

# The Surface Modification of Polyethylene by Solution-Phase Photochemical Grafting Using Short Irradiation Times

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## SYNOPSIS

The surface modification of low-density polyethylene by solution-phase photochemical grafting with acrylic acid and acrylamide is described. After irradiation for 3 min, the contact angles of the modified surfaces with water were ca. 20, 30, and 40°C and ca. 40, 40, and 80°C for grafting solutions containing 2M, 1M, and 0.1M of acrylamide and acrylic acid respectively. X-Ray photoelectron spectroscopy (XPS) and attenuated total reflectance infrared spectroscopy (ATRIR) of the modified polyethylene surfaces were consistent with the presence of grafts of polyacrylamide or poly(acrylic acid). Grafting using low concentrations of monomers, that is, 0.1M, resulted in a small, 20° decrease in contact angle for grafting with acrylic acid but a larger, 60° decrease for acrylamide. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The surface modification of polymers has attracted considerable interest in recent years. Techniques such as chemical oxidation,<sup>1</sup> plasma and corona discharge,<sup>2-4</sup> and treatment with ozone<sup>5</sup> have been widely used for this purpose. The surface properties of polyethylene have been modified using chemical<sup>6,7</sup> and radiative methods.<sup>8,9</sup> Photochemically induced grafting of vinylic monomers, such as acrylic acid, methacrylic acid, and acrylamide, has been shown to give materials that exhibit increased surface wettability.<sup>10-13</sup> However, earlier descriptions of these methods often involved relatively long irradiation times, of the order of hours, which limits the potential usefulness of the method as a practical process. A continuous process for the photochemical grafting of acrylic acid and acrylamide onto polyethylene tape at elevated temperature (ca. 70°C) using irradiation times of the order of seconds has been reported recently.<sup>14</sup> This process has also been used to modify the surface properties of ultra high-strength polyethylene fibers.<sup>15</sup>

Alternative approaches are also under investigation, for example, grafting of acrylic acid onto low-density polyethylene films treated by corona discharge has produced materials that exhibited improved surface wettability.<sup>16</sup> Nonradiative radically induced grafting where a peroxide initiator has been introduced into the swollen surface of LDPE resulted in a decrease in surface contact angle from 90 to ca. 30° after treatment with a boiling aqueous solution of acrylamide for 5 min.<sup>17</sup> Here we report some results for the photochemical grafting of acrylic acid and acrylamide onto low-density polyethylene using a solution-phase technique which allows effective grafting to be achieved at short experimental times without external heating.

## EXPERIMENTAL

### Reagents

Low-density polyethylene (LDPE, 75 μm thick, 54% crystallinity by differential scanning calorimetry) and poly(ethylene-terphthalate) (PET) were cleaned before use by immersion in boiling methanol for 45 min, followed by distilled water at room temperature for 30 min. The clean films were

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dried under vacuum. Acrylamide was recrystallized from acetone. Acrylic acid was distilled under reduced pressure (44°C, 4 mmHg) and stored at -20°C under nitrogen. Benzophenone and acetone (HPLC grade) were used as supplied.

### Apparatus

The ultraviolet lamp used was a Hanovia UVS 1000. The Pyrex filter employed absorbed ultraviolet radiation below about 300 nm. Contact angles (water, 2  $\mu$ L) were measured using a Rame Hart NRL 100 Contact Angle Goniometer. A minimum of six measurements were recorded. Core level X-ray photoelectron spectroscopy (XPS) were acquired using Kratos ES300 surface analysis instrument (base pressure  $8 \times 10^{-10}$  Torr). Mg  $K_{\alpha}$  (1253.5 eV) was used as the excitation source with the electron detection in the fixed retarding ratio (22 : 1) analyzer mode. The gold  $4f_{7/2}$  level at 83.8 eV had a full width at half maximum (FWHM) of 1.2 eV. XPS measurements were recorded with an electron take-off angle of 30° from the surface normal. No evidence was obtained for radiation damage to the samples during the typical time scale involved in these experiments. Data accumulation and component peak analysis were performed with an IBM PC computer, using linear background subtraction and Gaussian fits. For any particular experiment, all the different C(1s) environments were assigned a constant FWHM. The relative intensities of the peaks within any particular C(1s) envelope were fitted in accordance with the theoretical values expected from the monomer structures. All binding energies are referenced to the hydrocarbon component ( $-\text{C}_x\text{H}_y-$ ) at 285.0 eV,<sup>18</sup> and the instrumentally determined sensitivity factors were such that for unit stoichiometry, the C(1s) : O(1s) : N(1s) : Si(2p) intensity ratios are 1.00 : 0.55 : 0.74 : 1.02. Attenuated total reflectance infrared (ATRIR) spectra were recorded using a Perkin Elmer 1710 FTIR equipped with a KRS-5 crystal. 256 scans were collected for each spectrum to improve the signal to noise ratio. The relative intensity of the CO (ca. 1720  $\text{cm}^{-1}$ ) and CH<sub>2</sub> (ca. 1470  $\text{cm}^{-1}$ ) absorption bands was used as a measure of grafted acrylic acid and the CONH<sub>2</sub> (ca. 1650  $\text{cm}^{-1}$ ) and CH<sub>2</sub> (ca. 1470  $\text{cm}^{-1}$ ) for grafted acrylamide.

### Photografting

The grafting apparatus used has been described previously.<sup>19</sup> The grafting technique involved applying a nitrogen-purged (10 min) solution of

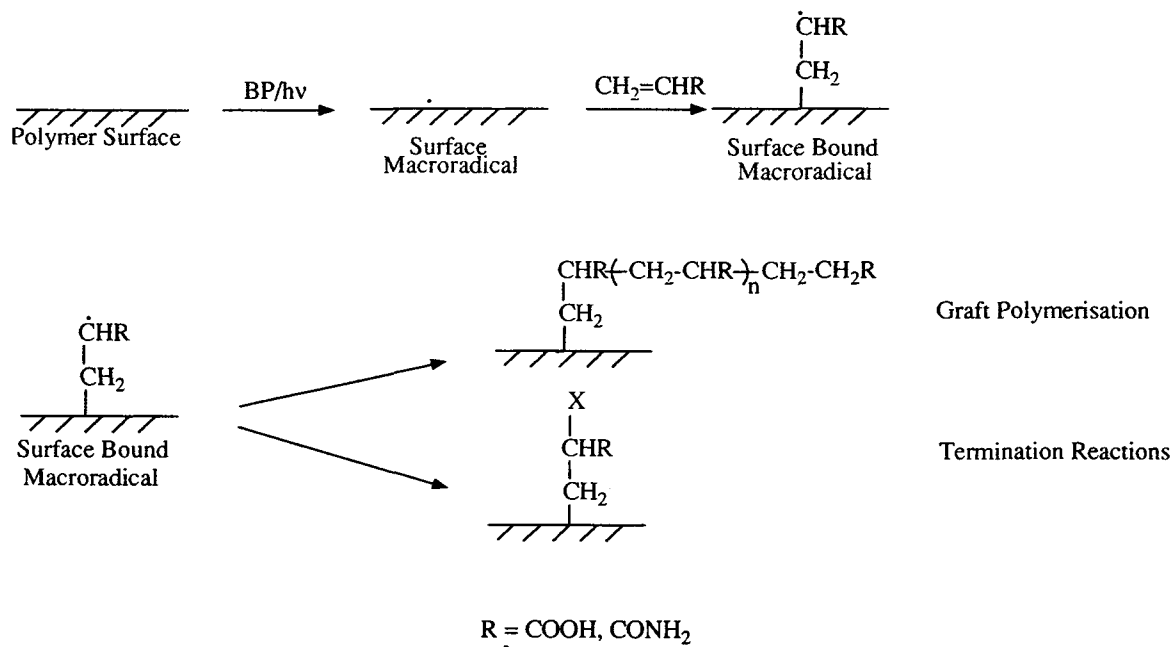
monomer and benzophenone (0.2M) in acetone to the PET substrate and placing a film of LDPE on top of the solution. The PET-grafting solution-LDPE sandwich was then flattened in order to remove gas bubbles and irradiated with ultraviolet light through a Pyrex window of a nitrogen-purged chamber so that the dry side of the LDPE film was facing the ultraviolet lamp. The temperature in the grafting chamber was ca. 20°C (measured using a thermocouple). After irradiation, the films were peeled apart, rinsed in methanol, and washed. The acrylamide-grafted samples were repeatedly washed in distilled water (60–90°C, 1 h) and then in methanol (room temperature, 10 min) to remove homopolymer. The acrylic acid-grafted films were washed in aqueous 0.1M NaOH solution at 70°C for 30 min. The films were occasionally removed from the washing solution and the grafted surface lightly rubbed with a cotton bud to aid the removal of the final traces of the homopolymer. The samples were then placed in aqueous 0.01M HCl for 30 min and then finally in distilled water (30 min). Before analysis, the films were dried under vacuum at room temperature for 1 h.

## RESULTS AND DISCUSSION

The photochemical grafting of vinylic compounds onto polyethylene can be achieved using a sensitizer such as benzophenone (Scheme 1).<sup>10,14</sup> In its excited triplet state, benzophenone can abstract hydrogen from polymer surfaces to produce a surface macroradical and a ketyl radical. The macroradical can react with a vinylic monomer to produce a surface-bound radical. This radical may then initiate graft polymerization of the monomer or undergo termination reactions such as hydrogen abstraction or cross-linking. The possibility of grafting onto a surface-bound radical will be dependent upon the temperature, reactivity of the radical, and the concentration of the monomer. Homopolymerization of the vinyl monomer also occurs and the material produced in this way is removed by thorough washing prior to characterization.

### Photografting of Acrylic Acid and Acrylamide onto LDPE

Grafting solutions that consisted of acrylic acid (AA) and acrylamide (AM) (2M, 1M, and 0.1M) and benzophenone (0.2M) in acetone were employed in order to determine the effect of monomer concentration on the degree of grafting.

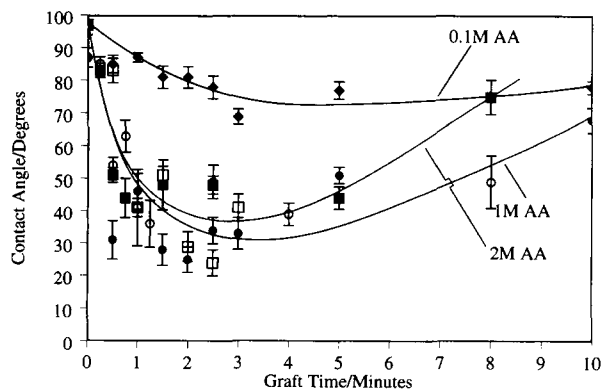


**Scheme 1** Photochemically initiated grafting onto polymer surfaces.

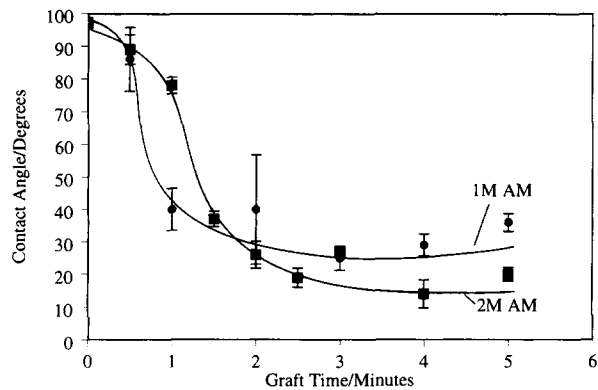
### Grafting Using Short Irradiation Times

Grafting onto LDPE using short irradiation times (< 10 min) was investigated first. The variation of contact angles with irradiation times for surfaces grafted with solutions of different monomer concentrations are shown in Figures 1 and 2. The error bars indicate the standard deviations associated with the measurements. Grafting employing 2*M*- and 1*M*-monomer solutions resulted in profiles that were typical for grafting by this approach in that an initial rapid decrease in contact angle is followed by a slow rise to a plateau value. The rate of change and time

of occurrence of the minimum value of the contact angle varies with experimental conditions and monomer and polymer structure. This kind of behavior has been observed for the solution-phase grafting of AA onto PE coated with benzophenone,<sup>13</sup> and was explained in terms of surface roughness. However, it is also possible that the carboxylic acid groups in the grafted polymer undergo photochemical or ground-state reactions, such as dehydration and decarboxylation, which reduce the number of free acid groups and hence increase the contact angle.<sup>20</sup> Grafting with the 1*M* AA acid solution gives approximately the same contact angle values (ca.



**Figure 1** The variation of contact angle with graft time. Acrylic acid. 0.2*M* benzophenone in acetone. 0.1*M* AA (◆). 1*M* AA (●, ○). 2*M* AA (■, □).



**Figure 2** The variation of contact angle with graft time. Acrylamide. 0.2*M* benzophenone in acetone. 1*M* AM (●). 2*M* AM (■).

30°) as a 2M solution for corresponding irradiation times (see Figure 1). Pure poly(acrylic acid) exhibits a contact angle of ca. 20°. The profiles of contact angle against time were reproducible with respect to the irradiation time at which the minimum value occurred. The error bars on repeat measurements were rather variable which may be attributed to small variations in the details of the experiment such as the nitrogen flow rate and the consequent cooling efficiency in the grafting chamber. Grafting for longer irradiation times (5 min) usually resulted in peeling of the LDPE film from the PET substrate which ruled out the use of this convenient experimental procedure for studies of the effect of longer irradiation times with this monomer solution.

In the case of grafting with AM, the LDPE surfaces exhibited a decrease in contact angle with graft time with a contact angle of ca. 20° (2.88) obtained after irradiation for 2.5 min in the presence of a 2M monomer solution (Fig. 2). A similar trend is observed for grafting using the 1M AM solution with a minimum contact angle of ca. 30° (2.67) obtained after irradiation for 3 min. Pure poly(acrylamide) exhibits a contact angle of ca. 25°. The contact angle after irradiation for 1 min had fallen from 97° (1.7) to 40° (5.2) which indicates a substantial modification of the LDPE surface which is consistent with the presence of grafted poly(AM). Grafting using a 0.1M solution of AM resulted in a decrease in contact angle from 97° to ca. 50° after irradiation for 5 min. This is in contrast to grafting using a 0.1M solution of AA where the contact angle decreases at most to 70° (typically 80°) over a similar irradiation period.

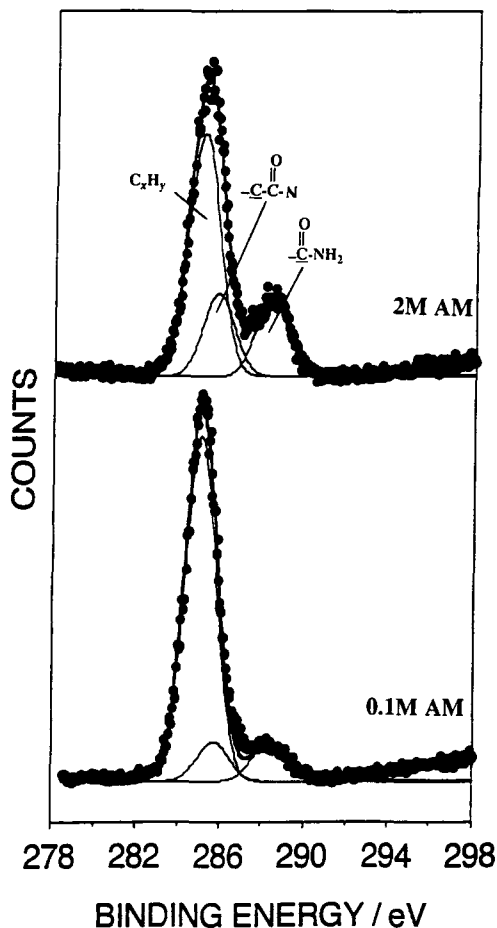
Exposure of the LDPE to irradiation in the presence of a solution of benzophenone (0.2M) in acetone for 10 min resulted in a material that exhibited a contact angle of ca. 85°–90°. These results are consistent with the grafting of the hydrophilic poly(acrylamide) onto the surface of the LDPE using this technique. The rapid drop in contact angle as a result of grafting and the variations with monomer structure are not surprising. The gradual rise in contact angle after the minimum implies that the initial grafted layer undergoes further physical or chemical modification. This may well be a function of monomer and grafted polymer structure and experimental conditions, including washing and drying protocols, humidity, and of the photochemical stability of the grafted chains.

ATRIR spectroscopy, which analyzes was ca. 1 μm of the polymer surface, of the samples grafted with AA indicated the presence of carbonyl absorp-

tion bands at ca. 1710 cm<sup>-1</sup> for all graft times when a 2M monomer solution was used except for the sample which had been irradiated for 15 sec, the spectrum of which contained no carbonyl absorption bands. In the case of the 1M solution, the ATRIR spectra exhibited carbonyl absorption bands at ca. 1710 cm<sup>-1</sup> for samples irradiated for more than 30 sec. Grafting with the 0.1M AA solution resulted in ATRIR spectra which exhibited little or no carbonyl absorption bands. In the case of grafting with AM the modified samples exhibited carbonyl absorption bands at ca. 1650 cm<sup>-1</sup> for irradiation times in excess of 30 sec. No carbonyl absorption bands were observed in the ATRIR spectra of the samples grafted using a 0.1M AM solution.

Detailed chemical information about the outermost layer of the modified polyethylene surfaces (sample depth ca. 30Å) was obtained by fitting the C(1s) XPS spectra with standard peaks corresponding to the known binding energies of carbon functionalities<sup>21,22</sup>: hydrocarbon ( $\underline{C}_xH_y \approx 285.0$  eV), carbon adjacent to a carboxylate group ( $\underline{C}-CO_2 \approx 285.7$  eV) or an amide group ( $\underline{C}-CONH_2 \approx 285.6$  eV), carboxylic acid groups ( $O=\underline{C}-OH \approx 289.2$  eV), and amide carbons ( $O=\underline{C}-NH_2 \approx 288.3$  eV). A N(1s) binding energy of 399.9 eV was obtained for photografted poly(acrylamide), and a O(1s) binding energy of  $\approx 533$  eV was measured for both types of surface modification. The C(1s) envelopes are shown in Figures 3 and 4 and the results are summarized in Table I.

Photografting was found to be dependent upon the monomer concentration. The most successful treatment appears to be using a 2M AA solution. Traces of oxygenated species were detected for the low-concentration experiments which could not be assigned to monomer residues. These may be due to the presence of some benzophenone but also may arise from competing photochemical reactions such as cross-linking *via* ether-type linkages. In the case of LDPE grafted with poly(AM), the O(1s) envelope exhibited a shoulder at ca. 534.6 eV, which indicates that more than one carbon-to-oxygen environment was present. There is also evidence in the C(1s) envelope (at ca. 287 eV) for such a structural feature. No such shoulder was observed in the O(1s) envelope for the samples grafted in the presence of AA. The presence of an unsymmetrical O(1s) envelope for polyester which had been photochemically grafted with AM has been reported by Uchida et al.<sup>23</sup> who explained the feature in terms of monomer impurity. A similar spectrum has also been reported for sensitizer-coated LDPE which had been pho-



**Figure 3** XPS C(1s) envelope of acrylamide grafted LDPE. 2M and 0.1M AM grafting solutions. Graft time = 5 min.

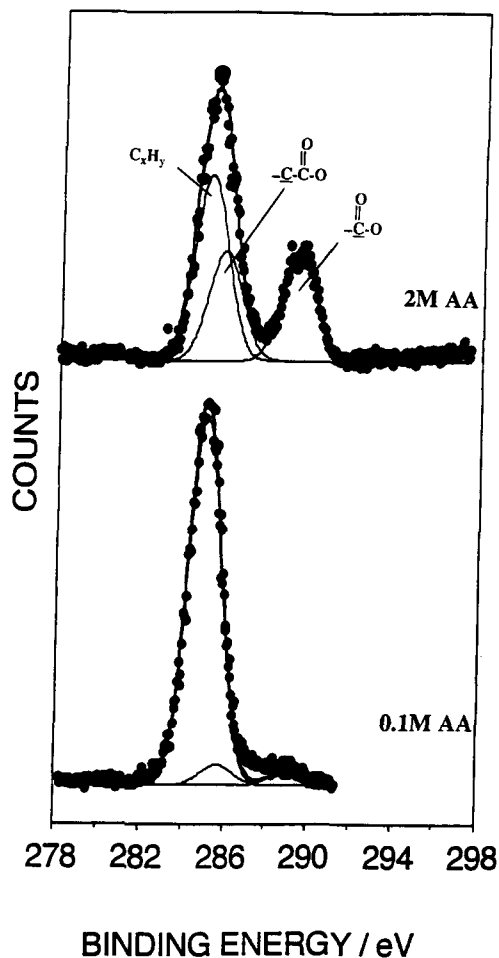
tochemically grafted with AM.<sup>13</sup> We carefully recrystallized our AM monomer prior to use and do not subscribe to the view that this feature results from monomer impurity. There was no anomaly in the corresponding N(1s) spectrum of the AM grafted sample. We propose that there must be a minor chain reaction leading to inclusion of AM residues in which the oxygen is not present as a carbonyl function, although, at present, we are unable to provide a satisfactory rationalization of these observations.

#### Grafting Using Long Irradiation Times

The possibility of grafting AM onto LDPE using 2M, 1M, and 0.1M solutions of monomer was investigated. The modified LDPE surfaces were an-

alyzed using contact angle measurements and ATRIR. As mentioned previously, it was not possible to study the grafting of AA using this procedure due to peeling of the LDPE from the substrate.

The variations of contact angle with irradiation time are shown in Figure 5. For all monomer concentrations (2M, 1M, and 0.1M) a rapid decrease in contact angle was observed after irradiation for ca. 5 min after which time the contact angle values remain constant before rising slowly after irradiation for 20 min. The minimum contact values obtained after irradiation for 5 min were ca. 20°, 30°, and 40° for grafting solutions containing 2M, 1M, and 0.1M of AM respectively. The results shown in Figure 5 are consistent with grafting of AM onto the LDPE surface. The plateau in the contact angle measurements after irradiation for ca. 5 min indicates that



**Figure 4** XPS C(1s) envelope of acrylic acid grafted LDPE. 2M and 0.1M AA grafting solutions. Graft time = 3 min.

**Table I** Summary of XPS Analysis of Grafted Samples

Treatment <sup>a</sup>	Area % of C(1s) Envelope Arising from Peaks Assigned to Photografted Material	Elemental Composition of Outer Layer. Atom %			
		C	O	N	Si <sup>b</sup>
0.1M Acrylic Acid	15	90	10	0	0
2.0M Acrylic Acid	82	68	32	0	0
0.1M Acrylamide	28	84	9	5	2
2.0M Acrylamide	61	69	15	13	3

<sup>a</sup> All samples were irradiated under the same conditions for 3 min for AA and 5 min for AM.

<sup>b</sup> The presence of silicon is probably due to silicon grease.

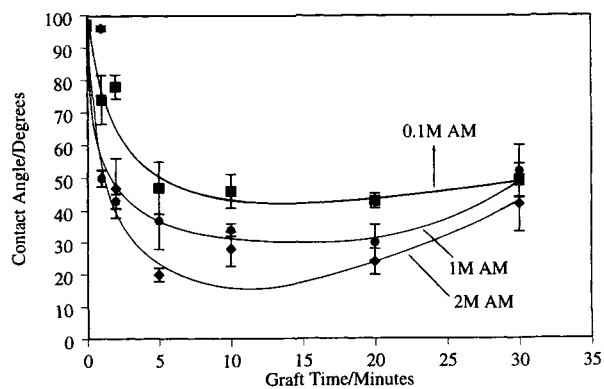
at this stage a stable-grafted layer has formed. However, there was an increase in contact angle for longer irradiation times, and the surface of the sample which had been irradiated for 30 min exhibited some discoloration. Both of these observations may be a result of degradation of poly(AM).

Variations in the CO (ca. 1710 cm<sup>-1</sup>)/CH<sub>2</sub> (ca. 1470 cm<sup>-1</sup>) absorbance ratio with irradiation time are shown in Figure 6. The ratio, as expected, increased with increasing irradiation time. The decrease observed after irradiation for 30 min may be due to degradation of the grafted layer or surface reorganization. There was, however, a shoulder in the in the C—H bend region (ca. 1450 cm<sup>-1</sup>) of the ATRIR spectra of grafted LDPE which became more pronounced at lower monomer concentrations. When irradiation was carried out in the absence of monomer for 5 min, a similar shoulder in the ATRIR spectrum was observed which may be due to reaction of benzophenone with the surface.

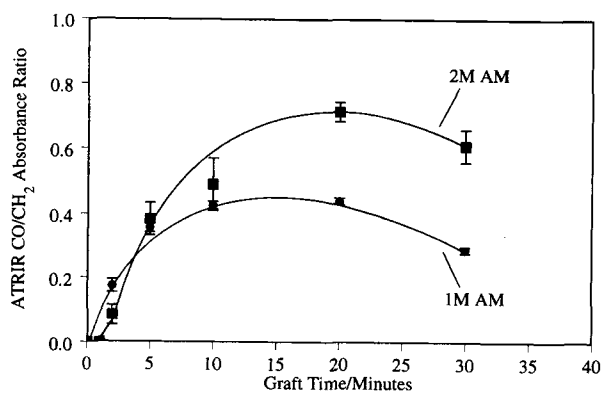
There were no significant carbonyl infrared absorption bands in the ATRIR spectra of the LDPE sample grafted using 0.1M AM solutions, although contact angle and XPS measurements indicated that grafting had occurred, suggesting that grafted layers were too thin to be detected by ATRIR measurements.

## CONCLUSIONS

Both AA and AM can be successfully grafted onto LDPE using irradiation times of the order of minutes. However, AM is more readily grafted when monomer solutions of 0.1M are employed since the surface of the AM grafted LDPE exhibits significantly increased wettability, whereas AA gives only a small decrease in contact angle. Grafting using longer irradiation times suggests that grafted



**Figure 5** The variation of contact angle with graft time. Acrylamide. 0.2M benzophenone in acetone. 2M AM (◆). 1M AM (●). 0.1M AM (■).



**Figure 6** The variation of ATRIR CO/CH<sub>2</sub> absorbance ratio with graft time. Acrylamide. 0.2M benzophenone in acetone. 2M AM (■). 1M AM (●).

poly(acrylamide) is more stable to ultraviolet light than is grafted poly(acrylic acid).

The authors thank British Petroleum International for financial support.

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Received May 29, 1993

Accepted October 13, 1993