

Surface Grafting of Polyacrylamide from Polyethylene-Based Copolymer Film

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ABSTRACT: Atom transfer radical polymerization (ATRP) was used to grow polyacrylamide from the surface of ethylene–acrylic acid copolymer (EAA) film. The surface functionalization constituted initiator immobilization and surface graft polymerization. All reaction steps were conducted at $24 \pm 3^\circ\text{C}$; polymerization was done in aqueous solution. For initiator immobilization, the carboxylic acid groups on EAA film were converted to acid chloride groups; further reaction with ethanolamines gave hydroxyl groups onto which 2-bromoisobutyryl bromide initiator was attached. ATR-FTIR data indicated that 1.64 ± 0.09 times higher initiator density was achieved by using diethanol-

amine, relative to ethanolamine. Acrylamide monomer was polymerized from the initiator by ATRP to yield nondistorted, transparent films with polymerization times of up to 1 h. For films prepared using diethanolamine, 1 h polymerization time reduced the static water contact angle by more than 50° , significantly increasing the hydrophilicity of the film surface. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1589–1595, 2004

Key words: polyethylene (PE); functionalization of polymers; surfaces; atom transfer radical polymerization (ATRP); hydrophilic polymers

INTRODUCTION

Graft polymerization is a well-known method to tailor the properties of solid surfaces for specific applications. When the surface is a polymer film, graft polymerization may improve film properties by changing chemical functionality only on the film surface. Polyethylene (PE) surfaces are relatively inert chemically, so surface treatments must first be done to create reactive sites that may be used for further surface modification. Examples of treatment techniques include electron-beam irradiation,¹ argon-plasma treatment,² ^{60}Co γ -radiation,³ and corona discharge treatment.⁴ Kildal et al.⁵ reported a chemical synthesis method in which peroxide initiator penetrated into a swollen polyethylene film, and then surface grafting of polyacrylamide was performed. A large volume of peroxide and a high temperature were used in this method to achieve grafting; such reaction conditions may raise potential safety problems. Additionally, high temperature may also be undesirable.⁶ Sarkar et al.⁷ reported a photochemical process to incorporate

succinic anhydride groups onto polyethylene film surfaces. Subsequent chemical reactions transformed these succinic anhydride groups to a variety of other functional groups.

Using a comonomer is another way to incorporate functional groups into polyethylene-based copolymers. The functional groups exposed on surfaces provide reactivity so that one may use them for the purpose of graft polymerization. Yao et al.⁸ and Kubota et al.⁹ described grafting of polyacrylamide on the surface of ethylene–vinyl alcohol copolymer (EVOH), where the hydroxyl groups served as initiation points by the interaction with Ce^{4+} in aqueous media. The graft efficiency was reportedly lower than 30%, indicating a large amount of homopolymer yield in the solution phase.

In a previous work,¹⁰ we immobilized 2-bromoisobutyryl bromide on the surface of EVOH film; the immobilized bromoester was used subsequently to initiate surface-confined ATRP of polyacrylamide at room temperature. Using acetone as a solvent, there was no detectable amount of polyacrylamide formed in solution even after 7 h of polymerization time, indicating high graft efficiency in this system. In this contribution, surface-confined ATRP is described for growing polyacrylamide from the surface of ethylene–acrylic acid copolymer (EAA) film. EAA is a polyethylene-based copolymer with carboxylic acid functionality. Unlike for EVOH, the bromoester initiator group cannot be attached directly onto the EAA film by the

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reaction with 2-bromoisobutyryl bromide. For this reason, a new reaction scheme was designed to functionalize EAA film with the bromoester initiator group (see **Scheme 1** below).

The goal of this study was to produce film with enhanced surface hydrophilicity, while maintaining transparency and other bulk properties. EAA was selected because of its greater clarity and toughness compared with those of LDPE and EVOH. Acrylamide was used because its polymer, polyacrylamide, is water-soluble and hydrophilic.

EXPERIMENTAL

Materials

EAA (9.5 mol % acrylic acid) films (thickness = 0.06 mm) were used as received from Cryovac Division of Sealed Air Corp. (Duncan, SC). All chemicals were purchased from Aldrich (Milwaukee, WI) and used as received: 2-bromoisobutyryl bromide (98%), phosphorus pentachloride (95%), ethanolamine (99+%), diethanolamine (99%), ethyl 2-bromoisobutyrylate (98%), CuCl (purified 99+%), and acrylamide (99+%, electrophoresis grade). Solvents were purchased from Aldrich as ACS reagent grade: toluene, acetone, methylene chloride, dimethyl formamide, and ethyl acetate. Hexamethyl tris(2-aminoethyl)amine (Me_6TREN) was synthesized from tris(2-aminoethyl)amine (96%), formaldehyde (37% in water), and formic acid (88%); all precursors were purchased from Aldrich and used as received.

Synthesis of Me_6TREN

Me_6TREN was synthesized by methylation of tris(2-aminoethyl)amine by a procedure modified from Ciampolini and Nardi.¹¹ A mixture was prepared of 300 mL of aqueous formaldehyde solution (37%), 20 mL of aqueous HCl solution (37%), and 270 mL of aqueous formic acid solution (88%); this mixture was then stirred for 1 h in a 2000-mL three-neck flask at 0°C. To this flask, a mixture consisting of 30 g of tris(2-aminoethyl)amine and 100 mL of deionized water was added dropwise. The final mixture was heated to $94 \pm 2^\circ\text{C}$ and maintained at this temperature for at least 48 h. Volatile fractions were removed completely by rotary evaporation, and the brown residue was washed with 400 mL of 20% aqueous sodium hydroxide solution, producing a two-phase aqueous-organic system. The organic layer was extracted into methylene chloride and then washed with about 500 mL of saturated aqueous sodium chloride solution, again producing a two-phase system. The organic phase was isolated and dried with anhydrous sodium sulfate overnight. After removing methylene chloride by evaporation, 37.2 g (79% yield) of Me_6TREN was ob-

tained. No N—H peak was shown in NMR spectra, supporting that no residual TREN remained.

$^1\text{H-NMR}$ δ : 2.67, 2.65, 2.64, 2.62 (6 H, CH_2); 2.44, 2.43, 2.41, 2.39 (6H, CH_2); 2.26 (18.2H, CH_3) ppm. ^{13}C δ : 57.5 (CH_2), 53.1 (CH_2), and 45.9 (CH_3) ppm.

Preparation of acid chloride-modified surface

EAA film ($\sim 1.5 \times 5$ cm) was placed into about 200 mL of a 3% (w/v) solution of PCl_5 in methylene chloride at room temperature for 15 min to convert the surface carboxylic acid groups to acid chloride groups. After reaction, the film was removed and washed sequentially with methylene chloride and ethyl acetate. Residual solvent on the surface was blotted with tissue paper. For a sample subjected to characterization, the film was allowed to air dry for at least 24 h. All other samples were used immediately in the next reaction step. The acid chloride-modified film is hereafter referred to as EAA-Cl.

Preparation of hydroxyl-modified surface

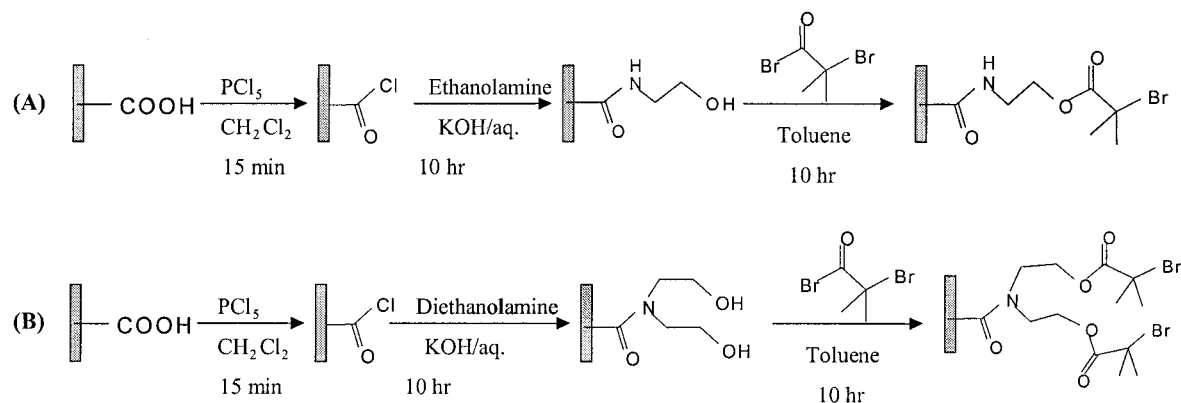
A total of 18 g of ethanolamine or diethanolamine was dissolved in 400 mL of 4% (w/v) KOH aqueous solution at room temperature ($24 \pm 3^\circ\text{C}$). One piece of the EAA-Cl film was placed in the solution to perform the reaction at room temperature for 10 h. After reaction, the film was removed and then washed with water. Tissue paper was used to absorb the residual solvent on the surface. For a sample subjected to characterization, the film was allowed to air dry for at least 24 h. All other samples were used immediately in the next reaction step. Hereafter, EAA-NOH and EAA-diNOH will denote ethanolamine- and diethanolamine-modified films, respectively.

Preparation of initiator-functionalized surface

EAA95-NOH or EAA95-diNOH film was put in 200 mL of a 3% (w/v) 2-bromoisobutyryl bromide solution in toluene to immobilize the initiator on the surface. The reaction was performed for 10 h at room temperature with stirring. The film was then removed, washed with 100 mL of ethyl acetate in an ultrasonicator, and then washed with a copious volume of water and then acetone. After drying in air, the initiator-functionalized film was characterized by ATR-FTIR spectroscopy. Hereafter, surfaces functionalized with initiator are referred to as EAA-NOH-Br and EAA-diNOH-Br.

Polymerization procedure

This step used an organometallic catalyst composed of Cu(I)Cl and ligand, Me_6TREN . All polymerizations were carried out in aqueous solution using a molar



Scheme 1 Reaction procedures for preparing initiator-functionalized EAA films: (A) linear structure; (B) bifurcated structure.

ratio of $\text{Cu(I)Cl} : \text{Me}_6\text{TREN}$ of 1 : 1, and a 3M concentration of acrylamide. Deionized water (18.2 M Ω ; Millipore, Milford, MA) was used as solvent to perform the polymerization.

A typical polymerization run follows: 1.725 g of Me_6TREN was added to 25.0 mL of dimethylformamide (DMF). A piece of EAA-NOH-Br film, 0.29 g of Cu(I)Cl , and 4.27 g of acrylamide were charged to a separate flask. To this flask, 20.0 mL of deionized water was added to dissolve the solid acrylamide. The solution was subjected to three freeze-thaw cycles with vacuum evacuation and nitrogen purging to remove oxygen. To begin polymerization, 1.0 mL of the $\text{Me}_6\text{TREN}/\text{DMF}$ solution was transferred to the flask containing the film, Cu(I)Cl , and monomer. The reaction solution volume was sufficient to fully submerge the film. Polymerization was performed at room temperature for a prescribed time up to 5 h. After removing the film from the polymerization system, it was sonicated in 400 mL of water for 15 min, and then washed with acetone. Surfaces functionalized with polyacrylamide films are referred to as EAA-NOH-PAAm and EAA-diNOH-PAAm.

Characterization

Attenuated total reflectance (ATR) FTIR spectra of the polymer films were obtained using a Nicolet Avatar 360 FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI) equipped with a nitrogen-purged chamber. ATR-FTIR spectroscopy was conducted with a horizontal multibounce attachment using a germanium crystal and a 45° angle of incidence. All spectra were taken at 4 cm^{-1} resolution and reported as an average of 540 scans.

Static contact angle measurements were conducted using a Krüss G10 instrument (Krüss, Hamburg, Germany) with a digital photo analyzer. With a syringe, a water drop (volume $\sim 1.4 \mu\text{L}$) was placed carefully

onto the film specimen of interest. At least nine drops were evaluated for each specimen to obtain an average contact angle and standard deviation.

X-ray photoelectron spectroscopy (XPS) data were collected using a Kratos AXIS 165 XPS spectrometer (Kratos Analytical Instruments, Ramsey, NJ) equipped with a monochromatic $\text{Al-K}\alpha$ (1486.6 eV) X-ray source and hemispherical analyzer. XPS characterization was done at Cryovac.

RESULTS AND DISCUSSION

Initiator structures on EAA surface

In contrast to conventional radical polymerization, ATRP uses alkylhalogen compounds as initiators, such as the widely used 2-bromoisobutyrylate structures. For surface-confined polymerizations, a common way to functionalize a surface with the bromoisobutyrylate structure is to react 2-bromoisobutyryl bromide with hydroxyl groups present on the surface.^{10,12} For EAA films, a first step is needed to convert the carboxylic acid functional groups to hydroxyl groups. **Scheme 1** shows our strategy to immobilize the bromoester group on the surface of EAA films. Using different ethanolamines, linear (A) and bifurcated (B) structures can be built on the EAA film. An advantage to this strategy over direct reduction of acid groups to hydroxyl groups (e.g., using borane) is that, using bifurcated structures, the concentration of initiator sites can theoretically exceed the concentration of surface carboxylic acid groups [see Scheme 1(B)].

Figures 1 and 2 present ATR-FTIR spectra that follow the reactions involved in initiator immobilization using linear and bifurcated structures, respectively. First, the carboxylic acid groups of EAA were converted to acid chloride groups; this conversion is marked by a shift of the carbonyl peak from 1702 cm^{-1}

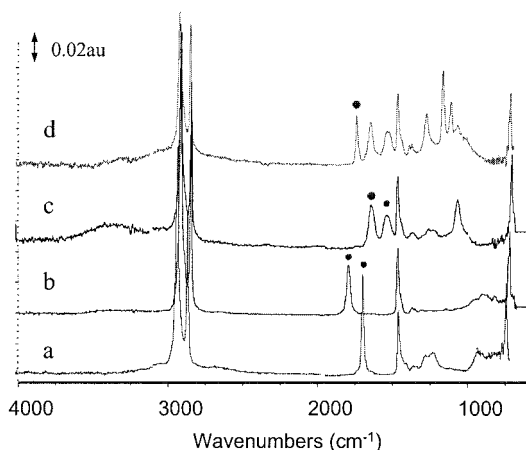


Figure 1 ATR-FTIR spectra of linear initiator functionalization on EAA film: (a) plain EAA film; (b) EAA-Cl; (c) EAA-NOH; (d) EAA-NOH-Br.

[Figs. 1(a) and 2(a)] to 1794 cm^{-1} [Figs. 1(b) and 2(b)] in the FTIR spectra. Next, either ethanolamine or diethanolamine was reacted with the acid chloride groups. These compounds have both amine and hydroxyl groups that can react with the acid chloride groups to form amide and ester groups, respectively. Reaction with the amine, however, is more favorable. After the second reaction step, amide formation was observed at 1655 cm^{-1} in the FTIR spectra [Figs. 1(c) and 2(c)], and ester formation was not observed in the spectra. Additional evidence of amide formation is the band at 1537 cm^{-1} [Fig. 1(c)], which is associated with N—H bending vibration from the secondary amide structure. No such band is seen in the spectrum associated with the diethanolamine reaction [Fig. 2(c)], consistent with the fact that reaction with diethanolamine generates a tertiary amide that contains no N—H bond. In the final step, 2-bromoisobutyryl bromide was reacted with the hydroxyl groups now present on the EAA films to form bromoisobutyrylate groups on the surface. FTIR data support the successful completion of this reaction; a band at 1740 cm^{-1} is seen [Figs. 1(d) and 2(d)] that indicates the existence of 2-bromoisobutyrylate on both linear and bifurcated initiator structures.

For surface-confined polymerization, the initiator density on surfaces affects polymerization kinetic behavior,¹³ morphology, and thickness of grafted polymer layers.¹⁴ Because the EAA films that we used had a low concentration of acid functional groups, we attempted to increase the initiator density by using diethanolamine to form a bifurcated structure, as described previously. Using FTIR measurements, and assuming Beer's Law, quantitative estimates were made to determine how initiator density for the bifurcated structure compared to that for the linear structure:

$$n = \frac{A_B(1740\text{ cm}^{-1})/A_B(2848\text{ cm}^{-1})}{A_L(1740\text{ cm}^{-1})/A_L(2848\text{ cm}^{-1})} \quad (1)$$

where n is the molar ratio of initiator groups for the bifurcated structure to that for the linear structure; A is absorbance at 1740 cm^{-1} (carbonyl group of initiator) or 2848 cm^{-1} (CH vibration as internal reference); and subscripts B and L represent bifurcated and linear structures, respectively. From FTIR measurements, we calculated $n = 1.64 \pm 0.09$ (the error represents the standard deviation calculated from multiple measurements of the samples.) The fact that $n \neq 2$ is reasonable because the proximity of the hydroxyl groups in the bifurcated structure might not allow for complete 1-to-1 reaction with 2-bromoisobutyryl bromide.

Graft polymerization conditions

Me_6TREN is a highly active ligand that allows a Cu-mediated ATRP at room temperature.^{15,16} ATRP systems with this ligand display distinct colors associated with the oxidation state of the metal. In the present system, when CuCl was mixed with Me_6TREN and ethyl 2-bromoisobutyrylate in 3M acrylamide aqueous solution, the system was pale green. After replacing CuCl with CuCl_2 , the color became pale blue. We examined the color changes associated with normal surface-confined polymerization (without addition of "sacrificial" solution-phase initiator); throughout the 30-min reaction period, the solution remained pale green. This result is consistent with the fact that for surface-confined polymerization from flat surfaces, too few initiator molecules are available to generate a significant concentration of Cu^{2+} under typical reaction conditions.¹⁷ When additional "sacrificial" initiator (ethyl 2-bromoisobutyrylate) was put in solution,

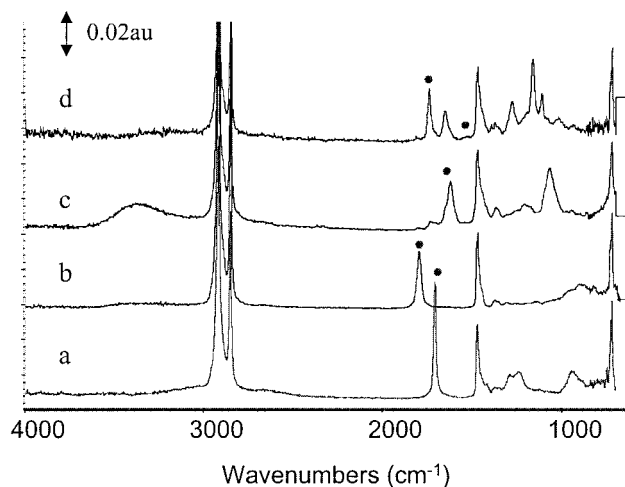


Figure 2 ATR-FTIR spectra of bifurcated initiator functionalization on EAA film: (a) plain EAA film; (b) EAA-Cl; (c) EAA-diNOH; (d) EAA-diNOH-Br.

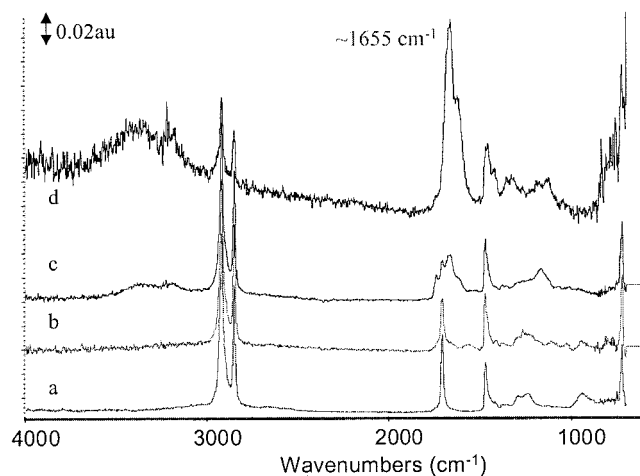


Figure 3 ATR-FTIR spectra: (a) plain EAA film; (b) plain EAA film immersed in polymerization solution for 7 days; (c) EAA-NOH-Br used in polymerization with sacrificial initiator, room temperature, 0.5 h; (d) EAA-NOH-Br used in polymerization without sacrificial initiator, room temperature, 0.5 h.

the system quickly turned pale blue because of the generation of Cu^{2+} species according to the mechanism of ATRP.

Figure 3 compares the graft results for different polymerization conditions. Growth of polyacrylamide from the EAA film surface is supported by the existence of the amide carbonyl band located at about 1655 cm^{-1} [Fig. 3(c), (d)]. Figure 3(a) is a spectrum of plain EAA film that did not undergo chemical treatment; Figure 3(b) is a spectrum of a plain EAA film (without initiator) that was put into a polymerization system with catalyst and monomer for 7 days. Those spectra show no major differences, demonstrating that no surface polymerization occurs without the initiator. Figure 3(c) and (d) are spectra obtained after surface-confined ATRP from initiator-immobilized film. The experiment associated with Figure 3(c) used sacrificial initiator. The role of sacrificial initiator is twofold: (1) it controls the radical polymerization by generating deactivator Cu^{2+} species¹⁸ and (2) it allows one to control polymer molecular weight (and thus surface graft thickness). The use of sacrificial initiator promoted solution-phase polymerization of polyacrylamide, thereby reducing the extent of polymerization on the surface, relative to the system that used only surface-confined initiator; this result explains the pronounced amide peak in Figure 3(d) relative to that for Figure 3(c).

XPS measurements were done on initiator-functionalized surfaces and polymer-grafted surfaces. Table I presents the C, O, N, and Br atomic compositions for EAA films functionalized with linear and bifurcated initiator groups, as well as polyacrylamide-grafted EAA films using a linear initiator group and 30-min

polymerization time. Of note, the initial C : O atomic ratio is 26.0 for plain EAA, consistent with the expected value of 20.1 for an EAA film with 9.5 mol % AA content. After initiator grafting, this ratio decreases slightly, which is consistent with the fact that the initiator C : O atomic ratio is lower than that for plain EAA. Also, the Br : N and O : N atomic ratios are roughly twice as high for the bifurcated initiator structure than for the linear initiator, as expected from their structures. For the polymer-grafted film, the measured C : N and C : O atomic ratios are 4.7 and 3.6, respectively; neat polyacrylamide has C : N and C : O atomic ratios of 3. This last result indicates that polyacrylamide graft layer has a thickness slightly less than the X-ray penetration depth, which is approximately 10 nm.

Graft impact on EAA films

Experiments were performed in aqueous solutions of acrylamide at room temperature and without sacrificial initiator. ATR-FTIR results in Figure 4 show that polyacrylamide was grafted from all of the EAA samples, as evidenced by an amide carbonyl peak at about 1655 cm^{-1} . Effective grafting of polyacrylamide was seen in the first sample taken at 30 min, and additional polymerization time had little effect on peak intensity for the bifurcated initiator structure. In Figure 4(A) for the linear initiator, the carbonyl peak area at 1655 cm^{-1} tends toward lower values at longer polymerization times, which is unexpected given that a thicker polyacrylamide layer should result at longer times. This behavior may be attributable to the films turning more opaque at longer times, thereby affecting the intensity of the reflected IR light.

Figure 5 shows typical photographs of the EAA films. All of the grafted films maintained a smooth surface and kept their original sizes and shapes. However, long polymerization times tended to reduce film clarity [Fig. 5(d)], obviating the need for shorter polymerization times (e.g., 30 min).

Because the goal of this study was to produce EAA film with enhanced surface hydrophilicity, water contact angle measurements were performed on the

TABLE I
XPS Atomic Composition Data for Initiator-Functionalized and Polyacrylamide-Grafted EAA Films

Film descriptor	C1s %	N1s %	O1s %	Br3d %
Plain EAA	96.3	—	3.7	—
EAA-NOH-Br (linear initiator)	93.4	1.8	4.6	0.3
EAA-diNOH-Br (bifurcated initiator)	88.3	1.6	9.5	0.6
EAA-NOH-PAAm (with polymer)	65.9	14.1	18.3	0.2

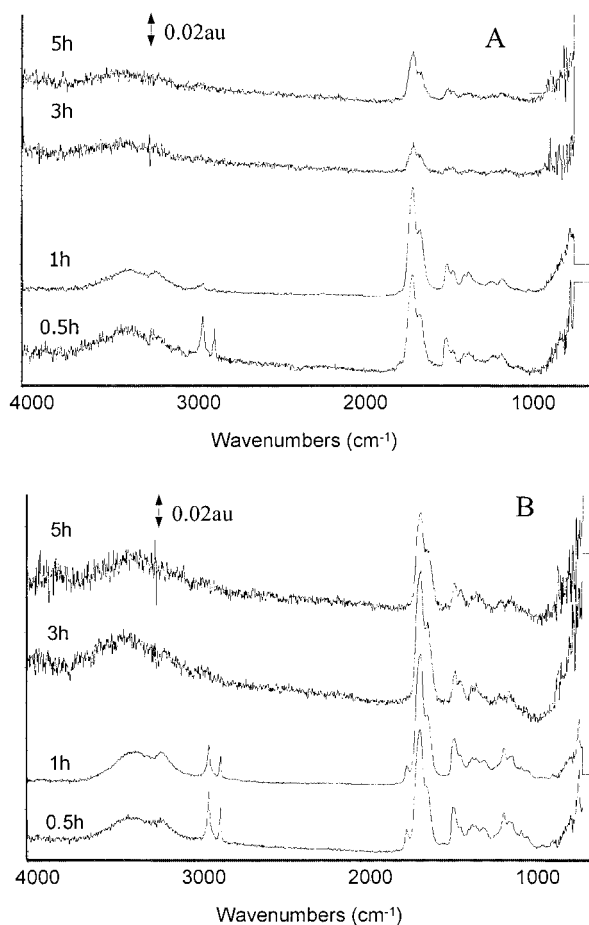


Figure 4 Time-dependent study of surface-confined ATRP of polyacrylamide on EAA films followed by ATR-FTIR spectroscopy: (A) Linear structure (EAA-NOH-Br); (B) Bi-furcated structure (EAA-diNOH-Br).

treated films. Figure 6 shows the differences of water contact angle on EAA films after each step used to functionalize the film with initiator. Before function-

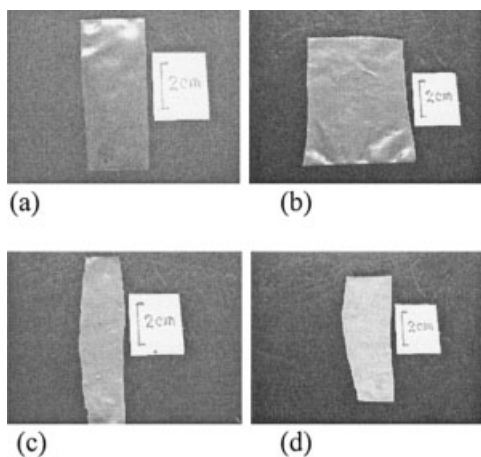


Figure 5 Typical images of surface-modified EAA films: (a) EAA-NOH-Br; (b) EAA-diNOH-Br; (c) EAA-diNOH-PAAm, polymerization for 1 h; (d) EAA-diNOH-PAAm, polymerization for 5 h.

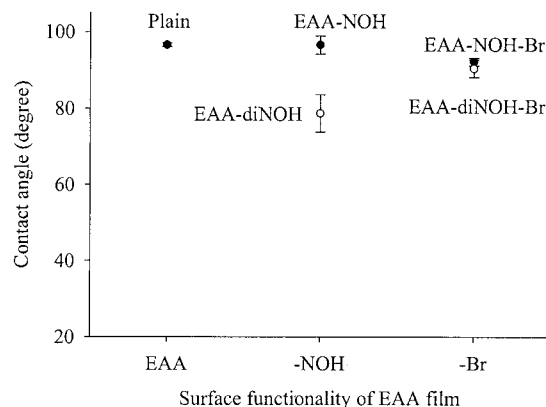


Figure 6 Static water contact angle on EAA films. -NOH represents the film after functionalization with an ethanolamine. -Br represents the film after functionalization with initiator.

alization, EAA had a hydrophobic surface with contact angle about 97° ($\cos \theta = -0.12$). This result is consistent with the fact that the starting film had only 9.5 mol % acrylic acid. Conversion of COOH groups to OH groups using ethanolamine (EAA-NOH) had a minor effect on contact angle ($\cos \theta = -0.21$). This result seems reasonable given that there is 1 : 1 conversion of COOH : OH by reaction with ethanolamine. When diethanolamine was used (EAA-diNOH), the number of hydrophilic functional groups (OH) increased relative to the starting COOH concentration. The result was a measurable decrease in water contact angle to about 79° ($\cos \theta = 0.19$), indicative of the increase in hydrophilicity of the surface. After initiator functionalization using 2-bromoisobutryl bromide, the surfaces were relatively hydrophobic.

Figure 7 shows static water contact angle data as a

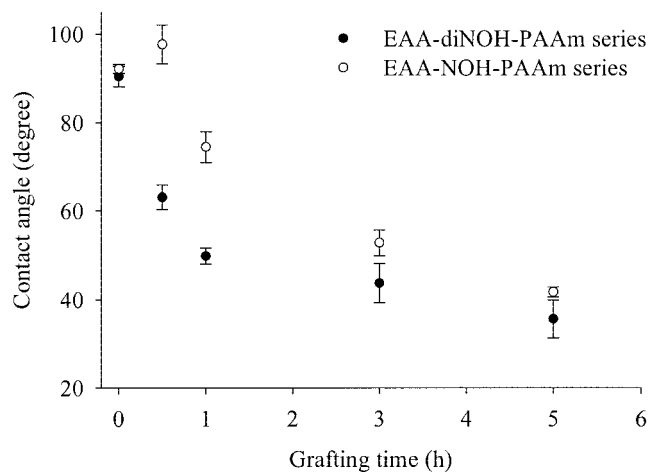


Figure 7 Static water contact angle as a function of grafting time for two initiator densities. Solid circles represent data for the bifurcated initiator structure; open circles represent data for the linear initiator structure.

function of polymerization time. Data were collected at various grafting times for EAA functionalized with both linear and bifurcated initiator structures. It is observed that the water contact angle decreased as grafting time increased, which has been reported extensively in the literature.^{3,19–21} For all times, EAA film functionalized with the bifurcated structure had a lower water contact angle than that of film functionalized with the linear structure. For the former, a rapid decrease of water contact angle was observed within 1 h. For the latter, 3 h of polymerization time was needed to achieve the same decrease in contact angle. To ensure that decreases in contact angle were a result of graft polymerization and not simply the result of contact with solvent water, EAA–NOH–Br and EAA–diNOH–Br films were treated in pure water for 5 h as a control. After water treatment, the contact angles were measured to be 81.5 ± 1.3 and $76.0 \pm 0.9^\circ$, respectively.

Neat polyacrylamide exhibits a water contact angle of about 25° ,²⁰ significantly lower than the $35\text{--}40^\circ$ observed after 5 h of grafting time. This disparity may be due to a combination of factors, including chain orientation, layer thickness, and surface coverage. The coverage is influenced by the density of initiator immobilized on the surface. An extreme case would be polymer chains grown from the terminal groups (initiator) on a well-organized self-assembled monolayer (SAM). Even in that case, the layer grafted to a SAM may give a contact angle different from that on a melted-and-resolidified plaque of polyacrylamide because of the difference in chain orientation in these two cases. In our experiments, the EAA film had an acid content of 9.5% and so extremely dense initiator packing was not expected. However, we purposefully increased the initiator density by using the bifurcated structure to increase the polymer grafting density, which led to lower water contact angle relative to layers grafted to the linear initiator structure (Fig. 7) at short polymerization times. It may be possible that the water contact angle would asymptote to the neat-polyacrylamide value of 25° at grafting times greater than 5 h and this possibility will be investigated further. It is noteworthy that the data in Figure 7 for the linear and bifurcated structures tend to converge at longer polymerization times, which one would expect as the polymer chain length increased to give similar random-coiled configurations, suggesting that surface coverage of polyacrylamide is greater for the bifurcated structure at shorter times.

CONCLUSIONS

ATRP was effective for surface-confined polymerization of polyacrylamide from EAA film. The graft polymerization occurred rapidly in aqueous solution at room temperature. Thirty minutes of polymerization was sufficient to obtain polyacrylamide-grafted EAA films. These films maintained their original size, shape, and transparency with short polymerization times. Linear and bifurcated initiator structures were prepared and characterized by ATR-FTIR spectroscopy. The bifurcated structure resulted in a 64% higher initiator density than did the linear structure. After 5 h of grafting, films with this high initiator density had water contact angles of 36° .

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