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The role of far UV radiation in the photografting process

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Summary

With low density polyethylene (LDPE) film as substrate, polyethyleneterephthalate (PET) film as filter, and an high pressure mercury (HPM 15) lamp as UV radiation source, the function of far UV radiation was examined. The results show that when the far UV (200–300 nm) was eliminated, the rate of polymerization of acrylic acid in the interlayer between two LDPE films initiated by benzophenone (BP) dramatically decreased, and the grafting efficiency became close to zero. The decisive effect of the far UV is further confirmed in UV–VIS spectra measuring the hydrogen abstraction reaction of the excited BP. For polymerization systems containing allylic hydrogens, this effect is smaller, while hydroxycyclohexyl phenyl ketone (HHPK) and benzoyldimethylketal (BDK), which are typical photocleaving initiators, show little sensitivity to the far UV. Based on an energy graph of the excited states, the bond energies and the relevant photochemical reactions a tentative interpretation of the results has been made.

Introduction

The pioneering work of photografting was made by Oster et al (1) in 1956, where monomers were photografted onto polyethylene with benzophenone added and with irradiation from low pressure lamps giving mainly far UV radiation (200–300 nm). During the past 40 years, there has been a significant change in the UV sources used in photografting experiments with a shift to the near UV region (300–400 nm). Most of the recent experiments were conducted with high pressure or medium pressure Hg lamps with special filters to cut off the far UV radiation (2–5). These operations were also applied in our earlier work (6,7). This change originated for two reasons: The first was the common opinion that the triplet state of the n→π transition is responsible for the photoinitiation and, therefore, its origin, the singlet state absorption (300-400 nm), should be in the near UV area. The second was the successful development of medium and high pressure Hg arc lamps in the UV-curing industry, which were used also for grafting experiments.

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In a series of experiments to optimise the conditions for photografting, we have, however, found that the far UV radiation plays a decisive role in the photografting process and studied its effects in separate experiments. This paper will present our experiments and new findings.

Experimental

Materials

Commercial low density polyethylene (LDPE) film 0.03 mm thick and with a transmission close to 100% for the UV radiation (200–400 nm) was used as polymer substrate and polyethyleneterephthalate (PET) film 0.256 mm thick was used as a special UV – absorption filter in this study. The PET film used has UV absorption properties similar to those of a Pyrex glass (Figure 1) with total absorption at 256 nm and high transmission for 320–400 nm radiation.

Acrylic acid (AA) and methyl methacrylate (MMA) without purification were used as monomers and 1,3-cyclohexadiene (CHD) was used as additive without purification.

Benzophenone (BP), hydroxycyclohexyl phenyl ketone (HHPK) and benzoyldimethoxyketal (BDK) were used as photoinitiators without purification.

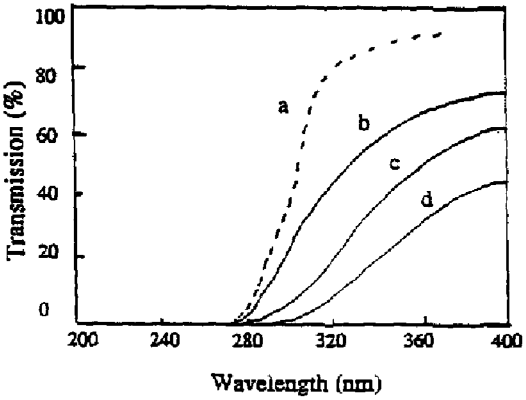


Figure 1. The transmission of 1 mm thick Pyrex glass (a) and the transmission of PET film: b, c, and d are one, two and three layers of PET film (256 μm), respectively.

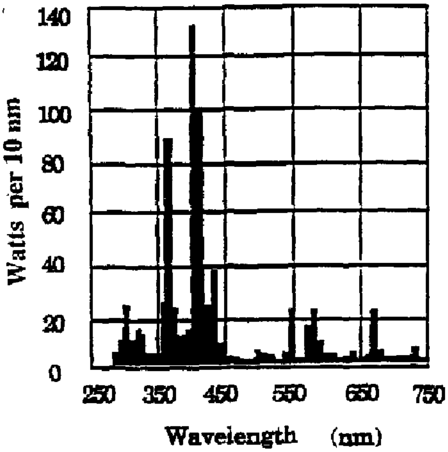


Figure 2. Absolute spectral energy distribution of HPM 15 lamp.

Experimental Procedure

Photopolymerization experiments were conducted in a photografting equipment (UV Cure) built in this laboratory and used extensively (6, 7, 8). The UV lamp used was a Philips high pressure mercury (HPM 15) (2 kW) with a spectral distribution as shown in Figure 2. The assembly for the photopolymerization experiments is shown schematically in Figure 3. A drop of a solution containing monomer and photoinitiator is deposited on the bottom

LDPE film with a micro-syringe. Another LDPE film is placed on top and the drop of solution is spread into an even and very thin (2–5 μm) liquid layer using suitable pressure with a quartz plate. The assembled unit is irradiated by UV radiation from the top side at a constant temperature. The extent of polymerization is controlled by varying the irradiation time manually.

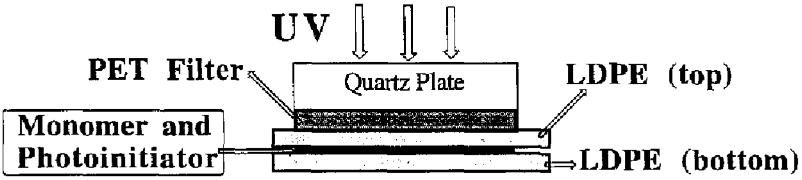


Figure 3. The assembly of Photopolymerisation.

A HP 8451A Diode Array Spectrophotometer was used to follow the hydrogen abstraction by measuring the decrease in BP concentration.

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

$$C_p = 100 \bullet (W_p/W_o) \qquad (1)$$

$$G_E = 100 \bullet (W_g/W_p) \qquad (2)$$

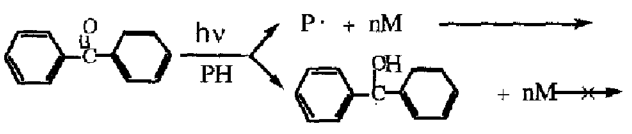
where W_0 is the weight of monomer and initiator between the two film layers, and W_p is the weight of polymer formed, obtained by weighing after vaporization of the residual monomer. The W_g is the weight of the grafted polymer, obtained by weighing after extraction of the homopolymer with proper solvents.

Results and Discussion

Under UV radiation, a photoinitiator between two LDPE films may undergo two photochemical reactions: one is photo-cleavage, which produces two radicals, and the other is hydrogen abstraction from the surface of LDPE film, which produces a ketyl radical and a surface radical. Only the surface radical can initiate surface photografting polymerization, whereas the other three small molecular radicals initiate homopolymerization.

The Benzophenone Photoinitiation System

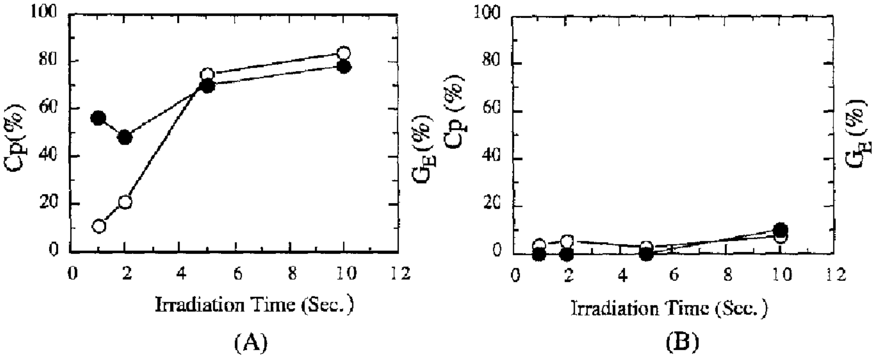
The photopolymerization of acrylic acid initiated by BP between two LDPE films is a highly efficient surface photografting system, as shown in Figure 4 (A). In 10 seconds the polymerization conversion reached 83% and the grafting efficiency was close to 80%. These results mean that the photoinitiation of BP proceeds mainly by the mechanism of photoreduction and the semipinacol free radical generated by the photoreduction has very low initiating reactivity,



(3)

(4)

When the far UV (200–300 nm) is eliminated by the PET film as filter, the rate of polymerization of acrylic acid decreases dramatically and the grafting efficiency approaches zero as shown in Figure 4 (B).



(A) (B)

Figure 4. The photopolymerization of acrylic acid initiated by benzophenone (2 wt-%) at 70°C without PET film (A) and with one layer of PET film (B) which excludes the far UV.
● is G_E (%) and ○ Cp(%).

The dramatic influence of the far UV radiation on the system can be attributed to an effect on the hydrogen abstraction, i.e. the initiation reaction. The interpretation is supported by UV–VIS spectrometer data for the rate of photoreduction of BP, measured by absorption at 256 nm (Fig. 5). The results show that the photoreduction of BP is strongly retarded when the far UV radiation is excluded

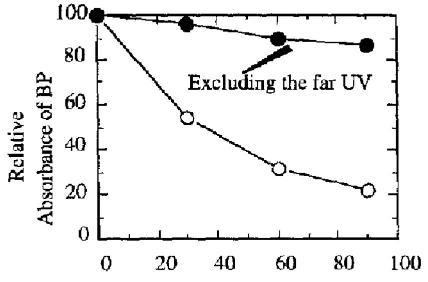


Figure 5. The effect of the far UV radiation on the photoreduction of BP (5 wt-%) at 70°C with AA as monomer.

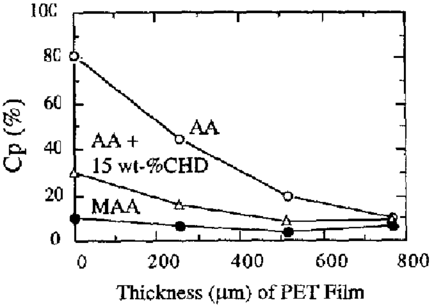
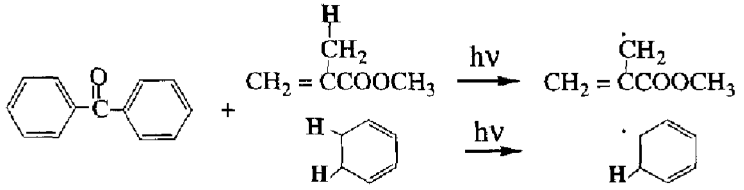


Figure 6. The effect of the thickness of the PET film as UV filter on polym-erization with 5 wt-% BP at 50°C.

The BP Photoinitiation System Containing Weak C–H Bonds

When methyl methacrylate (MMA) or a mixture of AA and 15 wt-% CHD were used as monomer system, the photopolymerization initiated by BP showed the following two features: 1) low polymerization rate as shown in Figure 6 with the 0 thickness of PET film, and 2) almost no grafted polymer was detected by gravimetric analysis. These results can be accounted for by allylic hydrogen abstraction of BP from the MMA or CHD:



(5)

(6)

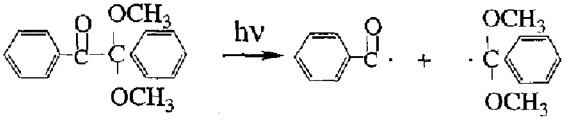
Since the bond energy of the allylic C–H bonds is lower than that of the surface-C–H bonds of LDPE film, the reaction (5) or (6) would strongly suppress the reaction (3). The formation of the allylic radicals, on the one hand, would retard the polymerization due to the low reactivity of the allylic radicals and, on the another hand, would result in the formation of homopolymer.

For the two systems containing the weak C–H bonds, when PET films were used to filter out the far UV radiation, the results are different from the pure AA system, as shown in Figure 6. In Figure 6 with increasing the thickness of PET film as filter, for pure AA, the suppression effect is large; for AA monomer mixed with 15 % CHD, the effect is smaller; and for MAA with three allylic hydrogens per molecule, the suppression effect is small.

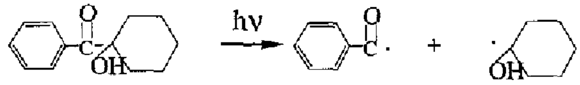
These results show that, when BP is used as photoinitiator, the far UV has a decisive role in the photografting polymerization but that its importance depends on the nature of the hydrogen donor.

The BDK,HHPK and PPD Photoinitiation Systems

BDK and HHPK are two commonly used photo-curing initiators. Under UV radiation they preferentially undergo photo-fragmentation as shown in the reactions (7) and (8). During photopolymerization with exclusion of the far UV radiation by an increased number of PET film as filter, the BDK and HHPK behave very differently from BP as shown in Figure 7. Excluding the far UV radiation has only a slight effect on the photopolymerization initiated by BDK and HHPK under the same experimental conditions as with BP.



(7)



(8)

These results demonstrate that the hydrogen abstraction reaction of BP and the cleavage reaction of BDK or HHPK have different requirements with regard to the wavelength range of the UV irradiation; the former requires far UV (200–300 nm) and the latter requires near UV radiation (300–400 nm). In other words, the photografting polymerization based on the photoreduction of aromatic ketones requires far UV (200–300 nm), while the homopolymerization or curing based on the photocleavage of ketones requires only near UV (300-400 nm).

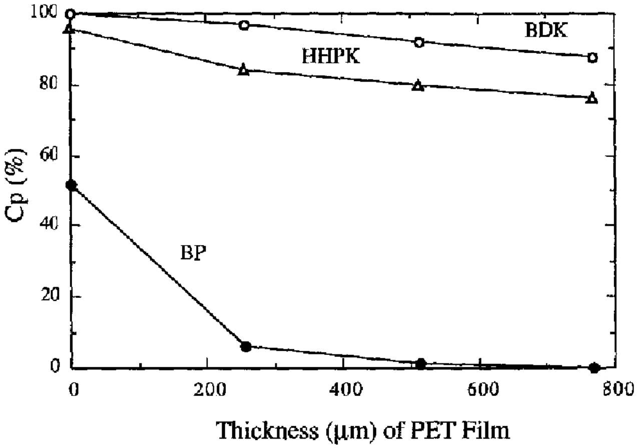


Figure 7. Photopolymerization of acrylic acid initiated by three different photoinitiators for 30 seconds at 50°C.

Energy Considerations

The decisive function of the far UV radiation in photografting polymerization shown in this study is not observed in previous studies. It is therefore appropriate to re-examine the photophysical and photochemical background of photografting polymerization.

The hydrogen abstraction reaction of BP is a bimolecular reaction process. The largest energy barrier of the transient states involved in the reaction is the cleavage of the C–H bond. The photoscission of BDK and HHPK is a monomolecular process in which the largest reaction barrier should be the cleavage of the –CO–C bond. The photoabsorption process in a molecule will result in the elevation of the molecular energy state (excitation) or the reduction of the reaction energy barrier. Energy considerations are therefore important for an understanding of the photochemical reaction.

For this purpose, the energy graph in Figure 8 was constructed. It shows the energy of the excited states of BP (9) and the bond strength of some relevant chemical bonds (10) placed on the curve of energy vs wavelength of UV radiation. A study of the positions of the excited states of BP and the energies of the chemical bonds in the graph in relation to the results obtained in our work, leads to several conclusions:

A. The C–H bonds have energies located in the upper reaches of the curve i.e., at about 300 nm. Their bond energies are obviously lower than the ($\pi \rightarrow \pi^*$) transition energy and higher than the ($n \rightarrow \pi^*$) transition energy. The ($n \rightarrow \pi^*$) transition has not enough energy to split these bonds, but that the ($\pi \rightarrow \pi^*$) transition energy is sufficient. As a result, only the far UV is effective in initiating the hydrogen abstraction from C–H groups.

B. The -CO–CO- and -CO–C- bonds have energies located in the lower reaches of the energy vs wavelength curve and their bond energies are lower than the $(n\rightarrow\pi^*)^1$, and even lower than the $(\pi\rightarrow\pi^*)^3$ and the $(n\rightarrow\pi^*)^3$ transitions. Therefore the $(n\rightarrow\pi^*)$ transitions have enough energy to split these bonds. Consequently, the $(\pi\rightarrow\pi^*)$ transitions and the far UV absorption is not necessary for the cleavage reaction.

C. The value of the bond energy of the weak C–H bonds, e.g. allylic hydrogens is close to that of the $(n\rightarrow\pi^*)^1$, and the effect of the far UV light absorption is low.

According to Figure 8, it appears that an energy requirement is necessary for a photoinitiated reaction, i.e. that only those molecules which have absorbed a photoquantum energy larger than the bond energy concerned can participate in the reaction.

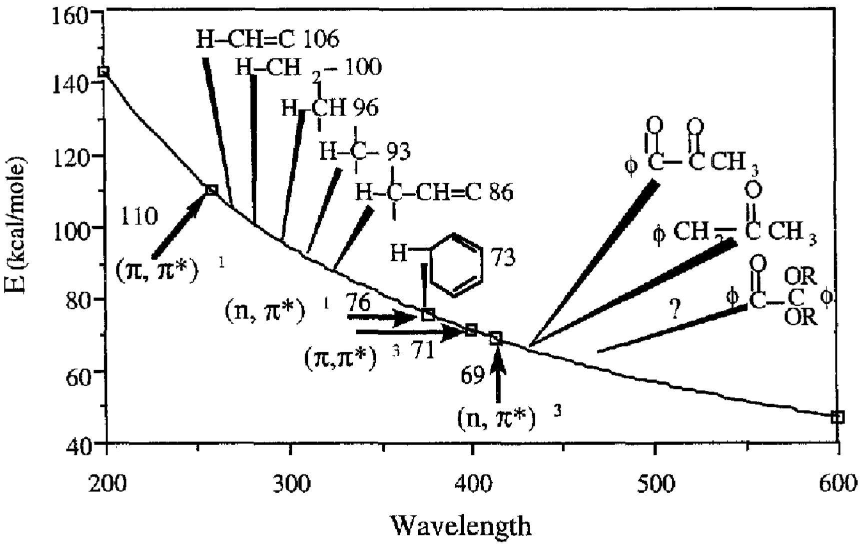


Figure 8. Energy vs wavelength of light quanta, the location of the various BP transitions and the bond energy of different chemical bonds.

The Function of the $\pi\rightarrow\pi^*$ Transition

The role of the far UV radiation is related to the $(\pi\rightarrow\pi^*)$ transition. Under UV radiation, BP undergoes well known photophysical processes (11). According to the photoexcitation pattern, the lowest excited state $(n, \pi^*)^3$ comes from the $n\rightarrow\pi^*$ (S_1) and $\pi\rightarrow\pi^*$ (S_2) transitions. The $n\rightarrow\pi^*$ (S_1) undergoes one intersystem crossing conversion and one internal conversion to reach the $(n, \pi^*)^3$ state, while the $\pi\rightarrow\pi^*$ (S_2) needs an additional internal conversion.

A reasonable assumption for the decisive role of the far UV radiation in the system is the participation of the $S_2\rightarrow S_1$ radiationless transition. The transition involves an excess energy which makes benzophenone molecule lie in an " overheated state ". The excess energy is transferred to molecules in the environment by collision. In the case of the present photografting system, the environment consists mainly of the surface of the LDPE film from which hydrogens are abstracted, and acrylic monomer present which are the components of the photoinitiation reaction. Hence the relaxation results in local activation of the reactants (hydrogen or monomer). Obviously the overheated BP, the locally activated C–H bond or the monomer are all favourable for a photografting process. Referring to the quite big energy value (30–40 kcal/mole) of the dissipation process, it is possible that the function of the ($\pi \rightarrow \pi^*$) transition comes partly from the $S_2 \rightarrow S_1$ radiationless dissipation process.

Conclusion

Radiation in the far UV region (200–300 nm) plays a decisive role in the photografting polymerization initiated by benzophenone. This influence decreases with decreasing C–H bond energy. No significant effect was observed in the polymerization of AA initiated by BDK or HHPK when the far UV radiation was excluded. The key function of the far UV radiation in the photografting process may be understood as the participation of radiationless transitions or energy dissipating processes in the photografting system.

Acknowledgement

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