

PHOTOINDUCED GRAFTING OF ACRYLIC AND ALLYL MONOMERS ON POLYETHYLENE SURFACE*

ZHANG Zhenfeng(张振峰) HU Xingzhou(胡兴洲)
and YAN Qing(严庆)

(Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing 100080)

ABSTRACT

Photoinduced grafting of acrylic and allyl monomers on polyethylene surface was generally studied by using benzophenone (BP) as a photoinitiator. The grafting process was carried out either in vapor-phase or in solution of the monomers. In the vapor-phase reaction with a filter used to cut off the short wavelength UV light, allyl amine is the most reactive of the four monomers used and acrylic amide is comparatively more reactive than acrylic acid and allyl alcohol. Acetone, as a solvent and carrier for initiator and monomers, however, shows its reactivity to participate the reaction. The solution grafting with a filter is much faster than the corresponding vapor-phase reaction, and a fully covered surface by the grafted polymer can be achieved in this way.

INTRODUCTION

In the polymer applications, it often occurs that a polymer surface needs to be modified to satisfy some specific requirements while its bulk properties should be kept unchanged. Photo-induced surface grafting is a good approaching in this area^[1]. With monomers containing active group grafted on the surface, further chemical reactions can be conducted; thus further modification can be pursued. This two-step procedure may find its utilization in bio-medical materials^[2-4].

In the previous works, polyethylene was photo-grafted in the acrylic acid vapor when a filtered high-pressure mercury lamp was used as the UV

* This work was supported by the Fund for Young Scientist from the National Advanced Materials Committee of China

source^[5,6]. We supposed that if no filter was applied, the grafting rate might be increased, and under the irradiation conditions, crosslinking would be promoted and the mechanical properties of polymer could be improved to some extent^[7,8]. In an attempt to do so, however, a side reaction arose. Acetone, the solvent we used in most cases, participates in the grafting and disturbs the whole process. Therefore, a new method of photografting in solution is proposed. In this case, because there is relatively concentrated initiator and monomer existed on the polymer surface, the rate of grafting is enhanced and the use of a filter becomes appropriate.

EXPERIMENTAL

Materials

Monomers (acrylic acid, allyl alcohol, allyl amine, and acrylic amide), initiator (benzophenone) and solvents (acetone and ethanol) were all commercial products of A. R. grade. Most of the materials were used as received without further purification. Low-density polyethylene pellet with no additives was provided by Yanshan Petrochemical Corporation. It was pressed into a film with the thickness of about 120 μ m at 150atm and 150°C for half a minute. The film was then extracted by hot acetone for four hours in a Soxhlet extractor before grafting.

Devices and Procedures

In the vapor-phase reactions (Fig. 1), a small vessel containing acetone solution of the photoinitiator (BP) and monomers was put in the dark part of the reaction chamber. The air was driven out by introducing nitrogen stream of 1 L/min for 20 minutes and then the box was sealed. With the help of a regulator, the chamber was kept at the temperature desired for vitalization of the solution, which was usually at 65°C, for at least 10 minutes before opening the shutter to start irradiation. A 500W high-pressure mercury lamp (GGU from Ya Ming, Shanghai) was used as the UV source. After a predetermined time, the shutter was closed and the sample removed, extracted with acetone for another 4 hours and washed with distilled water.

In solution grafting (Fig. 2), a filter was used to cut off the light with wavelength shorter than 317nm (the transmissivity of the filter at 317nm was

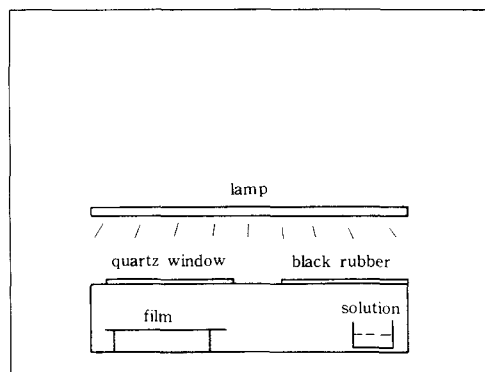


Fig. 1 Vapor-phase grafting device

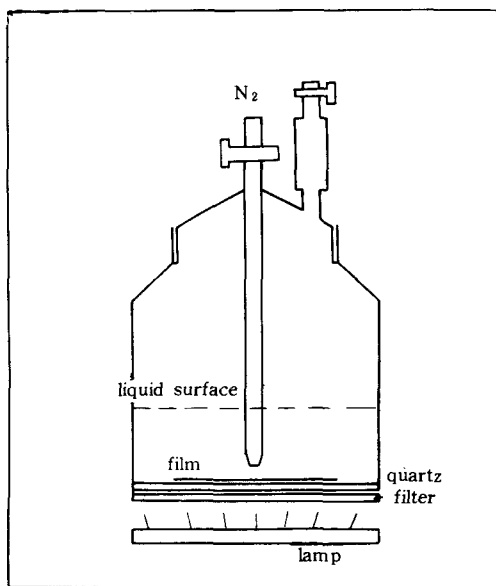
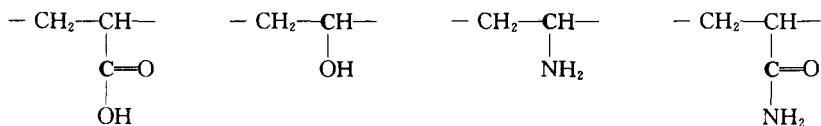


Fig. 2 Solution grafting device

10%). The filter was fixed at the bottom of the reaction bottle as an irradiation window. The sample film was immersed in the same solution as used in vapor-phase reaction, and the solution was purged with nitrogen bubble to expel air for 20 minutes before the bottle was sealed. After irradiation for a period of time through the filter, the film was soaked in 0.1 mol/L potassium hydroxide solution twice, 8 hours each time. After that, the film was rinsed in 0.05 mol/L hydrochloride acid solution for another 8 hours. Finally, the film was washed with distilled water and acetone successively.

Measurements

ESCA can be used for semi-quantitative analysis of the grafted surface^[9]. Taking carbon atom for example, its normal position of C_{1s} electrons is at 285.0 eV for polyethylene. When the polymer surface is modified by a monomer with certain electron attractive groups on it, a shoulder peak with a higher bonding energy will appear beside the normal position. This shoulder peak comes from the carbon atoms connected directly with one or two oxygen or nitrogen atoms, as shown in the following schemes:



Theoretically, the shoulder peak is proportional to the coverage of the surface within certain depth until the whole surface is completely covered by the grafted polymers, when the saturation is reached.

In the grafting process, some products other than the grafted polymer will be produced. Their peaks of C_{1s} usually appear between the peak of the body polymer and that of the grafted polymer^[10]. To reduce the interference of these noises, S_1 and S_2 , the outmost halfparts of the C_{1s} peaks, were chosen to represent the corresponding peak areas of the grafted and body polymer respectively (Fig. 3). So the ratio R of S_1 over S_2 was used as a measure of the grafting degree.

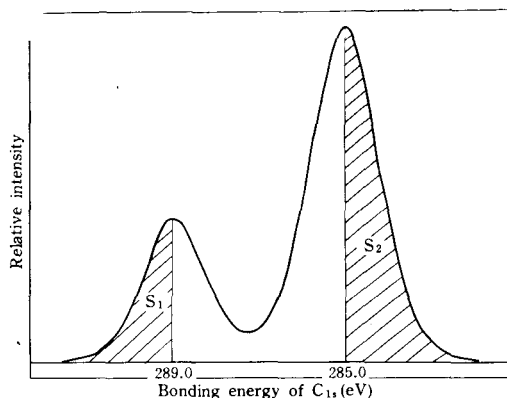


Fig. 3 The calculation of R value from C_{1s} peaks

For quantitative calculation of the surface coverage, poly(acrylic acid) was prepared for calibration by photo-polymerization in a similar condition of grafting. The R value of this homopolymer is around 0.365. It showed a wide difference with the theoretical value of 0.5 (1:2) as used in the previous work^[5].

ESCA was carried out on a photoelectron spectrometer, Model ES-300. Transmission IR spectra were obtained on a Perkin-Elmer 983GIR spectrophotometer and ATR on an FTIR spectrophotometer, BRUKER IFS 113V.

RESULTS AND DISCUSSION

Vapor-phase grafting

(1) Relative reactivity of the different monomers

At the first beginning, we tried to introduce the reacting vapor into the reaction chamber by bubbling the N_2 through an external hot bottle with acetone solution of the photoinitiator and monomers inside. Its vapor was expected to be carried by the N_2 flow. This idea could serve for a continuous grafting processing. But it was found that only allyl amine showed a detectable and rather strong ESCA C_{1s} shoulder peak in this method (Table 1). This demonstrates the high reactivity of allyl amine, which is probably from its high volatility, comparing with the other monomers.

After we brought a solution vessel inside the reaction chamber to introduce the reactive monomer, all the other three monomers could be successfully grafted onto the polyethylene surface. It is found that acrylic amide grafts faster than acrylic acid and alcohol (Table 1).

Table 1 Comparison of the R values in ESCA for different grafted monomers^{a)}

	Acrylic acid	Allyl alcohol	Acrylic amide	Allyl amine ^{b)}
$T=15\text{min}, d=6\text{cm}$	0.123	0.072	0.112	$T=15\text{min}, d=10\text{cm}$
$T=60\text{min}, d=10\text{cm}$	0.087	0.143	0.140	0.224

a) 0.2 mol/L BP and 2 mol/L monomers; b) N_2 bubble through method

(2) Grafting of acrylic acid

After the film was grafted in the vapor phase, an ESCA shoulder peak of C_{1s} at 289.0 eV was found and IR measurement showed a carbonyl absorption at 1719cm^{-1} . As shown in Fig. 4, the ratio R in ESCA increased with the increasing irradiation time, but the most prominent factor that affects the ESCA signal is the irradiation distance. When the lamp changed from 10cm to 6.5cm apart from the film, the shoulder peak increased rapidly at the same reaction conditions. The back side of the film was also grafted but only to a less extent. In the conditions of irradiation distance of 6.5cm, irradiation time 30 minutes,

and the solution concentration of acrylic acid and benzophenone 2mol/L and 0.2mol/L respectively, the ratio R of the front side is 4.8 times higher than that of the back side of the film.

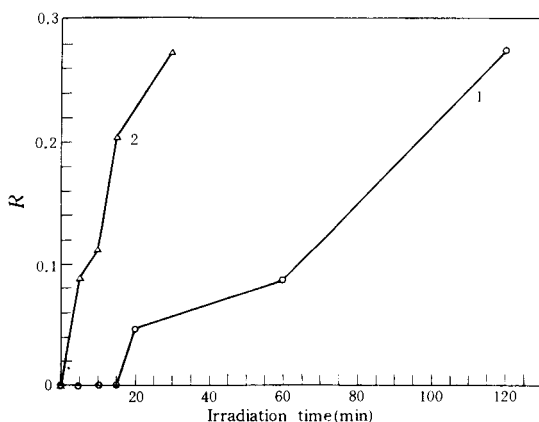


Fig. 4 Irradiation distance and time dependence of R value of acrylic acid. Curve 1: $d=10\text{cm}$; curve 2: $d=6.5\text{cm}$. In both curves $C_{\text{acid}}=2\text{mol/L}$; $C_{\text{BP}}=0.2\text{mol/L}$

From Fig. 5, it was found that the ratio R increased with the increase of the concentration of acrylic acid in solution, but in a rather insignificant manner. It was also found that with the increase in BP concentration, the R first increased then declined (Fig. 6). It is suggested that with the increase of BP concentration, more BP can participate in the photo-initiation of the reaction, but simultaneously, it also brings about other effects, e. g. , more homopolymerization and rapid termination of the free radicals.

(3) Acetone involvement

In the Figs. 5 and 6, it is noticed that when no monomer or no BP existed in the acetone solution, the ESCA results also show a remarkable R . To confirm this observation, an experiment with only the film sample and acetone vapor in the reaction chamber for irradiation was carried out. The ESCA C_{1s} shoulder was still present at 289.0 eV. And the IR spectrum showed an appreciable carbonyl absorption that did not change its shape and position after treated by potassium hydroxide. However, no carbonyl peak appeared at all if the film was irradiated in nitrogen or in an ethanol atmosphere instead.

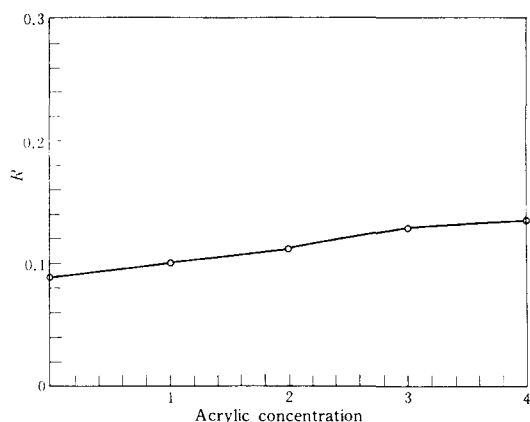


Fig. 5 Dependence of R value on acrylic acid concentration. In this curve, $T = 10\text{min}$, $d = 6\text{cm}$, $C_{\text{BP}} = 0.2\text{mol/L}$

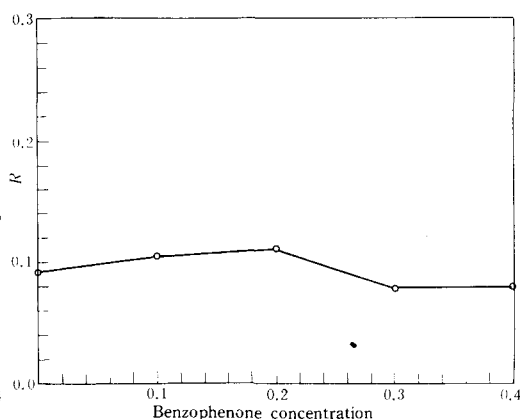


Fig. 6 Dependence of R value on BP concentration. In this curve, $T = 10\text{min}$, $d = 6\text{cm}$, $C_{\text{acid}} = 2\text{mol/L}$

Another experiment ruled out the possibility that the absorption of acetone by the polymer film caused this unusual phenomenon. A polyethylene film was dipped in acetone vapor without irradiation under the same conditions as used for irradiation. No IR carbonyl peaks were observed. So, the carbonyl peak must come from some photoreactions of acetone with polyethylene under the UV irradiation. Acetone is well known as a photoinitiator itself at the short wavelength irradiation^[5] ($< 300\text{nm}$), but its participation in the grafting is rarely reported.

Solution grafting

With a solution of 0.2mol/L BP and 2mol/L acrylic acid, a sample was irradiated through the filter for 30 minutes at a distance of 20cm , the ratio R in ESCA reached a value of 0.369 , while in vapor phase grafting it never exceeded 0.3 even the irradiation time was longer. That means a full coverage of the film surface by acrylic acid can be achieved, since the value of the prepared acrylic acid homopolymer is just about 0.365 . Compared with the vapor-phase grafting, the rate of the photoreactions in solution is much higher. That is reasonable because the concentrations of the initiator and monomers can be much higher than those in vapor.

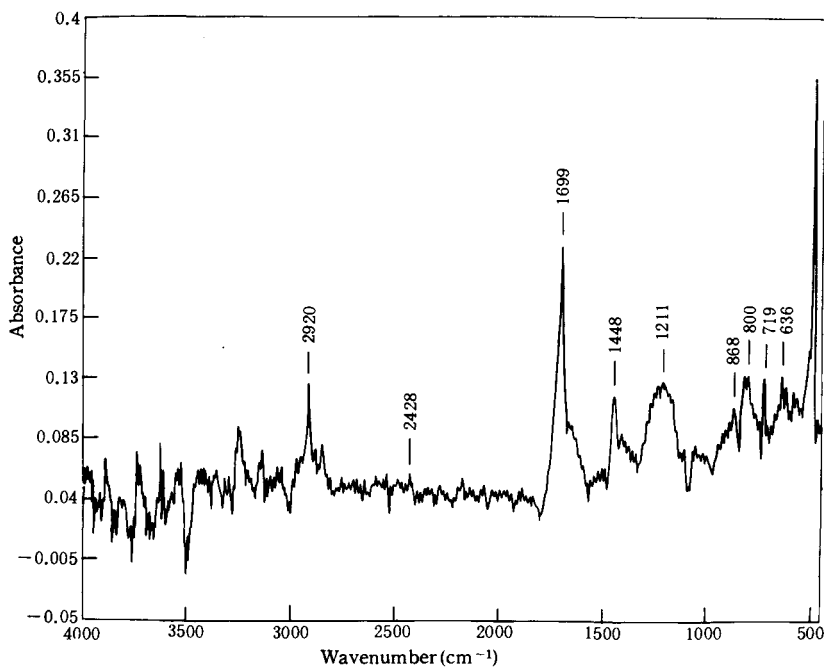


Fig. 7 ATR spectra of solution grafted film with acrylic acid

Conditions $C_{\text{acid}} = 2\text{mol/L}$, $C_{\text{BP}} = 0.2\text{mol/L}$, $T = 30\text{min}$ and $d = 20\text{cm}$

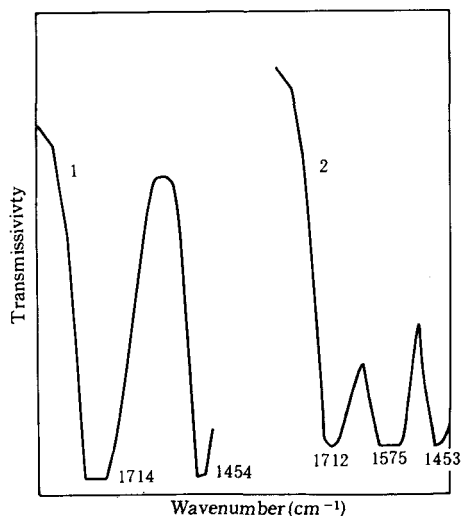


Fig. 8 IR spectra of solution grafted film with acrylic acid before (1) or after (2) treatment with potassium hydroxide

ATR shows a strong absorption at 1699cm^{-1} on the surface of grafted films (Fig. 7). This carbonyl peak can also be found in transmission IR at the position of 1714cm^{-1} . And when the film was treated with potassium hydroxide, the peak split into a twin peak of equal intensities at 1712 and 1575cm^{-1} , which is typical for a salt of carboxylic acid (Fig. 8). This result confirms that the carbonyl absorption of the grafted film comes from the acid group in acrylic acid, which is supposed to be grafted onto the sample surface, and the acetone involvement is eliminated to a negligible extent after the filter applied.

CONCLUSIONS

In the vapor phase reaction, allyl amine is the most reactive of the four monomers used. And acrylic amide is comparatively more reactive than acrylic acid and allyl alcohol.

In the vapor-phase grafting of acrylic acid onto polyethylene surface, the light intensity affects the grafting rate most significantly. Irradiation time and the monomer concentration in the solution supplying the vapor also have the effect. With the increase of these three factors, both the grafting rate and degree rise monotonously. The concentration of photoinitiator (BP) has an optimum value for grafting.

Acetone will participate the photo-grafting as both initiator and grafting substance onto the polymer surface under the irradiation when no filter is applied to cut off the short wavelength components from the UV lamp, especially in vapor-phase where the concentration of the initiator and monomers are much lower than that of acetone.

Compared with the vapor-phase reaction, grafting in solution is favorable because a higher grafting rate and full coverage can be achieved.

Keywords:

UV light; Surface grafting; Polyethylene; Acrylic acid; Allyl alcohol; Allyl amine; Acrylic amide

Acknowledgement The ESCA analysis was supported by and performed in the United Center of Analysis and Measurement of Zhongguan-Cun Area, Beijing.

REFERENCES

- [1] Ranby, B., *Makromol. Chem., Makromol. Symp.*, **1992**, 63,55.
- [2] Allmer, K.; Hult, A. and Ranby, B., *J. Polym. Sci., Polym. Chem.*, **1989**, 27,1641.
- [3] Allmer, K.; Hilborn, J.; Larsson, P.H., et al., *J. Polym. Sci., Polym. Chem.*, **1990**, 28,173
- [4] Yang, N. C. and Teng, C-L. C., in "Biomimetic Polymers", Gebelein, C. G. Ed., Plenum Press, New York, **1990**, p. 175.
- [5] Allmer, K.; Hult, A. and Ranby, B., *J. Polym. Sci., Polym. Chem.*, **1988**, 26,2099.
- [6] Zhang, P.-Y. and Ranby, B., *J. Appl. Polym. Sci.*, **1990**, 40,1647.
- [7] Yan, Q.; Xu, W. and Ranby, B., *Prog. Mater. Sci.*, **1990**, 4,277.
- [8] Yan, Q.; Xu, W. and Ranby, B., *Polym. Eng. Sci.*, **1991**, 31,1567.
- [9] Yamamoto, F. and Yamakawa, S., *J. Polym. Sci., Polym. Phys. Ed.*, **1979**, 17, 1581.
- [10] Clark, D. T. and Thomas, H. R., *J. Polym. Sci., Polym. Chem. Ed.*, **1976**, 14, 1671.