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Novel Surface Graft Copolymerization Method with Micron-Order Regional Precision

Takashi Sugawara and Takehisa Matsuda*

Department of Bioengineering, National Cardiovascular Center Research Institute, 5-7-1 Fujishirodai, Suita, Osaka 565, Japan

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ABSTRACT: This paper presents a novel graft copolymerization method which allows for surface modification with micron-order regional precision. The essential feature of the method is based on surface photoprocessing leading to immobilization of radical initiators. This method consists of the following steps: (1) derivatization of amino groups onto a polymer surface *via* photochemical fixation of poly(allylamine) partially derivatized with photoreactive phenylazido groups, (2) chemical fixation of carboxylated radical copolymerization initiators *via* condensation reaction with poly(allylamine), and (3) surface radical graft copolymerization under reduced pressure. Two examples were demonstrated to verify the effectiveness of this method. One was surface graft copolymerization of styrene on poly(vinyl alcohol) (PVA) film, and the other was surface graft copolymerization of acrylamide on poly(ethylene terephthalate) (PET) film. Electron spectroscopy for chemical analysis (ESCA) and water contact angle measurement before and after sequential surface reactions provided evidence that graft copolymerization proceeded successfully. The microprocessing of a substrate surface using a photomask with micron-level spaces was demonstrated. Microscopic observations of modified surfaces using an atomic force microscope (AFM) showed that surfaces were grafted on only UV-irradiated regions, resulting in the formation of a micropatterned graft polymer, which was clearly visualized by staining of hydrolyzed acrylamide units with a dye. The scope of potential applications is discussed.

Introduction

The surface design of polymers has become increasingly important in various industrial fields such as printing, coating, fiber, membrane, and biomedical technologies, where surface properties play a decisive role in their function. Currently available surface modification methods are as follows: surface chemical reactions in solutions,[1,2] physical deposition or coating,[3] and surface graft polymerization.[4–12]

Of these methods, the surface graft copolymerization method has been extensively studied in conjunction with biomedical applications[7,8] where the surface structure and properties at the outermost layer determine the biological responses. For example, polyacrylamide-grafted surfaces have been proven to impart highly antithrombogenic potential, especially in acute-phase implantation, which is attributed to a highly swollen diffuse layer composed of nonionic graft chains.[7] These surface grafts are usually attained by the formation of radical-generating highly reactive species such as peroxide groups *via* γ-ray irradiation[7] or plasma or glow discharge[9] treatment and subsequent graft copolymerization.

However, the following drawbacks of surface graft copolymerization *via* the above-mentioned methods have been claimed: (1) surface modification of only a given portion of device surfaces is difficult and (2) the facility of free radical generation *via* corona or glow discharge treatment depends upon the kind of materials used. Although these methods have been used industrially for surface modifications of films, their application to surface modification of complex-shaped fabricated devices has not been successful.

This paper presents a novel surface graft copolymerization method which permits surface modification at a given region of devices with micron-order precision as follows. First, an aminated polymer partially derivatized with a photoreactive phenylazido group in its side chains is coated on a polymer surface. Then ultraviolet (UV) light is irradiated on the coated surface for chemical fixation of the aminated polymer *via* the conversion of the phenylazido group to the highly reactive phenylnitrene. Carboxylated radical initiators are then condensed with the primary amino groups of the photochemically fixed aminated polymers. Finally, radical polymerization initiated by surface-fixed initiators results in surface grafting. Since the radical polymerization initiators are covalently bonded only on UV-irradiated portions, the surface graft copolymerization method developed here can provide micron-order precision.

Experimental Section

Materials. Solvents and reagents, all of which are special reagent grade, were obtaiend from Wako Pure Chemicals Inc. (Osaka, Japan) and used without further purification. Bis[4-(dimethylamino)phenyl]phenylmethylium hydroxide (malachite green carbinol base) was obtained from Aldrich Chemical Co. Inc. (Milwaukee, WI). Poly(allylamine hydrochloride) was purchased from Nitto Boseki Co., Ltd. (Tokyo, Japan). Poly(vinyl alcohol) (PVA) film was donated by Nitigo Film Ltd. (Osaka, Japan). Polystyrene film was obtained from Asahi Chemical Industry Co., Ltd. (Tokyo, Japan). Poly(ethylene terephthalate) (PET) film was obtained from Bellco Glass Inc. (Vineland, NJ). Seamless cellulose tube for dialysis (cutoff MW: approximately 12 000) was purchased from Viskase Sales Corp. (Chicago, IL). A photomask with a striped pattern arrayed with slits whose widths were 0.50 and 0.35 mm was donated by Hirai Co. Ltd. (Osaka, Japan).

Preparation of Photoreactive Poly(allylamine) (Az-PhPAL). Poly(allylamine hydrohcloride) (2.32 g, 25 mmol equiv for each monomer unit), 4-azidobenzoic acid (0.82 g, 5.0 mmol), and $KHCO_3$ (0.50 g, 5.0 mmol) were dissolved in deionized water (150 mL) under cooling in an ice bath. A solution of 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (WSC; 1.20 g, 5.5 mmol) in dimethylformamide (DMF; 50 mL) was added to the mixture under stirring and cooling in an ice bath. The reaction mixture was allowed to stand overnight under continuous stirring. After the reaction mixture was concentrated under reduced pressure, an exten-

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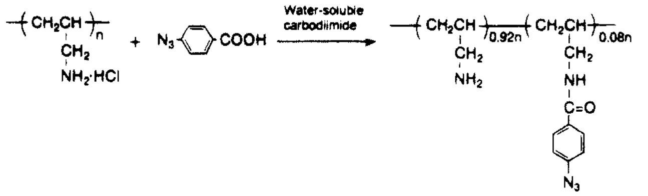

Figure 1. Synthetic route of a photoreactive aminated copolymer, AzPhPAL, and its chemical structure.

sive dialysis using a seamless cellulose tube was conducted in deionized water for 3 days. The dialyzed polymer was freeze-dried *in vacuo* to obtain a white solid (yield 0.78 g, 26%). The degree of substitution (8%), of the phenylazido group was determined by ^{1}H-NMR spectroscopy from the peak intensities of the phenylazido protons around 7 ppm and those of the methylene protons of the AzPhPAL main chain at 1.3 ppm. The synthetic route used to prepare AzPhPAL and its chemical structure are shown in Figure 1.

Surface Graft Copolymerization. A water/methanol (2/3 v/v) mixed solution containing AzPhPAL (0.5 wt %) was cast on PVA film (20 × 20 mm, thickness 25 μm) and air-dried. The film was UV-irradiated for 40 s using a Toshiba UV lamp (H-400P; 400 W) at the distance of 30 cm (intensity 2.22 mW/cm^2). The irradiated film was immersed in a DMF (50 mL) solution of 4,4′-azobis(4-cyanovaleric acid) (0.20 g, 0.72 mmol) and WSC (0.15 g, 0.78 mmol) under stirring at 0 °C for 3 h. The film was thoroughly washed with acetone. The film was immersed in benzene solution containing styrene (50% v/v) in a tube. After four freeze–thaw cycles under reduced pressure, the tube was sealed under reduced pressure. Graft copolymerization of styrene was carried out at 60 °C for 4 h. The films were washed with benzene to remove unreacted monomers and homopolymers of styrene. The graft copolymerization of acrylamide (5.0 wt % aqueous solution) on PET film (18 × 18 mm, thickness 50 μm) was carried out in the same manner.

Microprocessing. Surface microprocessing was carried out using a photomask. As previously mentioned, AzPhPAL was photochemically fixed by UV irradiation of a photomask with a striped pattern arrayed with slits whose widths were 0.50 and 0.35 mm. After derivatization of the carboxylated initiator, graft copolymerization of acrylamide was performed according to the method described above. The amide groups on the side chains of the graft copolymer were hydrolyzed in a dilute NaOH aqueous solution (12 mM) for 5 min. Hydrolyzed groups of the graft copolymer were stained by a dilute hydrochloride solution of malachite green carbinol base (1.0 wt %) for visualization under a light microscope.

Physical Measurements. ^{1}H-NMR spectra were measured on a JEOL GX-270 (Tokyo, Japan) [in $(CD_3)_2SO$ at 30 °C; ppm from $(CH_3)_4Si$]. Electron spectroscopy for chemical analysis (ESCA) spectra were recorded on Shimadzu ESCA 750 (Kyoto, Japan). The C1s spectra were deconvoluted into subpeaks by computer-aided processing. Static advancing contact angles toward deionized water were measured by a Kyowa contact angle meter (Kyowa Kagaku Co., Ltd., Tokyo, Japan) at 25 °C by the sessile drop method. Atomic force microscope (AFM) images were obtained on a NanoScope II (Digital Instruments Co. Ltd., Santa Barbara, CA) using 200 μm cantilevers (narrow-leg type) with a calculated force constant of 0.06 N/m and operating at a voltage of −1.0 V and scanning rate of 1.34 Hz. All data manipulations and image processing were carried out with Digital Instruments software. Microscopic observation was carried out on an Olympus Vanox-S system (Tokyo, Japan).

Results

The sequential surface reactions involved in the photochemical fixation of photoreactive poly(allylamine), surface derivatization of azo-bis-type radical initiator, and subsequent surface radical polymerization were carried out on PVA and PET films. We measured ESCA spectra at each step. Static advancing contact angles toward water on polymer surfaces before and after surface graft copolymerization were measured.

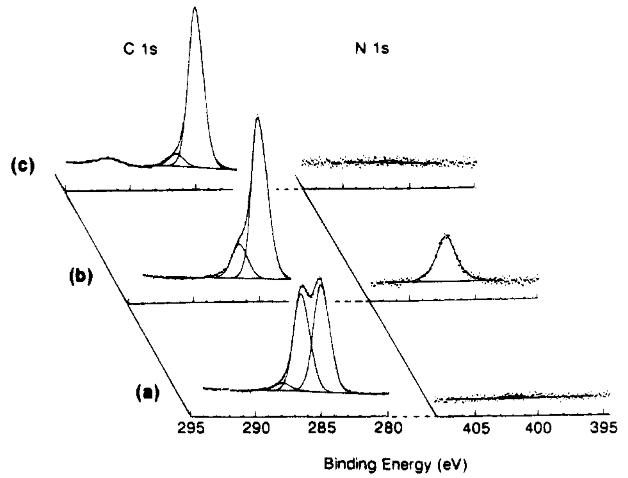

Figure 2. ESCA spectra of nontreated PVA film surface (a), AzPhPAL photochemically fixed surface (b), and styrene-grafted surface (c). Conditions: [styrene], 50% (v/v); solvent, benzene; temperature, 60 °C; polymerization time, 4 h.

Surface Graft Copolymerization. Photoreactive aminated polymer (AzPhPAL) was prepared from the partial condensation of poly(allylamine) with 4-azidobenzoic acid in the presence of water-soluble carbodiimide (WSC) in DMF. The degree of derivatization of the phenylazido group was found to be 8%, which was determined from ^{1}H-NMR spectroscopic measurement. A thin-layer coating of AzPhPAL on a polymer surface was obtained by casting of the water/methanol mixed solution of AzPhPAL. Subsequently, UV light was irradiated for a short period at an incident light power of 2.2 mW/cm^2. After extensive washing with water, the condensation reaction between the amino groups of surface-fixed poly(allylamine) and 4,4′-azobis(4-cyanovaleric acid) was performed. Then surface graft copolymerization in solutions was carried out under reduced pressure.

We demonstrated two examples of surface graft copolymerization. One was graft copolymerization of styrene on the PVA film and the other was that of acrylamide on the PET film. At first, the surface graft copolymerization of styrene in benzene solution was conducted on treated PVA film. Figure 2 shows the ESCA spectra of a nontreated PVA film surface, the AzPhPAL photochemically fixed surface, and the styrene-grafted surface. The nontreated PVA film (Figure 2a), which was subjected to extensive Soxhlet extraction with methanol, showed almost equal intensities of the peaks at 285.0 and 286.5 eV. These are ascribed to hydrocarbon-like C and C−O, respectively. In addition, only a very slight signal was observed in the N1s spectrum. These indicate that the surface region of nontreated PVA film is composed of PVA.

UV irradiation on the AzPhPAL-coated surface resulted in the ESCA spectral changes shown in Figure 2b. The N1s signal appeared and C1s subpeaks were markedly changed. Extensive washing with water did not cause any appreciable changes in the C1s or N1s spectra. These results indicate that AzPhPAL is chemically fixed on the PVA film. The ESCA spectra of the styrene-grafted surface (Figure 2c) differed significantly from the AzPhPAL-fixed surface in the following points. (1) The content of the lowest binding energy component in the C1s subpeaks, which is assigned to hydrocarbon-like C, was extremely high (92.8%). (2) A well-resolved

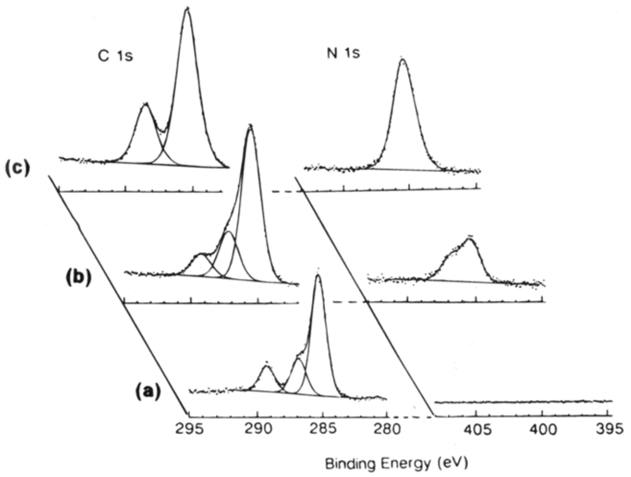

Figure 3. ESCA spectra of nontreated PET film surface (a), AzPhPAL photochemically fixed surface (b), and acrylamide-grafted surface (c). Conditions, [acrylamide], 5.0 wt %; solvent, water; temperature, 60 °C; polymerization time, 1.5 h.

high-energy satellite peak was observed at 292 eV, which is due to shake-up phenomena characteristic of unsaturated hydrocarbons. (3) Almost no N1s signal was observed. The spectrum resembles that of polystyrene.

The water wettability measurement showed that the surface nature was drastically changed from hydrophilic to hydrophobic upon surface graft copolymerization; that is, the advancing water contact angles were 31.2 ± 0.4° for nontreated PVA film and 89.6 ± 1.5° for the styrene-grafted surface. The latter value is very close to that of commercially available polystyrene film surface (91.4 ± 1.4°). Taken together with ESCA spectral results, it can be said that the graft copolymerization of styrene on PVA film was performed successfully.

Next we demonstrated the surface copolymerization of acrylamide on PET film. Figure 3 exhibits the ESCA spectra of the nontreated PET film surface (Figure 3a), the AzPhPAL photochemically fixed surface (Figure 3b), and the acrylamide-grafted surface (Figure 3c). The C1s spectrum of nontreated PET film shows subpeaks at 285.0, 286.6, and 289.0 eV, which are ascribed to signals derived from hydrocarbon-like C, C−O, and C=O, respectively. The intensity ratio of these subpeaks was determined as 4.3:1.3:1.0, whereas the theoretical intensity ratio of PET is 3:1:1. Although a higher content of hydrocarbon-like C was observed for the PET surface, the observed O/C ratio (0.36) was close to the theoretical value (0.40), indicating that the PET surface is mainly composed of poly(ethylene terephthalate) with only a slight contamination by hydrocarbons. (Note that hydrocarbon-like contamination has often been observed for commercially available processed polymer films into which ingredients such as antioxidants and lubricants are usually incorporated.) Upon UV irradiation on an AzPhPAL-coated surface, the N1s signal appeared. Similarly to the previous photochemically treated surface, no appreciable spectral changes were observed even after extensive washing with water. After carboxylated radical initiators were coupled to the photochemically fixed surface, surface graft copolymerization of acrylamide was carried out in water. This was followed by extensive washing with water, after which the ESCA spectrum was recorded (Figure 3c).

Two subpeaks, which can be assigned to carbon atoms corresponding to carbonyl and hydrocarbon, were observed in the C1s spectrum. The intensity ratio between subpeaks at 285.0 and 288.1 eV was 2.6:1.0, which was close to the theoretical value (2:1) of polyacrylamide. Furthermore, the observed elemental ratio of C:O:N was found to be 3.5:1.1:1.0, which was in agreement with the theoretical ratio (3:1:1) of polyacrylamide.

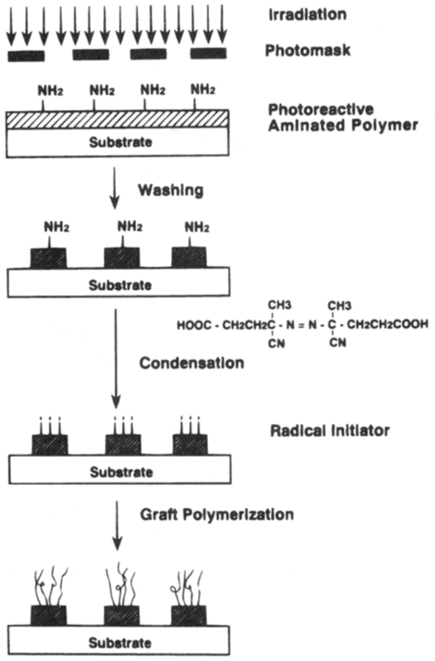

Figure 4. Microprocessing of material surfaces by the surface graft copolymerization method.

The static advancing contact angles of water were 70.5 ± 1.1° for the nontreated surface and 25.7 ± 0.5° for the grafted surface. These results indicated that the surface graft copolymerization of acrylamide proceeded on the PET surface.

Microprocessing. To examine whether surface graft copolymerization can provide micron-order precision, we attempted micropattern processing with the use of a photomask having a striped pattern with slits of widths 0.50 and 0.35 mm. The schematic of microprocessing is illustrated in Figure 4. Surface graft copolymerization was carried out in a manner similar to the grafting of acrylamide to PET film except that this time, a photomask was used. UV light was irradiated through the photomask, which was in contact with the PET film. After extensive washing with water, the grafted film was immersed in dilute NaOH aqueous solution (12 mM) to hydrolyze the amide groups to carboxyl groups. The immersion of the hydrolyzed film in a dilute HCl solution of malachite green carbinol base, which is a dye sensitive to negatively charged ions, resulted in the formation of a surface pattern where only the carboxylated graft region was stained (Figure 5). The observed widths of the stained lines were 0.50 and 0.35 mm under the light microscope, which are in good agreement with the widths of the slits of the photomask used. This visualization clearly showed that AzPhPAL was chemically fixed only on the UV-irradiated region and that graft copolymerization proceeded only on the irradiated portion.

The atomic force microscope (AFM) provides topographic images by scanning with a sharp tip over a surface. It has been used to produce atomic-resolution images of synthetic and biological polymers such as polyalanine and fibrin as well as images of a photoresist on silicon.[16,17] An attempt was made to obtain images

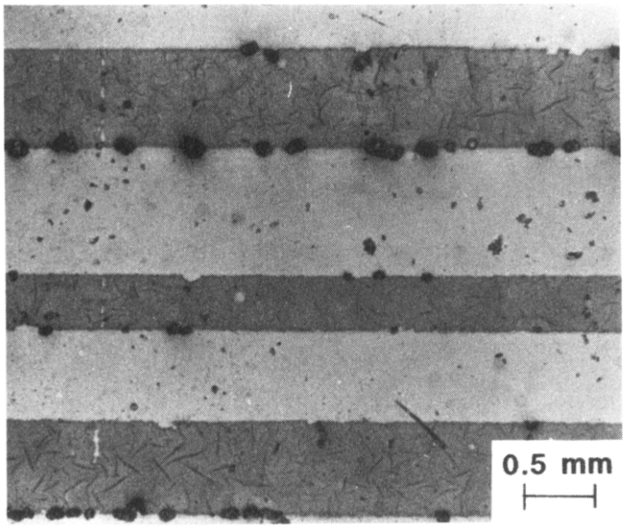

Figure 5. Micrograph of malachite green stained microprocessing surface. The amide groups on the side chains of the acrylamide graft polymer were hydrolyzed in dilute NaOH aqueous solution (12.5 mM) for 5 min at room temperature and stained by a dilute hydrochloride solution of malachite green carbinol base.

of the micropatterned acrylamide-grafted PET surface by AFM. The computer-constructed three-dimensional surface of grafted PET film was recorded under the height mode for operation and the line-scan mode for imaging, which allows easier visualization of the boundary region. Figure 6 shows AFM images of the nontreated PET film surface (Figure 6a,b), acrylamide graft surface (Figure 6c), and boundary area between nongrafted and grafted portions (Figure 6d) projected 30° for viewing. As can be seen in Figure 6a,b, the nontreated PET surface was a relatively flat surface, with the roughness estimated to be within 20–30 nm over the horizontal range of 2000 nm. On the other hand, the acrylamide graft surface showed a large undulation which is covered with dense graft polymer without any pinholes (Figure 6c), the roughness of which was around 200–300 nm. Observation of the boundary gives us some information on the dimensional precision of the surface graft copolymerization (Figure 6d). The border was almost a linear feature with a very sharp edge on the submicron order. The thickness of the acrylamide graft polymer layer, which includes the thickness of the photochemically fixed poly(allylamine) layer, was estimated to be 200–300 nm. A more detailed AFM study is now in progress.

Discussion

The increasing demand for providing surface functional properties such as adhesivity, wettability, printability, lubricatability, launderability, or biocompatibility has led to the development of numerous methods of polymer surface modifications with minimum deterioration of bulk properties. Surface modification of polymers to improve serviceability may involve exposure to γ-rays,[7] UV light,[4,5,11] or glow discharge.[9] Under suitable conditions, such excitation can generate free radical sites for the initiation of graft copolymerization. Generally, surface graft copolymerization requires surface pretreatment to produce reactive species capable of the generation of free radicals which can initiate radical or peroxide polymerization. Free radical generation and its polymerization-initiating capability largely depend upon the kind of materials used, as pointed out in the Introduction. Since the surface region modified by the glow discharge method is limited to the range of 10–20 Å to a submicron depth depending on the method and treatment conditions, surface graft copolymerization proceeds within this range of depth without significant alterations of bulk structure or properties. On the contrary, γ-ray irradiation produces radicals throughout the interior of samples, resulting in the formation of a graft layer at much deeper regions.

An alternative method for surface graft copolymerization is to introduce radical initiators on a surface *via* derivatization. In fact, it was reported that the surface hydroxyl group of PVA was derivatized with 4,4′-azobis(4-cyanovaleroyl chloride), which initiated radical graft copolymerization with various vinyl monomers.[12]

On the other hand, the surface modification method developed here involves chemical immobilization of radical initiators to an aminated polymer which is photochemically fixed on a material surface. It is known that photoreaction of the phenylazido group upon UV irradiation involves the loss of nitrogen and concomitant generation of highly reactive nitrene.[13–15] Nitrene in the triplet state is so reactive that it induces various

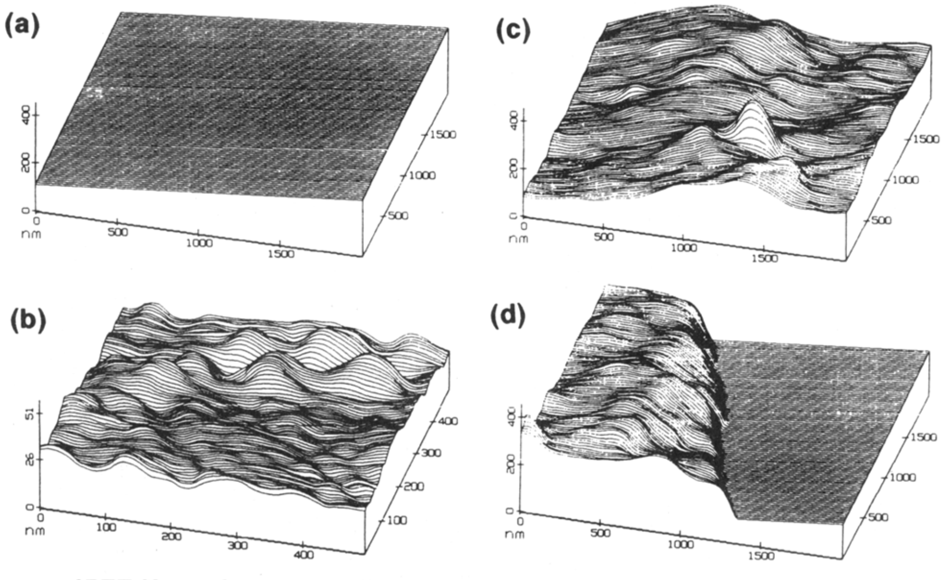

Figure 6. AFM images of PET film at the nonexposed region (a), its higher magnification image (b), acrylamide graft surface at the exposed region (c), and borderline of the exposed and nonexposed regions (d).

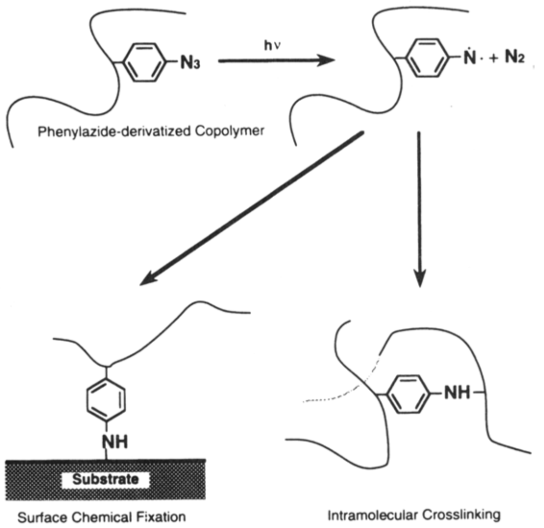

Figure 7. Schematics of molecular events of photochemical reaction upon UV irradiation (a highly reactive nitrene generated upon irradiation leads to the chemical fixation on substrate as well as intermolecular cross-linking *via* subtraction of hydrogen and formation of covalent bonding).

reactions including insertion, addition, and abstraction. The well-known photoreaction of azide to produce insoluble cross-linked polymers as negative resists has been utilized over the years for microlithography. If such reactions effectively take place at an interface between a thinly layered photoreactive coating and a polymer surface, then the coating is chemically fixed on the surface. In fact, we have successfully derivatized polymer surfaces with phenylazido-derivatized polymers upon coating and subsequent UV irradiation.[16-21] The general scheme of the photochemical fixation process is shown in Figure 7. The chemically modified surface layer is expected to be heavily cross-linked.

As can be clearly seen in Figures 2 and 3, poly(allylamine) partially derivatized with the phenylazido group was chemically fixed on both PVA and PET surfaces. The chemical fixation process is shown in Figure 7. Subsequent coupling reaction of carboxylated azo bis radical initiator resulted in the formation of a layer with a high density of radical initiating sites which are essentially localized on the surface. Following a typical radical copolymerization procedure, surface grafting of styrene and acrylamide was successfully achieved on PVA and PET surfaces, respectively. These were evidenced in ESCA spectral measurements and wettability studies. Therefore, if a vinyl monomer which can be polymerized by an azo bis initiator is employed, the surface graft copolymerization *via* the present method can proceed. Since phenylnitrene can react with most organic materials, photochemical fixation of photoreactive poly(allylamine) will proceed on various polymers, the surfaces of which can be wetted by its cast solution. Our experiences with photochemical fixation of phenylazido-derivatized polymers showed that, except for very hydrophobic polymers such as poly(tetrafluoroethylene), photochemical fixation of various photoreactive synthetic polymers partially derivatized with the phenylazido group was attained on polymers which include poly(dimethylsiloxane), polyethylene, and polystyrene.[16-21] Therefore, at the outermost layer of a surface, the present surface graft copolymerization method can be considered to be the least surface-destructive method among the currently available ones.

The most striking feature of this surface graft copolymerization method is its regional precision. As visually demonstrated in Figure 5, the dimensions of the surface grafted pattern were in agreement with those of the photomask used. The AFM images shown in Figure 6 provide additional proof of the dimensional precision. Although the dimensional precision observed in this study was on the submicron order, it is within the limitations required for precision microlithography using deep UV.

In summary, the surface graft copolymerization method *via* photochemical fixation of aminated polymer on a polymer surface and subsequent coupling of radical initiator provides the following advantages over conventional ones: (1) much less limitation in the choice of polymer surfaces to be modified and monomers to be polymerized, (2) less surface destruction, (3) higher dimensional precision, and (4) uniform grafting of a given region of complex-shaped devices. Since UV energy can be transmitted by a quartz optical fiber, surface graft copolymerization of a complex-shaped device is feasible. In fact, our ongoing study of blood compatibility of artificial heart surfaces showed that graft copolymerization of acrylamide at the interior chambers of the heart is uniformly achieved, resulting in a marked improvement of antithrombogenicity of the implanted device.

Furthermore, it must be stressed that since this method allows for surface graft copolymerization with micron-order regional precision, surface microprocessing of micromachines or biosensors is feasible in principle. Thus, the surface graft copolymerization developed here has a wide scope of potential applications.

Conclusions

We explored a novel surface graft copolymerization method *via* the following steps: photochemical fixation of an aminated polymer on a substrate, coupling reaction of radical initiators, and subsequent graft copolymerization of a vinyl monomer. This work has, for the first time, verified that surface microprocessed grafting can be achieved with micron-order precision. The entire process is simple and inexpensive. With its advantages over conventional surface graft copolymerization methods, it can be said that the method is substantially valuable, especially since surface modification is required for fabricating devices or micromachines.

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