechanism could be proposed:



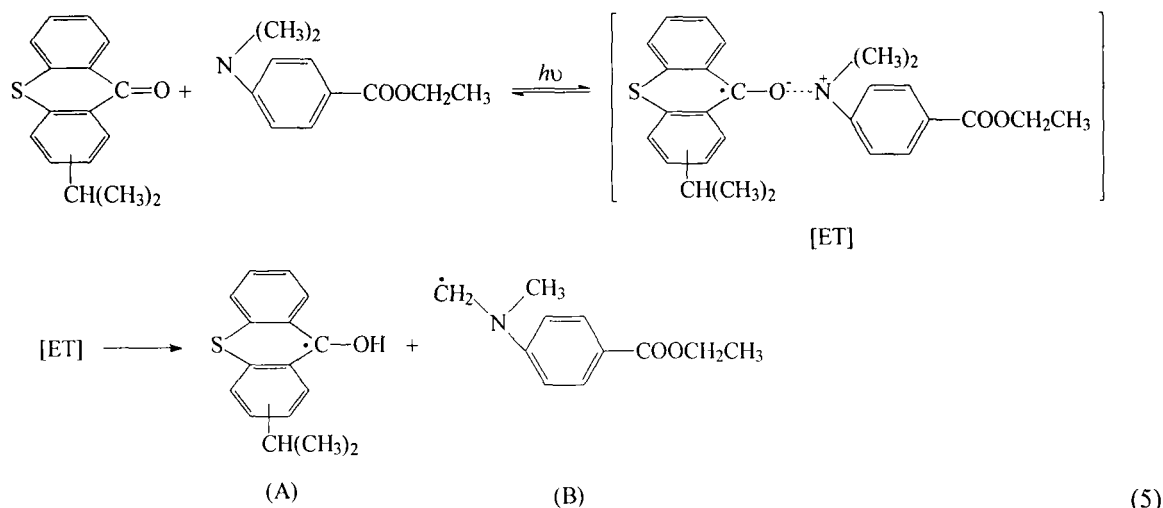
Both radical (I) and (II) can initiate a homopolymerization. The initiation reactivity of radical (II) is much higher than that of radical (I) due to the stereo and conjugating effect, this being the main reason why the G_E of ITX is lower than that of BP.



The surface radical (A) initiates the monomer and produces a surface-grafting polymer. Because the initiation reactivity of radical (I) is very low, most of polymers formed are graft polymers.



When EDAB is added, it will react with ITX, The reaction is shown as follows:



It is well known that the hydrogen abstraction reaction of a carbonyl compound with an amine proceeds very easily due to the formation of a charge transfer (CT) complex. The complexing effect induces two results: (1) the polymerization speed is strongly increased; (2) the grafting efficiency decreases significantly because the reaction suppresses and over the ITX-LDPE hydrogen abstraction.

CONCLUSIONS

ITX is a hydrogen abstractable photoinitiator therefore and can be used for surface grafting application. Its advantages over BP are that it still has appreciable grafting reactivity in the near UV range (300~400 nm).

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