

# Functionalization of Polypropylene Film by Radiation Grafting of Acryloyl Chloride and Subsequent Esterification with Disperse Red 1

Emilio Bucio, Guillermina Burillo, María del Pilar Carreón-Castro, Takeshi Ogawa

Instituto de Ciencias Nucleares, and Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México DF 04510, Mexico

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**ABSTRACT:** Polypropylene (PP) films were grafted with acryloyl chloride by  $\gamma$ -irradiation, and the grafted films were reacted with an azo dye, Disperse Red 1. The films were characterized by X-ray diffraction, scanning electron microscopy, atomic force microscopy, and differential scanning calorimetry. It was found that the grafting takes place first on the film surface, and with increase in the radiation dose the grafting penetrated inside of the film, decreasing the crystallinity of the PP film. The surface of the films was homogeneous, and a mesophase was observed for the film

grafted with the dye through a polarized optical microscope. The dye underwent *trans* to *cis* photoreaction, whereby the red films became colorless by the irradiation of UV light at room temperature, although the color was recovered on standing, and more quickly when heated. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 172–178, 2004

**Key words:** irradiation; graft copolymers; polypropylene (PP); films; Disperse Red 1

## INTRODUCTION

Polar dye-containing polymeric systems have been a topic of great interest in the last decades. The principal interest was to obtain second-order nonlinear optical (NLO) materials, and a great number of works have been reported in the literature in the past few decades.<sup>1–3</sup> However, because of rather poor NLO susceptibility and inevitable relaxation of orientated dye molecules, studies of the NLO materials have recently faded from mainstream interest. Apart from applications in NLO, photoresponsive polymers, which are susceptible to isomerization or structural changes upon irradiation of light, are attractive materials as photofunctional materials and devices. There are also various studies on liquid crystalline polymers containing azo dyes in their side chains.<sup>4–7</sup> Recently polymers containing polar azo dyes (azopolymers) have been investigated for their light-induced *trans*–*cis* isomerization, and the formation of surface grafting by interference light is one of the recent applications.<sup>8–11</sup> In these studies polymethacrylates containing polar azo dyes such as Disperse Red 1 have widely been used. Methacrylates that have bulky groups, however, are

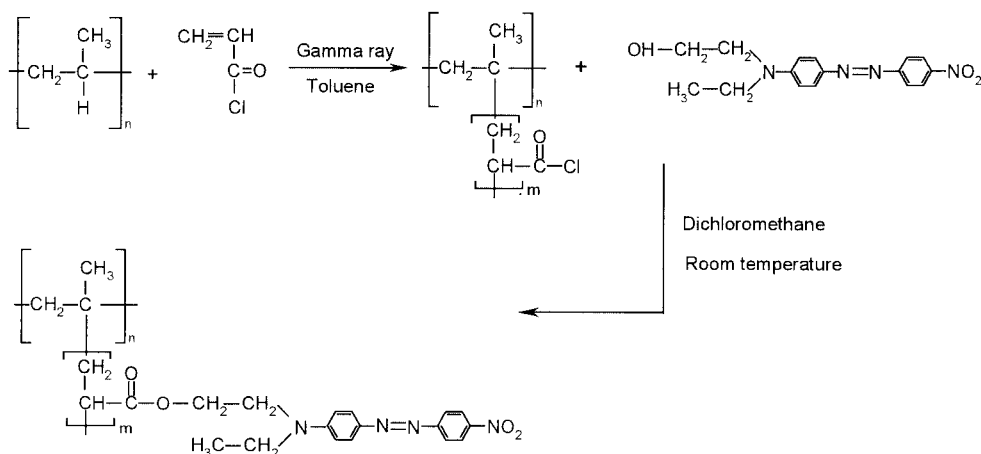
difficult to polymerize to high molecular weight polymers with good mechanical strength, and it is difficult to obtain free-standing flexible films. When flexible free-standing films are required, grafting functional polymers onto thin flexible films is a solution. Thin polymer films may be used as substrates for functional materials instead of inorganic substrates such as glass. Thus radiation grafting is an important method of obtaining novel functional polymeric materials. The present authors have been studying the  $\gamma$ -ray-induced graft polymerization of functional monomers onto common polymer films, and have previously reported the methods of grafting acryloyl chloride onto hydrocarbon polymers.<sup>12</sup> In this work, a polypropylene film was grafted with poly(acryloyl chloride), which was then converted to polyacrylate containing Disperse Red 1, which is commonly available at a relatively low cost. The preparation, characterization, and some properties of the grafted films are reported in this article.

## EXPERIMENTAL

### Materials

The polypropylene (PP) film used was a commercial product (PEMEX, Mexico) with molecular weight of 39,000 ( $M_n$ ) and 179,000 ( $M_w$ ), density of 0.902, crystallinity of 88%, and thickness of 70  $\mu\text{m}$ . The films was washed with methanol for 2 h and dried in vacuum. It was cut into pieces of 1  $\times$  5 cm and their weights were recorded exactly. Acryloyl chloride, supplied by Al-

Correspondence to: T. Ogawa (ogawa@servidor.unam.mx).  
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Scheme 1 Preparation route.

drich (Milwaukee, WI), was distilled before use. 2-[4-(4-Nitrophenylazo)-*N*-ethyl-phenylamino]ethanol (Disperse Red 1) was also supplied by Aldrich and was used as received.

### Grafting

A  $^{60}\text{Co}$  gamma-beam 651 PT, with activity of 45,000 Curies, was used for irradiation of PP films. The experimental procedure of grafting of poly(acryloyl chloride) was reported previously.<sup>12</sup> The PP film and acryloyl chloride (70%) in toluene were placed in a Pyrex ampoule, and the ampoule was sealed off in vacuum after degassing by repeated freeze/thaw cycles, and irradiated at a dose rate of 4 kGy/h (Direct method). The irradiation was also carried out for the PP film but in the vapor of acryloyl chloride (Vapor phase method). To estimate the grafting yield, after the irradiation the homopolymer of acryloyl chloride was extracted with dichloromethane, and the remaining films were treated with methanol and triethylamine to convert the grafted poly(acryloyl chloride) to the poly(methyl acrylate). Although the esterification cannot be quantitative, the grafting yields were calculated from the weight increase of the films. Then, the PP film, irradiated under the same conditions, was reacted with Disperse Red 1 in dichloromethane with triethylamine. The mixture was stirred for 24 h at room temperature, and then methanol was added to convert the remaining chloride to the methyl ester. The product films were washed with methanol and dried under vacuum. The preparation route is shown in Scheme 1. The amount of Disperse Red 1 bonded to the film was estimated by elemental analysis (Desert Analytics, Tucson, AZ) of nitrogen contents of the films. From the weight increase, the amount of grafted polymer is known, and it is possible to obtain approximate amounts of acrylates containing Disperse Red 1

as copolymers of methyl acrylate and acrylate with Disperse Red 1 (Scheme 2).

### Characterization

FTIR-ATR (attenuated total reflection) spectra were taken using a Perkin-Elmer Paragon 500 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT). The scanning electron microscopy (SEM) of the cross section of the films was performed using a JEOL model JSM 5200 apparatus (JEOL, Tokyo, Japan). The samples were prepared by the transversal cryogenic fracture method. The X-ray diffraction patterns of the films were obtained by an X-ray diffractometer (Model Bruker-AXS D8-Advance; Bruker Instruments, Billerica, MA). The observation of surface of the films was made using an atomic force microscope (AFM; Model Autoprobe-CP, Park Scientific Instruments, division of Veeco Instruments GmbH, Unterschleissheim, Germany), with 10- $\mu\text{m}$  scanner (contact mode) and an autocalibration by Scanner Master. The obser-

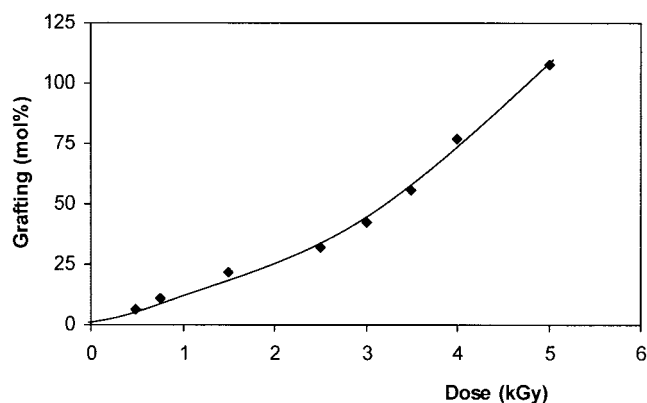
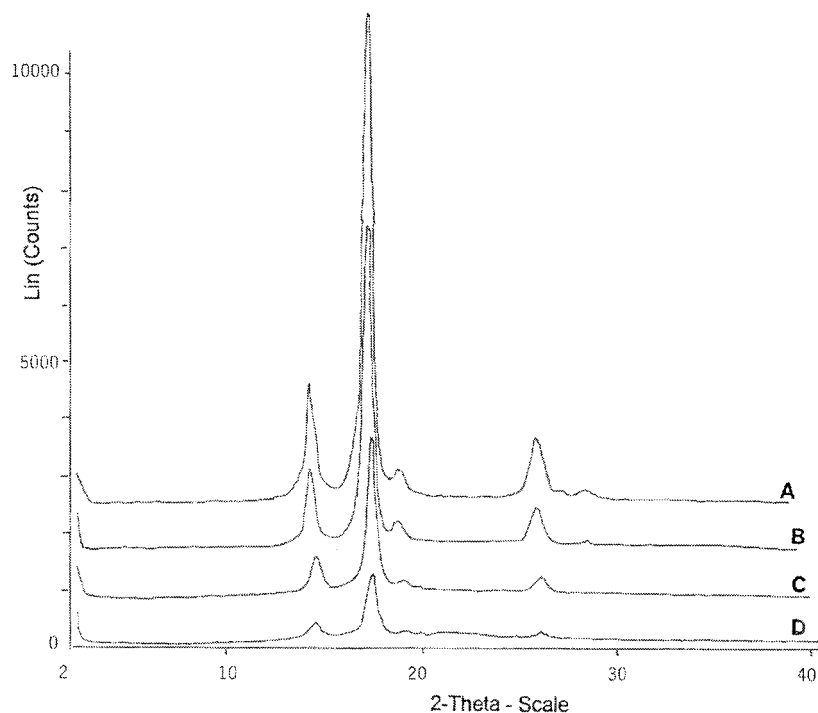


Figure 1 Relationships between given dose and grafting yield (Direct method).



**Figure 2** X-ray diffraction patterns of PP films grafted with poly(methyl acrylate): (A) D1; (B) D2; (C) D3; (D) D4 (Table I).

vation of the surface texture of the films was made using a polarized optical microscope (Model BH-2, Olympus, Osaka, Japan) fitted with a hot stage. Differential scanning calorimetry was performed using a DSC 2010 calorimeter (TA Instruments, New Castle, DE). A Varian Cary Model 100 UV-visible spectrophotometer (Varian Associates, Palo Alto, CA) was used to observe the *trans*-*cis* transformation of the azobenzene group in the films. A 450-W medium pressure mercury lamp of Ace Glass was used to irradiate the films, which had the following spectra:

Far UV 220–280 nm	Middle UV 280–320 nm	Near UV 320–400 nm	Visible 400–600 nm	Infrared 1000–1400 nm	Total radiated energy
27.0	28.7	28	75.7	16.4	175.8

## RESULTS AND DISCUSSION

### Grafting of PP films

Figure 1 shows the results of grafting of acryloyl chloride on the PP by the direct method. The grafted films were reacted with methanol to convert into methyl ester. The amount of the grafted poly(methyl acrylate) increased with the irradiation time (i.e., irradiation dose). This observation is normal for radiation-induced grafting. Although the esterification cannot be quantitative, the grafting (%) yields were calculated from the weight increase of the films, from  $[(w - w_0)/w_0] \times 100$ , where  $w_0$  is the original weight of the PP film and  $w$  is the weight of film after grafting and esterification with methanol. The mole percentage, based on the PP, was calculated from  $100 \times [(w - w_0)/86]/(w_0/41)$ , where 86 and 41 are molecular weights of methylacrylate and PP, respectively. It can be said that

**TABLE I**  
PP Films Grafted with Poly(methyl acrylate)

Sample	Dose (kGy)	Graft (wt %)	Graft (mol %)	Thickness (mm)	Crystallinity (%)
Blank	0	0	0	0.060	88
D1	1	40	4.4	0.060	77
D2	2	85	9.4	0.080	63
D3	3	100	11.1	0.110	54
D5	5	240	26.7	0.170	31

TABLE II  
Relationships Between Grafting and Crystallinity of PP Films Grafted with Disperse Red 1

Sample	Dose (kGy)	Total graft (wt %)	Molar ratio DR-1/MA	Thickness ( $\mu\text{m}$ )	Crystallinity (%)
Blank	0	0	0	60	88
1	1	32	1/9	60	—
2	2	85	1/10	75	71
3	3	146	1/8.9	100	—
4	4	238	1/7	100	61
6	6	281	1/7	170	—
8	8	452	—	220	—

acryloyl chloride can be readily grafted to the PP films. Acryloyl chloride is a monomer that gives a polymer with reasonably high molecular weight by free-radical polymerization. When it was irradiated with  $\gamma$ -rays under the same conditions, but in the absence of PP film, the number-average molecular weights of the polymers treated with methanol, poly(methyl acrylate), was found to be 32,200 ( $DP \approx 370$ ) and 74,000 ( $DP \approx 860$ ), with doses of 4 and 12 kGy, respectively, determined from the equation:  $[\eta] = 2.58 \times 10^{-3} M^{0.85}$  mL/g.<sup>13</sup> The increase in the molecular weight with dose is the usual observation in the radiation-induced polymerization. Therefore, it is assumed that relatively high molecular weight poly(methyl acrylate) chains are grafted.

X-ray diffraction patterns of PP and its films grafted with poly(acryloyl chloride) and converted to poly(m-

ethyl acrylate) are shown in Figure 2. The crystallinity of films decreased as expected, and Table I shows the relationships between the applied doses, grafting yield, changes in film thickness, and crystallinity. The measured crystallinity is based on the film thickness, and the decrease in the crystallinity is mainly attributed to the increase in the film thickness by the grafted poly(methyl acrylate).

Table II shows the grafting yields with Disperse Red 1. The amounts of Disperse Red 1 grafted were estimated from the elemental analysis of nitrogen. Because the weight ratios of PP film and the polyacrylates are known from weight % of grafting, the found nitrogen contents were converted to those for the grafted polymers, and the ratios of poly(methylacrylate) to polyacrylate of Disperse Red 1 were calculated. The amounts of Disperse Red 1 in the grafted polymers were rather small: 1 for 7–9 methylacrylate units. This is probably attributable to the poor reactivity of the hydroxy group of Disperse Red 1 with poly(acryloyl chloride). It seems that the reaction of Disperse Red 1 with poly(acryloyl chloride) takes place mainly at the surface of the film. The crystallinity somewhat decreased with the increase in the weight of grafted polymers because of the increase in the film thickness

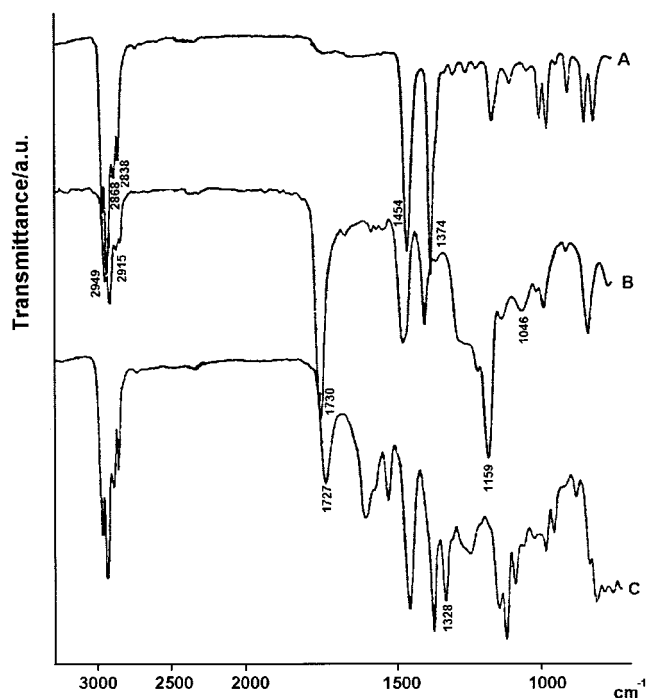


Figure 3 FTIR spectra of PP (A), grafted with poly(methyl acrylate) (B), and with Disperse Red 1 (C).

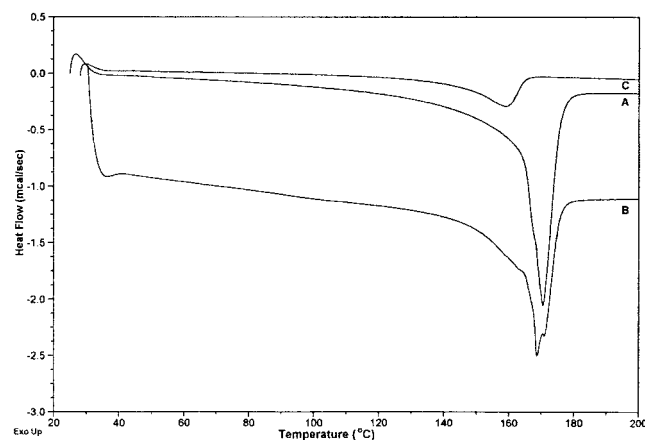
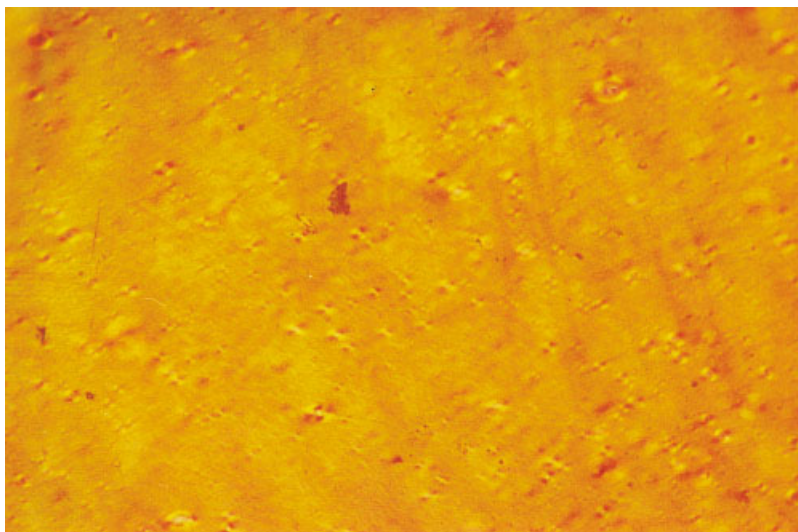


Figure 4 DSC curves of PP (A), grafted with poly(methyl acrylate) (B), and PP with Disperse Red 1 (C).



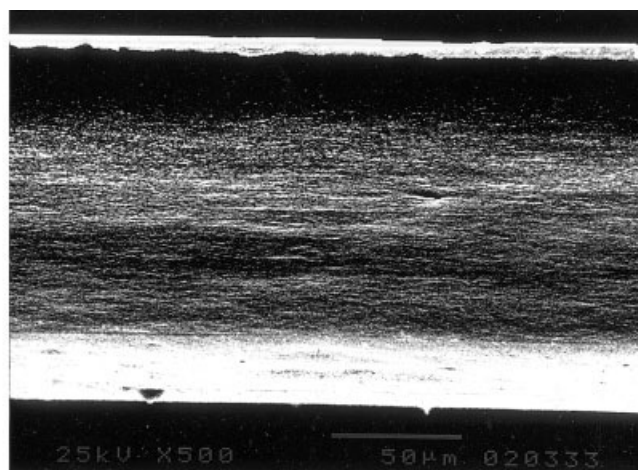
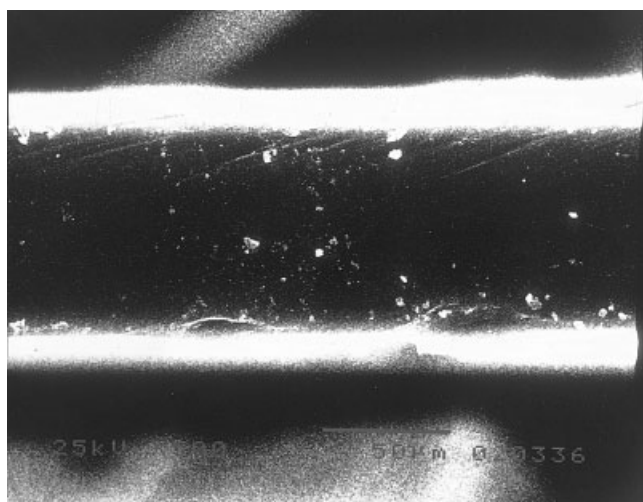
**Figure 5** Polarized light optical microscope picture of PP film grafted with Disperse Red 1 (sample 2, Table II).

by grafting, and it seems that the crystalline region of PP films is almost intact.

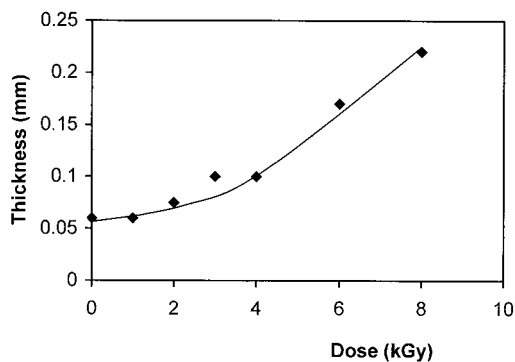
The transmission FTIR-ATR spectra of the films are shown in Figure 3. The PP shows its characteristic peaks at 2948, 2915, 2868, and 2837  $\text{cm}^{-1}$  of CH stretching; 1454  $\text{cm}^{-1}$  of  $\text{CH}_2$ ; and 1374  $\text{cm}^{-1}$  of  $\text{CH}_3$   $\delta_{\text{si}}$ . The PP grafted with methyl acrylate has, in addition to the above, peaks at 1730  $\text{cm}^{-1}$ , attributed to C=O stretching, and 1159 and 1046  $\text{cm}^{-1}$ , attributed to C(=O)-O and O-C-C stretching vibrations of the ester, respectively. The PP with Disperse Red 1 contains characteristic peaks at 1716  $\text{cm}^{-1}$  (O=C), 1600 and 1500  $\text{cm}^{-1}$  (aromatics), as well as 1328  $\text{cm}^{-1}$  ( $-\text{NO}_2$  stretching), in addition to those attributed to the ester group.

DSC thermographs of PP, the PP grafted with poly(methyl acrylate), and that with Disperse Red 1, are

shown in Figure 4. The melting of PP crystals at 170°C [Fig. 4(B)], remained unchanged [Fig. 4(C)] when the film was grafted with poly(methyl acrylate). The melting temperature of the PP crystals shifted to 159°C [Fig. 4(C)] with Disperse Red 1. The heat of melting decreased considerably by grafting, and this is because of a decrease in the relative volume of PP by the grafting. This observation is in agreement with the apparent decrease in crystallinity observed by X-ray diffraction. Although the DSC did not reveal any thermal transitions apart from melting of PP, observations with a polarized optical microscope indicated the existence of a mesophase. When the film grafted with Disperse Red 1 (sample 2 in Table II) was heated to 150°C, a nematic birefringent texture (minute shining Maltese crosses of 10–20  $\mu\text{m}$ ) appeared (Fig. 5). On heating to 175°C the crosses disappeared, and on cool-



**Figure 6** SEM micrographs of cross section of PP films grafted with Disperse Red 1. Sample 1 (left) and sample 4 (right) of Table II.

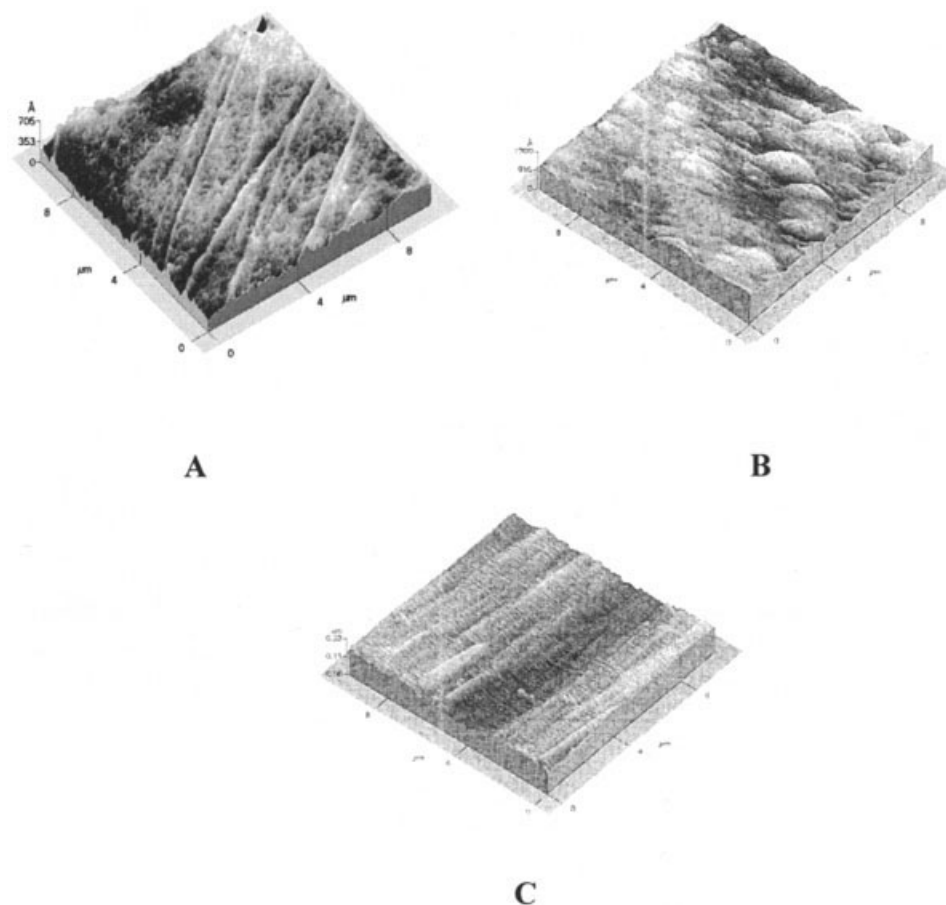


**Figure 7** Increase in film thickness with irradiation dose (grafting yield).

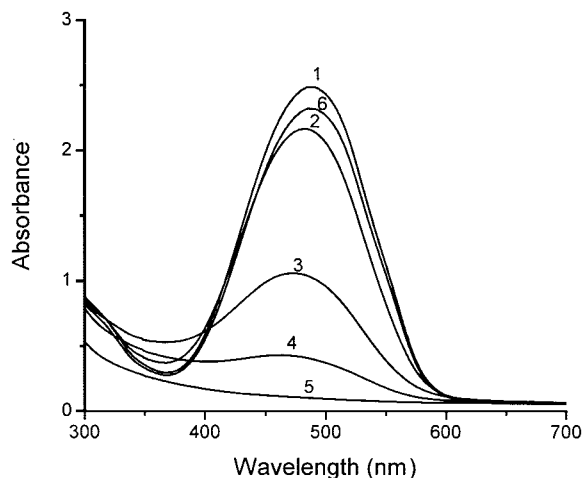
ing from 200°C to room temperature, a typical blurred schlieren texture (as black thin lines in the red film) was obtained. It seems that polyacrylate containing Dispersed Red 1 forms the mesophase. However, the amounts of Disperse Red 1 in the grafted polymers were low, as mentioned above. It seems that Disperse Red 1 reacted mainly with poly(acryloyl chloride) on the surface of the film.

Figure 6 shows scanning electron microscope topographies of the cross section of the films grafted with acryloyl chloride and esterified with Disperse Red 1. When the given irradiation dose is 1 kGy (25 min irradiation, 23% grafting), the grafting mainly takes place on the surface of the film (white parts) (Fig. 6, left). However, with higher dose (4 kGy, 100 min, 230% grafting) (Fig. 6, right), it can be seen that grafting penetrated into the inside of film. The PP film is not soluble in toluene and acryloyl chloride, and the grafting is considered to take place only at the amorphous region. When the surface is covered with poly(acryloyl chloride), the monomer penetrates inside the film through amorphous region between the crystallites; thus grafting takes place inside the film as well. This is commonly observed for many radiation-induced graftings on polymer films.<sup>14,15</sup> It can be seen that with high doses the thickness increases drastically as grafting penetrates the inside of film, as shown in Figure 7.

Figure 8 shows AFM topographies of the PP film and the films grafted with poly(acryloyl chloride) then esterified with Disperse Red 1. The surface of PP film-[Fig. 8(A)] contains line peaks with average roughness



**Figure 8** AFM topographies of PP film (A), grafted with Disperse Red 1 [sample 1 (B) and sample 4 (C) in Table II].



**Figure 9** Changes in visible absorption spectra of PP film with Disperse Red 1 (sample 2 in Table II) with UV irradiation time: 1, 0 h; 2, 2 h; 3, 8 h; 4, 12 h; 5, 48 h; 6, sample 5 after 5 min heating at 110°C.

of 17.5 Å. When the surface is grafted (sample 1, Table II) many lumps with size of a few micrometers appeared on the surface, in which the average roughness was 0.133  $\mu\text{m}$  [Fig. 8(B)]. When grafted with a higher dose (sample 4, Table II), the surface became very smooth and regular, and the average roughness decreased to 486 Å [Fig. 8(C)]. It can be seen the surface texture changes significantly by grafting, and that the surface is homogeneously covered with the polyacrylate containing Disperse Red 1.

Figure 9 shows the absorption changes of the visible spectra of the film grafted with Disperse Red 1 after irradiation with the UV lamp at room temperature. The peak at 489 nm of the dye decreased slowly with irradiation, and the red color disappeared completely after 48 h irradiation, resulting from the *trans* to *cis* transformation of the azo dye. However, when the discolored film was heated at 110°C the *trans* form was recovered within a few minutes. The irradiated film regained its coloring when allowed to stand at room temperature, although it was a slow process.

## CONCLUSIONS

An azo dye, Disperse Red 1, was successfully grafted onto polypropylene film by radiation grafting of acry-

loyl chloride, and the grafted films were characterized. SEM showed that with low irradiation dose, grafting takes place on the surface of film, but with higher doses, grafting penetrates inside the films. AFM and polarized optical microscope observation indicated that the film surface is homogeneously covered with the grafted material. The azo dye undergoes *trans-cis* photoisomerization, whereby the color of the films was lost, although the process is thermally reversed. This method is useful for obtaining flexible polymer films covered with functional materials in general, and the grafted amount can be controlled by irradiation dose.

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