

Distribution of Acrylic Acid Grafted Chains Introduced into Polyethylene Film by Simultaneous Radiation Grafting with Water and Ethanol as Solvents

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ABSTRACT: The graft copolymerization of acrylic acid onto low-density polyethylene films by simultaneous γ -ray irradiation was carried out. The effect of water and ethanol as grafting solvents on the distribution of grafted poly(acrylic acid) in the low-density polyethylene films was studied with optical microscopy observations of dyed and sliced samples and attenuated total reflection/Fourier infrared spectroscopy analysis. When no vigorous homopolymerization occurred, both polyethylene and poly(acrylic acid) existed in the grafted layer, and the thickness of the grafted layer and the poly(acrylic acid) concentration in the grafted layer increased with an increasing degree of grafting, regardless of the grafting conditions, the former increasing faster than the latter. In comparison with water as the sol-

vent, in the absence of the inhibitor, homopolymerization could be suppressed to a certain degree in the ethanol solvent system, whereas in the presence of the inhibitor, obvious homopolymerization occurred at a lower monomer concentration, and both the degree of grafting and the thickness of the grafted layer were lower. Such differences could be explained by the chain transfer and the relatively low solubility of poly(acrylic acid) in ethanol. In addition, an experimental scheme using optical microscopy to observe the dyed and sliced polymers was optimized. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1570–1577, 2007

Key words: graft copolymers; irradiation; polyethylene (PE); radiation

INTRODUCTION

Radiation-induced graft copolymerization is one of the most effective methods for obtaining materials with tailored properties.¹ When grafting chains form on the surface of a polymer substrate, the bulk properties of the substrate will remain the same with improved surface properties, whereas they are likely to change dramatically when grafting chains penetrate the substrate.² Therefore, it is of great significance to study the distribution of grafted chains in substrates.

There exist various methods for analyzing the distribution of grafted chains in polymer substrates.^{3–6} Among them, dyeing and slicing a copolymer, followed by the observation of the obtained cross section by optical microscopy, is a simple and direct means of gaining information about the penetration profile of grafted chains in a polymer substrate that especially suits situations in which the substrate and the grafted chains are of opposite polarity. For a copolymer with a nonpolar-polymer substrate and polar-polymer grafted chains, a certain dye can be selected to color only the grafted chains, with the substrate unchanged. Slicing the colored copolymer and ob-

servicing the distribution of color on the obtained cross section, we can acquire relevant information on the distribution of grafted chains in the substrate. However, the optical microscopy observations can hardly provide information on the concentration in the grafted layer. This can be remedied with spectroscopic analysis.³ Among them, Fourier transform infrared is a well-established and widely used method because of its sensitivity to chemical groups. Moreover, attenuated total reflection/Fourier transform infrared (ATR-FTIR) spectroscopy can be used to obtain quantitative information on the near-surface composition.⁷

As is well known, the grafting conditions have considerable influence on the grafting process² and can lead to subsequent changes in the corresponding grafting structure. Thorough studies of the effects of grafting conditions on the distribution of graft chains in polymer substrates are lacking, although there are some. Acrylic acid (AA) grafting into polyethylene (PE) films, as a typical radiation grafting system, has been studied in this respect. Lawler and Charlesby⁴ studied the effects of the dose, dose rate, and monomer concentration on the thickness of a grafted poly(acrylic acid) (PAA) layer. Sidorova et al.⁵ studied the effect of the degree of grafting (DG) on the distribution of grafted PAA in PE films by simultaneous irradiation grafting. Kaji⁶ studied the effect of the grafting system with and without an inhibitor on the dis-

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tribution of grafted PAA in PE films by preirradiation grafting. However, the grafting solvent was water every time. The use of an organic solvent has not been reported to the best of our knowledge.

In this study, poly-ethylene-*graft*-acrylic acid (PE-*g*-AA) films with different DGs were prepared by simultaneous radiation grafting with water and ethanol as solvents through changes in the concentrations of the inhibitor and monomer. The distribution of AA-grafted chains introduced into PE films was studied by the optical microscopy observation of dyed and sliced samples and ATR-FTIR analysis. For a finer analysis of the penetration profile of grafted chains, the dyeing and slicing conditions were optimized.

EXPERIMENTAL

Materials

Films with a thickness of 250–320 μm were prepared from commercial low-density polyethylene (LDPE) with a heat press. The AA monomer (chemical-grade; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was purified by distillation under reduced pressure.

Ethanol (analytical-grade; Shanghai Chemical Co., Shanghai, China) and copper acetate [$\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$; analytical-grade; Shanghai Zhenxing Chemical Plant, Shanghai, China] were used without further purification. Cationic red, cationic blue, acid blue, and acid red dyes were purchased from Shanghai Luo Jing Dyestuff Co., Ltd. (Shanghai, China). The water used in all the experiments was deionized.

Preparation of the graft copolymer

LDPE films were cut into rectangular pieces ($3.5 \times 10 \text{ cm}^2$), thoroughly washed with water and then ethanol, dried in an oven at 65°C to a constant weight, and immersed in glass ampules with an AA solution and with water and ethanol as the solvents. The inhibitor was $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$. The ampules were deaerated with bubbling nitrogen for 15 min, sealed, and exposed to γ -ray irradiation. The dose rate and total dose of γ radiation were 0.61 kGy/h and 10 kGy, respectively.

After the irradiation, the grafted films were purified by Soxhlet extraction with a mixed solvent of water and ethanol (2 : 1 v/v) to remove the homopolymers and residual monomers in the films. The grafted films were dried at 60°C in a vacuum oven to constant weight. Because the films' thickness was uncertain, DG of the grafted LDPE films was calculated as follows:

$$\text{DG (mg/cm}^2\text{)} = (W_g - W_0)/S$$

where W_g and W_0 are the weights of the starting and grafted films, respectively, and S is the sample area (70 cm^2 , the sum of both sides).

Dyeing, slicing, and optical microscopy observations

The grafted LDPE films were cut into rectangular pieces ($1.5 \times 1 \text{ cm}^2$), soaked in 1 wt % dye solutions at 40°C for some time, taken out, washed thoroughly with hot deionized water, and air-dried.

The dyed films were put in self-made paper boxes with melted paraffin. After they became solid, the embedded films were cut perpendicularly to the film surface with a rotary paraffin microtome (Shanghai Medical Equipment Fourth Plant, Shanghai, China). The slices' thickness was controlled to about 100 μm because excessively thin films were likely to fold and excessively thick films would be hard to observe. The cross section was observed with an optical microscope at a magnification of $400\times$ (Zoom-620E stereomicroscope, Shanghai Changfang Optical Instrument Co., Ltd., Shanghai, China). The images were then collected by a computer linked to an Olympus digital camera (Tokyo, Japan), which directly shot the microscopic images. The dyeing thickness was measured with a self-made ruler.

ATR-FTIR spectroscopy analysis

Attenuated total reflection/infrared analysis of the surfaces of the LDPE films before and after γ -radiation grafting was performed with ATR-FTIR (Avatar 360, Nicolet Corp., Waltham, MA) with a germanium crystal at a 45° angle of incidence.

RESULTS AND DISCUSSION

Effect of the solvent on DG

For the simultaneous radiation grafting of AA onto PE films, the common solvent is water.^{4,5,8} Gupta et al.⁹ tried using methanol as a grafting solvent and found that no grafting occurred in pure methanol. However, using ethanol as a solvent has not been reported.

For a water solvent grafting system without an inhibitor, vigorous homopolymerization can take place from the very beginning of the reaction because AA is one of the monomers that polymerize fastest under radiation initiation;¹⁰ this causes a significant reduction in the monomer available for the grafting reaction. In addition, intensive homopolymerization leads to a high viscosity of the grafting solution, which will lower the diffusivity of the monomer. For these reasons, only homopolymerization can be observed even at very low monomer concentrations. In this study, intensive homopolymerization was observed for a 5 vol % AA aqueous grafting solution without an inhibitor. To reduce homopolymerization, inhibitors are usually added to the grafting solution. The commonly used inhibitors for AA are cupric salt and Mohr's salt. Anions have no effect on grafting or homopolymerization, both of which are suppressed by the cations in

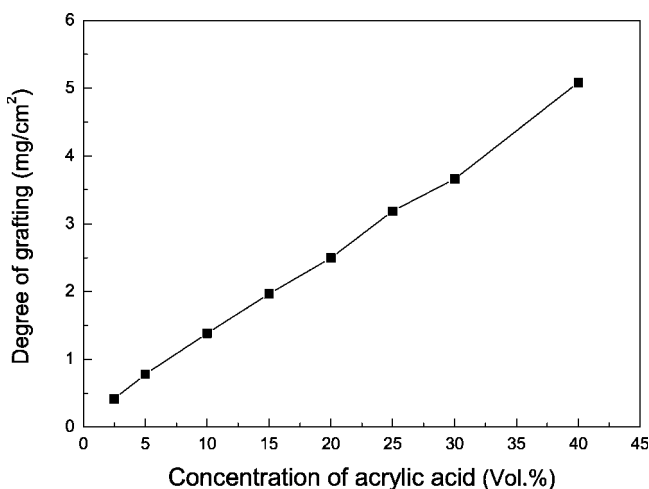


Figure 1 Effect of the AA concentration on DG (solvent = water; concentration of the inhibitor = 2.5×10^{-3} mol/L; absorbed dose = 10 kGy; dose rate = 0.6 kGy/h).

the following order of effectiveness: $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Fe}^{3+}$.¹¹ In this study, $\text{Cu}(\text{CH}_3\text{COO})_2$ was used as the inhibitor because it is reasonably more soluble in ethanol than other cupric salts, such as CuSO_4 .

When water was used as the grafting solvent and the inhibitor concentration was 2.5×10^{-3} mol/L, PE-g-AA films with different DGs were prepared by changes in the monomer concentration. Figure 1 shows that DG rises with an increasing monomer concentration, ranging from 2.5 to 40 vol %.

With ethanol as the solvent, PE-g-AA films with different DGs were prepared by changes in the monomer concentration and inhibitor concentration. The obtained DG value was lower compared with that obtained with water as the solvent (Fig. 2). Figure 2 shows that for different inhibitor concentrations, DG rises with increasing monomer concentration when the AA concentration is less than 20 vol %, and when the AA concentration is more than 20 vol %, DG decreases with increasing monomer concentration. In the presence of the inhibitor, the obtained DG value is higher than that in the absence of the inhibitor. The fact that the DG values of the PE-g-AA films obtained with an inhibitor concentration of 1.25×10^{-3} mol/L were higher than those obtained with an inhibitor concentration of 2.5×10^{-3} mol/L indicates that the amount of the inhibitor should be less for an ethanol solvent system than for a water solvent system. For the grafting system without the inhibitor, the monomer concentration at which obvious homopolymerization could be observed in the ethanol solvent system was higher than that in the water solvent system. This shows that ethanol can reduce AA copolymerization to some extent.

The difference in the homopolymerization behavior for the ethanol solvent grafting system and the water solvent grafting system can be explained as follows.

The side reaction involving chain transfer is minimal in water because water is insensitive to most organic radicals.¹² Compared with water, ethanol has a higher chain-transfer constant to AA (at 80°C, chain-transfer constant = 4.38×10^{-4}).¹³ Therefore, the growing chains terminate by chain transfer in the process of polymerization; that is, after growing chain radicals extracting H from the OH group of ethanol, the growing chains terminate, and radicals ($\text{CH}_3\text{CH}_2\text{O}\cdot$) are formed. Chain transfer leads to a decrease in the molecular weight of PAA, and in turn, the viscosity of the graft solution is reduced. Therefore, the partial suppression of AA homopolymerization by ethanol is due to the fact that ethanol can reduce the molecular weight of the AA homopolymer. However, when the AA monomer concentration is high, homopolymerization is predominant, and this leads to an increase in the viscosity of the graft solution because chain transfer competes with chain growth.

Optimization of the dyeing and slicing conditions

Selection of the dye

In this study, four dyes were tested: cationic red, cationic blue, acidic red, and acidic blue. Figure 3 shows the dyeing thickness of grafted PE films with DG = 3.04 mg/cm^2 , which were immersed in four 1 wt % dye solutions at 40°C for 12 h. The dyeing thickness of acidic blue and acidic red is less than that of cationic blue and cationic red. In the case of the acidic dyes, the boundary between the dyed and nondyed portions is unclear, whereas in the case of the cationic dyes, the boundary is distinct. These results prove that a cationic dye has better dyeing effects (color and thickness) on PE-g-AA films than an acidic dye

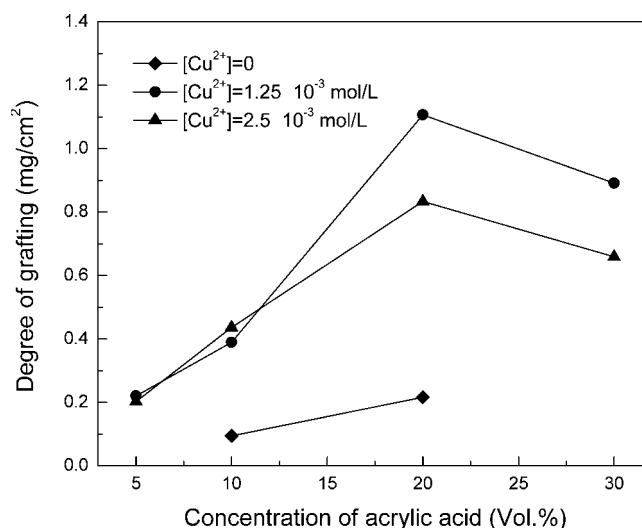


Figure 2 Effect of the AA concentration on DG (solvent = ethanol; concentration of the inhibitor = 0, 1.25×10^{-3} , or 2.5×10^{-3} mol/L; absorbed dose = 10 kGy; dose rate = 0.6 kGy/h).

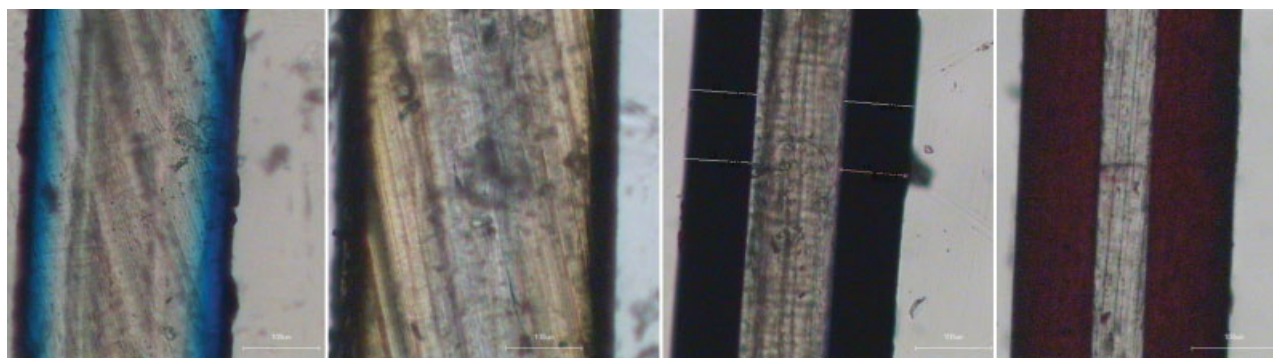


Figure 3 Comparison of the dyeing of AA-grafted PE films ($DG = 3.0 \text{ mg/cm}^2$) with four types of dyes: acidic blue, acidic red, cationic blue, and cationic red (from left to right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

because cationic dye ions with positive charges forming in an aqueous solution bind with PAA by substituting the proton of grafted PAA. Further comparing the dyeing effects of cationic blue and cationic red, we have found that the dyeing thickness by these two dyes is almost the same. However, the difference in the shades is more obvious when cationic red is used than when cationic blue is used. Evidently, the darkness of the color is related to the grafting density. The bigger the grafting density is, the darker the shade is. Thus, the samples followed in the study were dyed with cationic red.

Selection of the dyeing time and dyeing temperature

The grafted PE films were dyed at room temperature ($10\text{--}18^\circ\text{C}$). The variation of the dyeing thickness with the dyeing time is given in Figure 4. The dyeing thickness increases sharply for the first several hours until it reaches its maximum. Then, it remains unchanged despite the lapse of time. The higher the DG is, the less time it takes to reach the maximum dyeing thick-

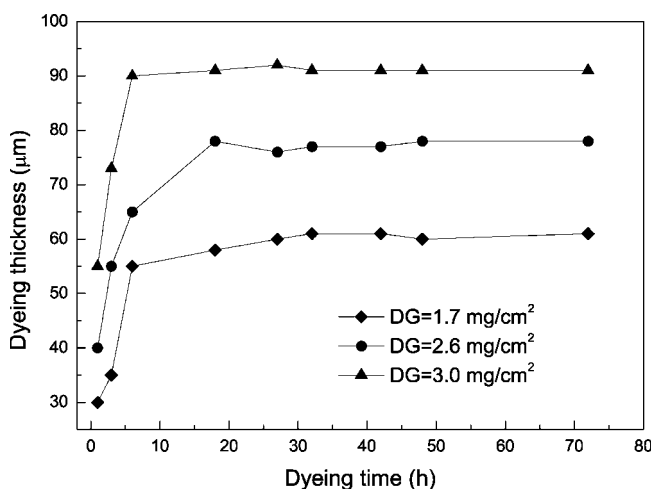


Figure 4 Effect of the dyeing time on the dyeing thickness at room temperature ($10\text{--}18^\circ\text{C}$).

ness. For samples with different DGs, the maximum dyeing thickness can be reached within 32 h.

To better control the dyeing experiment and reduce the dyeing time, the grafted films were dyed at 40°C . The maximum dyeing thickness was reached after the films were dyed 30 min for all samples with various DGs. This indicates that the diffusion of the dye molecules in the films is faster at higher temperatures. With an increase in the dyeing time, the dyeing thickness remains unchanged but the color darkens and the difference in the shades becomes less obvious. As experiments show, further dyeing at 40°C after 12 h would not produce new dyeing effects. Therefore, the optimum dyeing time at 40°C is 12 h, which was applied to all the following samples.

Study of the distribution of grafted chains by optical microscopy observations

Grafted PE films with different DGs, which were prepared in a water solvent grafting system, were dyed, and the variation of the dyeing thickness with DG is

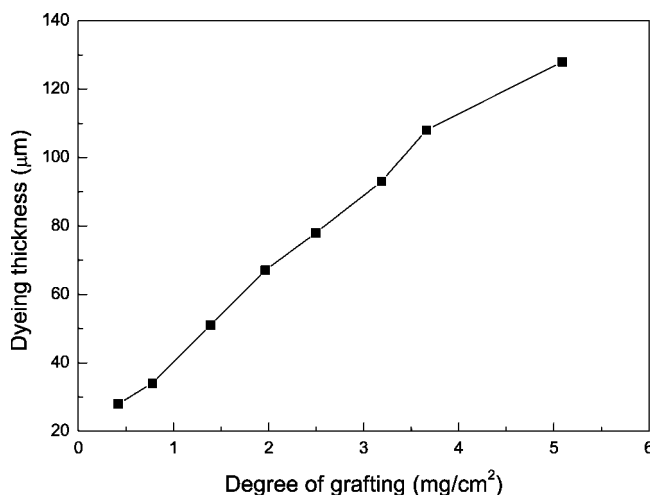


Figure 5 Effect of DG on the dyeing thickness with water as the grafting solvent.

given in Figure 5, which shows that the dyeing thickness increases with increasing DG. The dyeing thickness does not increase to the same extent as DG; for example, when DG increases 4.6 times from 0.8 to 3.7 mg/cm², the corresponding dyeing thickness increases 3.2 times from 34 to 108 μm. This implies that the concentration of the grafted PAA in the grafted layer also increases with increasing DG. In this study, the penetration rate of the grafted layer into PE is about 1.4 times less than the rate of the increase in DG, and this is in agreement with the work of Sidorova et al.⁵ In their study, the penetration rate of the grafted layer into PE was about 1.5 times less than the rate of the increase in DG, which was obtained by X-ray microanalysis coupled with electron microscopy.

For an ethanol solvent grafting system with different inhibitor concentrations, the variation of the dyeing thickness with DG is demonstrated in Figure 6. The grafted PE films used in Figure 2 were dyed and used as samples for Figure 6. Comparing Figure 6 with Figure 2, we find that the variation of the dyeing thickness with DG in Figure 6 follows the same trend shown in Figure 2. Replotting the dyeing thickness against DG for the samples in Figure 6, we find (Fig. 7) that the dyeing thickness increases almost linearly with increasing DG, even though the DG values were obtained with different monomers and inhibitor concentrations. Similarly to the case of a water solvent system, the concentration of the grafted PAA in the grafted layer also increases with increasing DG.

These results indicate that when the other grafting conditions are the same, both the DG and the dyeing thickness of the grafted PE films prepared in an ethanol solvent grafting system are obviously less than those prepared in a water solvent grafting system.

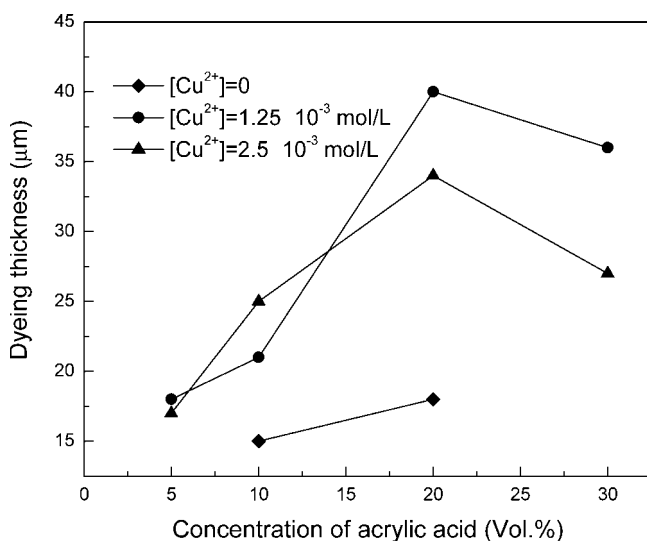


Figure 6 Effect of the AA concentration on the dyeing thickness with ethanol as the grafting solvent.

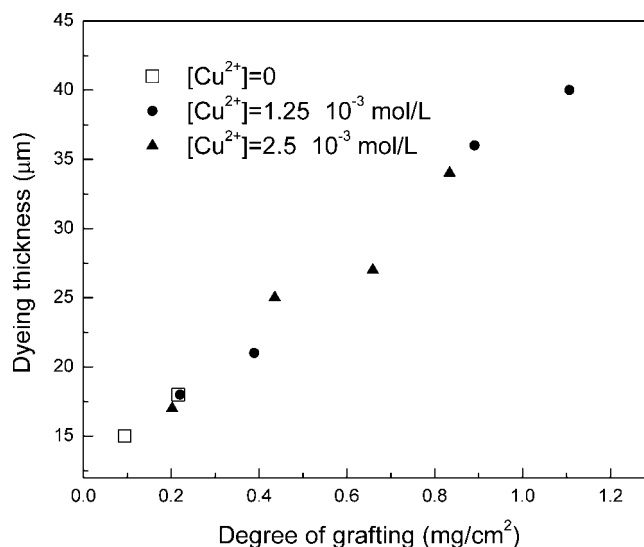


Figure 7 Effect of DG on the dyeing thickness with ethanol as the solvent.

Furthermore, as shown in Figure 8, which reflects typical dyeing interface features of grafted PE films prepared in ethanol and water grafting systems, the dyeing interface for those films prepared in an ethanol solvent grafting system is unclear, whereas the dyeing interface for those films prepared in a water solvent grafting system is distinct. These differences mainly result from the diffusibility of the monomer into the PE substrate in the grafting process. As a nonpolar polymer, PE is incompatible with the polar AA monomer, and this means that AA can hardly diffuse into PE films. However, once grafting starts on the surface of a PE film, the grafting will follow the grafting front mechanism by the progressive diffusion of the monomer through the grafted layers because the radicals that form on the surface of the PE film, induced by irradiation, can be accessed by the monomer and thus initiate the grafting copolymerization.⁴ Within a certain monomer concentration range, with increasing monomer concentration, the probability of interaction between PE and AA molecules increases, so DG increases. However, when homopolymerization occurs, the high viscosity of the grafting solution makes it hard to diffuse the monomer into the PE film, so DG decreases. When water is used as the solvent, as the solubility of the formed PAA in water with high polarity is high, the viscosity of the grafting solution will be low, and this favors the diffusion of the monomer into the PE film and an increase in DG. When ethanol is used as the solvent, however, PAA solubility in ethanol is lower than that in water. Once PAA forms, it is likely to increase the viscosity of the grafting solution and thus make it harder for the monomer to diffuse into the PE film. Therefore, with ethanol as the solvent, DG is low, and the dyeing interface is unclear and not uniform. This can be veri-

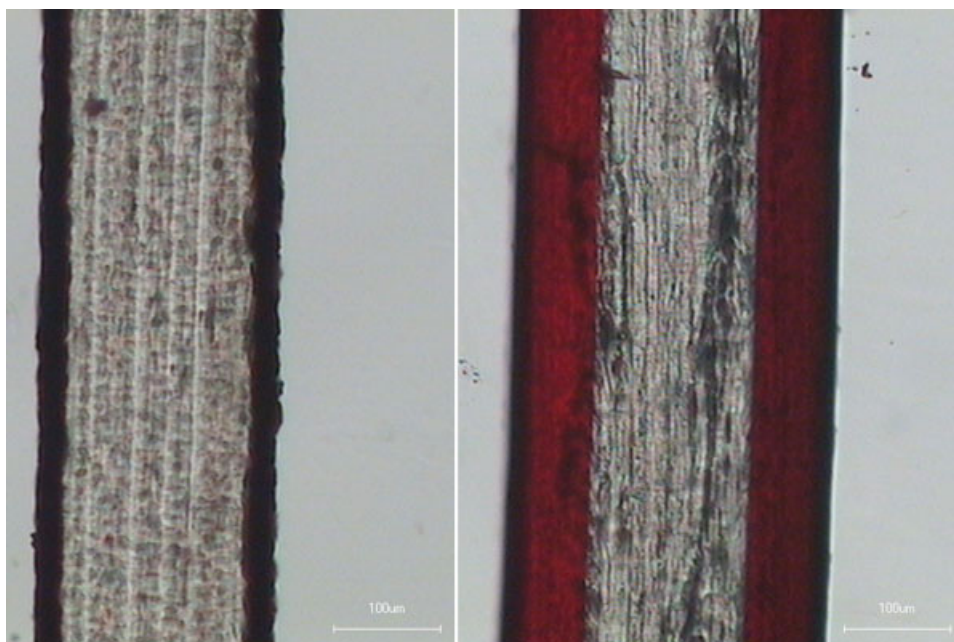


Figure 8 Dyeing images of grafted PE films prepared in an ethanol solvent system (left) and in a water solvent system (right) with an AA concentration of 20 vol % and a Cu^{2+} concentration of 2.5×10^{-3} mol/L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fied by a straightforward experiment. Water and ethanol (10 mL) were used to dilute about 3 mL of a post-grafting solution with an appreciably high viscosity, which was taken from an ampule in which there was a 30% AA ethanol solution with 1.25×10^{-3} mol/L inhibitor. In comparison with water as a diluter, ethanol took longer to dissolve the solution thoroughly, and the viscosity of the diluted solution in ethanol was apparently higher than the viscosity in water.

Study of the distribution of grafted chains by ATR-FTIR spectroscopy

As optical microscopy observations do not provide information on the density of the grafted layer, ATR-FTIR was used to obtain quantitative information on the surface composition. In Figure 9, the spectrum obtained by ATR-FTIR of the starting PE film is different from those of the grafted PE films. A marked difference between the AA-grafted PE films and the starting film occurs at 1710 cm^{-1} , which is assigned to the carbonyl ($\text{C}=\text{O}$) stretching absorption of the carboxyl group, indicating that AA has been grafted onto the PE films. Besides, the bands at 2918 and 2848 cm^{-1} , typical PE absorption bands due to CH_2 stretching, can also be found in all the spectra of the grafted PE films used in this study. This means that both PE and PAA exist in the grafted layer because the penetration depth of the incident beam of ATR-FTIR is estimated to be $10 \mu\text{m}$ at most, and the dyeing thickness for all the grafted films in this study is greater than $10 \mu\text{m}$.

We studied the concentration of PAA in the surface layer of the PE film by working out for all the samples the intensity ratio of the band at 1710 cm^{-1} , typical of AA, to the band at 2918 cm^{-1} , typical of PE (A_{1710}/A_{2918}). This is feasible because the intensity of the peak at 2918 cm^{-1} is not influenced by irradiation and that of the peak at 1710 cm^{-1} in ATR-FTIR spec-

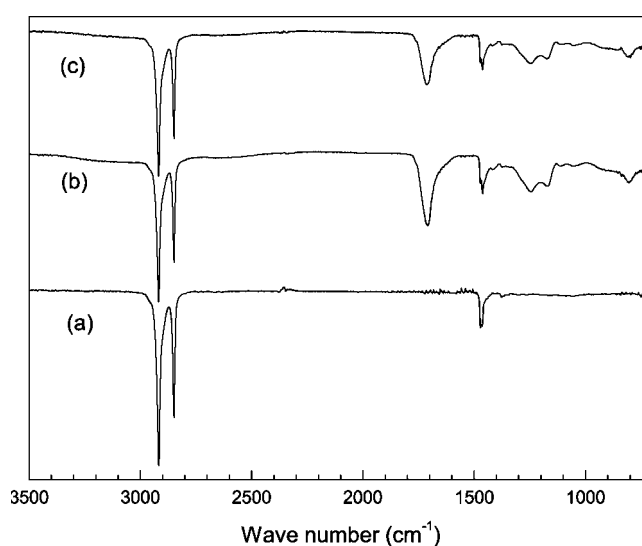


Figure 9 ATR-FTIR spectra of the LDPE films: (a) starting PE, (b) grafted PE prepared in a water solvent system with an AA concentration of 20 vol % and a Cu^{2+} concentration of 2.5×10^{-3} mol/L, and (c) grafted PE prepared in an ethanol solvent system with an AA concentration of 20 vol % and a Cu^{2+} concentration of 2.5×10^{-3} mol/L.

tra should correlate with the concentration of PAA in the near-surface layer of the grafted PE film. Figures 10 and 11 show the variation of A_{1710}/A_{2918} with the AA concentration in a water solvent system and in an ethanol solvent system, respectively. It can be deduced from these two figures that the concentration of PAA in the surface layer of the grafted PE film increases with increasing monomer concentration. Moreover, Figure 10 shows that, in a water solvent grafting system, with the monomer concentration increasing from 2.5 to 40 vol %, A_{1710}/A_{2918} increases almost linearly from 0.43 to 0.56, whereas the corresponding DG value increases from 0.4 to 5.1. Obviously, the increased rate of the concentration of PAA in the surface layer is much less than that of DG, and this indicates that the grafted PAA chains do not accumulate on the surface of the PE film but instead penetrate the film; that is, using water as a solvent together with an inhibitor is conducive to the homogeneous distribution of grafted chains in the PE substrate. In an ethanol solvent grafting system, Figure 11 shows that within the monomer concentration range of 20 vol %, both DG and A_{1710}/A_{2918} increase with increasing monomer concentration; this behavior is similar to the case of a water solvent system. However, for the monomer concentration of 30 vol %, DG drops and A_{1710}/A_{2918} increases sharply with increasing monomer concentration. This indicates a high PAA concentration in the surface layer because of the hard diffusion of AA into the PE film in an ethanol solvent grafting system at a high monomer concentration.

CONCLUSIONS

The experimental method of using optical microscopy to observe dyed and sliced polymers to study the distribution of grafted chains in a polymer substrate by

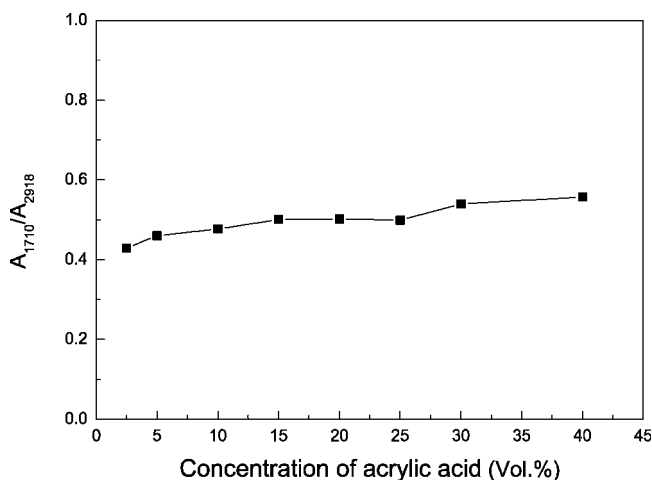


Figure 10 Variation of A_{1710}/A_{2918} with the AA concentration in a water solvent system.

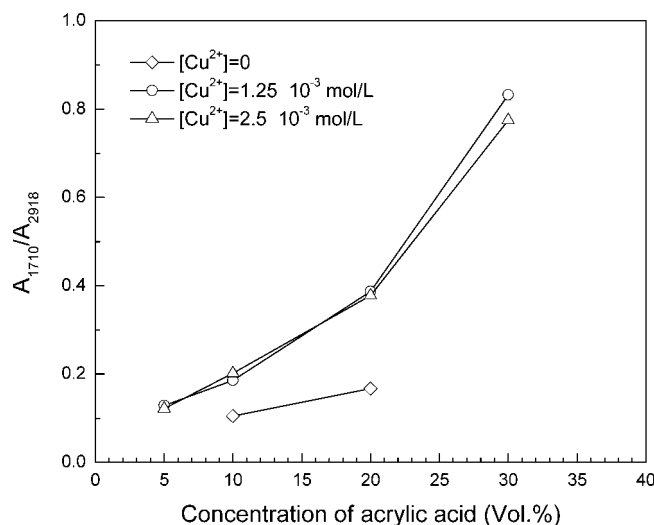


Figure 11 Variation of A_{1710}/A_{2918} with the AA concentration in an ethanol solvent system.

graft copolymerization was optimized as follows. The grafted PE films were immersed in 1 wt % cationic red aqueous solutions at 40°C for 12 h. The dyed films were embedded in paraffin and cut perpendicularly to the film surface. The slices' thickness was controlled to about 100 μm .

The effects of water and ethanol as solvents on the distribution of grafted PAA in PE films by simultaneous radiation grafting were studied by optical microscopy observation of dyed and sliced samples and ATR-FTIR. The following can be concluded:

1. In the absence of an inhibitor, in comparison with water as a solvent, ethanol as a solvent can suppress AA homopolymerization to some extent because of chain transfer. In the presence of an inhibitor, when the other grafting conditions remain unchanged, homopolymerization is likely to happen at a lower monomer concentration in ethanol than in water because of the lower solubility of PAA in ethanol than in water.
2. In cases of no vigorous homopolymerization, there exist both PE and PAA in the grafted layer. The thickness of the grafted layer and the PAA concentration in the grafted layer increase as DG rises, regardless of the grafting conditions, with the former increasing faster.
3. In comparison with ethanol, water as a solvent is more conducive to the uniform distribution of grafted chains in the substrate. DG is higher.

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