Macromolecules **2005,** *38,* 6592−6597

Surface Grafting on Polymer Surface Using Physisorbed Free Radical Initiators

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Received October 10, 2004; Revised Manuscript Received March 16, 2005

ABSTRACT: A new strategy for creation of radicals on an inert polymer surface has been developed. This new method combines free radical polymerization with a surface graft polymerization. The polymer film, poly(dimethylsiloxane) (PDMS), was selected as an inert model material and was immersed into acetone containing azo-bis-isobutyrylnitrile (AIBN). We speculate that the AIBN becomes physically adsorbed or partially penetrates the hydrophobic polymer surface. The polymerization of water-soluble monomers was initiated by the absorbed initiator and polymer surface became modified by the hydrophilic monomers. We speculate this process was facilitated by the poor diffusion of physisorbed radicals derived from AIBN into an aqueous medium. ATR−IR, XPS, and contact angle measurements were used to characterize the surface modification. This method provides a potential modification method for the coating of many polymer surfaces possessing complicated geometrical shapes. The principle relies on the insolubility of the physisorbed initiator and the medium of the polymerization mixture.

Introduction

Polymer surface modification has been a significant issue over two decades in many fields.[1,2] The polymer surface is the phase boundary that resides between the bulk polymer and the outer environment. The performance of polymeric materials relies largely upon the properties of the boundaries in many applications.[3] As most polymer surfaces are hydrophobic, untreated nonpolar polymer surfaces often have adverse problems in adhesion, coating, painting, lamination, packaging, and colloidal stabilization.[4] The biomedical application of polymeric materials have also faced many of the same critical obstacles, such as undesirable protein adsorption and cell adhesion, because of the poor biocompatibility of a conventional polymer surface.[5] To solve these problems, considerable basic and applied research has been devoted to the surface modification of polymeric materials. Polymer surface modifications have been developed using different techniques that include both chemical and physical processes.[6,7] Among these techniques, surface grafting has several advantages that include easy and controllable introduction of grafted chains with high density accompanied by minor changes in the bulk properties. Furthermore, covalent attachment of graft chains onto a polymer surface avoids desorption and ensures long-term chemical stability of grafted chains.

Many different synthetic routes can be employed to introduce graft chains onto the system of interest. The grafting methods can be generally divided into two classifications known as grafting-from and grafting-to.[8] Grafting-from utilizes active species existing on the polymer surface to initiate the polymerization of monomers from the surface. In the case of grafting-to method, performed polymer chains carrying reactive groups at the end or the side chains are covalently coupled to the surface. Plasma treatment can introduce active species on the surface of polymer, followed by the polymerization of monomers.[9] The limitation of the grafting-to method is that plasma treatment is slow and expensive and has found only limited applications, even though the surface properties of polymer can be changed in a few minutes.[9] UV energy has been extensively applied for surface graft polymerization of polymers with the aid of a photoinitiator or photosensitizer. Various kinds of monomers were attached onto polymer surfaces such as poly(ethylene terephthalate), polyethylene, poly(dimethylsiloxane) (PDMS), polypropylene, polystyrene, and poly(methyl methacrylate) (PMMA).[10] Other methods have also been studied extensively, such as γ-ray and microwave exposure. But the primary limitation is that these laboratory processes are difficult to scale up in industry because the irradiation can damage the polymer structures over long time exposures and the UV light is harmful to human health.[11] Furthermore, all of the current grafting methods are incapable of easily modifying the interior walls of tubing or pipe because the radicals are primarily generated on the outer surface.

Azo and peroxide initiators are typical free radical initiators for solution polymerization. Monomers, such as methyl methacrylate (MMA), are easily initiated and propagate with a growing polymer in organic solution. In this paper, a versatile surface grafting method is described: (1) preadsorb a hydrophobic initiator (e.g., azo-bis-isobutyrylnitrile (AIBN)) onto the bulk polymer surface, (2) exploit the polarity disparity between the initiating hydrophobic radicals and an aqueous polymerization medium, and (3) perform surface grafting of hydrophilic monomers via the physisorbed free radical species. By using this technique, it is possible to easily modify complex object geometries, including the inner walls of a tube.

Experimental Section

Reagents. Sylgard 184 was purchased from Dow Corning (Midland, MI). Acrylic acid (AA), *N*,*N*-dimethyl acrylamide (DMA), 2-hydroxyethyl acrylate (HEA), and 2-hydroxyl methacrylate (HEMA) were passed through a column of activated basic alumina (Aldrich, 150 mesh). Acrylamide (AM), Rhodamine B, $K_2S_2O_8$ and AIBN were all obtained from Aldrich and used without further purification. All other reagents and materials were purchased from Fisher Scientific.

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10.1021/ma0479060 CCC: $30.25

Characterization Methods. FT-ATR spectra of the surface of modified and unmodified samples were obtained on a Nicolet model 730 FT-IR spectrometer using an attenuated total reflection apparatus (Harrick Scientific). Spectra were recorded at 4 cm^{-1} resolution. A single-beam reference spectrum of a freshly cleaned germanium crystal was recorded before the measurements and used as background spectrum. X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer instrument using Al α radiation at The MAT-NET Surface Analysis Center at Case Western Reserve University. Before measurement, the samples were vacuum dried for 24 h. During the measurement, the takeoff angle was 45°. Film thicknesses were determined using a Gaertner model L116C ellipsometer with a He−Ne laser ($\lambda = 632.8$ nm) and a fixed angle of incident of 70°. For thickness calculations, we used refractive index values of 1.45 for PDMS,[12] 1.50 for poly(acrylamide) (PAM),[13] 1.51 for poly(2-hydroxyethyl acrylate) (PHEA),[14] 1.53 for poly(acrylic acid) (PAA)[15] and 1.50 for poly(2-hydroxyethyl methacrylate) (PHEMA).[16] Contact angles were determined using a Rame Hart NRL-100 contact angle goniometer equipped with an environmental chamber and tilting base mounted on a vibrationless table (Newport Corp.). A 10 μL droplet of deionized water was placed on the surface of a film at room temperature, and after 30 s, the contact angle was measured. Each reported value is the average of five independent measurements. Scanning electronic microscopy (SEM) was performed with a JEOL JSM-5300 scanning microscope. The samples were coated with gold/platinum using a SPI sputter (model 12121, SPI Supplies Division of Structure Probe, Inc.). Molecular weight analysis was determined by size exclusion chromatography using a Waters 501 pump, Waters HR4 and HR2 Styragel columns, a Waters 410 differential refractometer, and a Viscotek 760A dual light scattering and viscosity detector.

Graft Polymerization of Polymer with Preadsorbed Initiator. A polymer film (2 cm × 4 cm × 0.2 cm) was immersed into an acetone solution of 5% AIBN (w/w) for 15 min. The polymer film was dried in a vacuum oven 24 °C for 24 h. A solution of monomers (10% total monomer concentration in water, w/w) and the AIBN-treated polymer were transferred into the sealed glass vessel and reacted at 80 °C for several h. The polymer samples were washed in distilled water at 80 °C under constant stirring for 48 h and then exhaustively extracted with a water/tetrahydrofuran mixture to remove physisorbed monomer and polymer. The PDMS films were vacuum dried for 48 h.

To determine the thickness of grafted layers, a 1% solution (w/w) of PDMS in toluene was coated onto silicon wafer using a spin-coater to yield a final thickness of approximately 50 nm. After the sample was dried, it was immersed into the AIBN/acetone solution for 5 min and then put into a monomer solution containing 10% (w/w) of monomer. After grafting, the sample was extracted in a Soxhlet extractor with water for 24 h. Thickness measurements were performed by ellipsometry. Graft yield (GY) was defined as: $GY = W_a - W_b/A$; where W_a and W_b represent the weight of the membrane before and after grafting and A is the area of the membrane.[10] To determine the penetration depth of the AIBN initiator, the PDMS film was immersed into 2% of Rhodamine B/5% of AIBN/acetone (w/w/w) solution for 15 min. A double-edged razor blade was then used to slice the PDMS film. Optical microscopy was used to study the penetration of the initiator and dye into the polymer matrix.

Results and Discussion

Surface Grafting onto Polymer Using Physisorbed Free Radical Initiators. To modify the surface of a hydrophobic polymer, such as PDMS, a variety of monomers were grafted by initiating a preadsorbed initiator. The penetration of the initiator was investigated by dissolution of a 2% solution of Rhodamine B dye in acetone to help identify the location of AIBN in the PDMS matrix. From the microscope image (Figure 1), we estimate that the dye remains localized at the surface of the PDMS, and the thickness of the penetrated edge (dye) is less than 1μm, indicating the penetration of the initiator into the polymer matrix is relatively limited. We studied the polymerization of hydrophilic monomers including AA, AM, HEA, HEMA, and DMA on the basis of their polarity and biocompatibility. We speculate that the preadsorbed initiator at the PDMS surface decomposed into radicals and the formed radicals transferred to the most local "neighbor", i.e., the methyl group of PDMS (Scheme 2). The diffusion of hydrophobic radicals was inhibited by the hydrophilic liquid environment relative to the hydrophobic surface to which they were originally adsorbed. Despite the lower reactivity of the AIBN-induced radicals relative to radicals generated from PDMS, we speculate that the hydrophobic/hydrophilic barrier trapped a sufficient number of radicals at the surface that ultimately reacted with PDMS to result in a grafted polymer. The polymer samples were exhaustively extracted by a mixture of THF and H_2O to remove the unreacted or noncovalently attached polymers. The transparent PDMS film became "cloudy" if the surface was extensively reacted with HEMA, DMA, or AA. In some cases, the flexible PDMS film became rigid after the modification. These results suggest that the polymer was "covalently" attached to the bulk PDMS surface. The number average molecular weight of free PHEA polymer (polymer generated simultaneously in solution) was approximately 625 000 g/mol and the $M_w/M_n = 2.05$. However, to account for the qualitative observation of changes in the PDMS stiffness, it is important to consider that the interior bulk properties of the PDMS may have also been affected by radical diffusion to the interior. At this stage of the investigation, we cannot discount surface reactions versus cross-linking of the interior of PDMS.

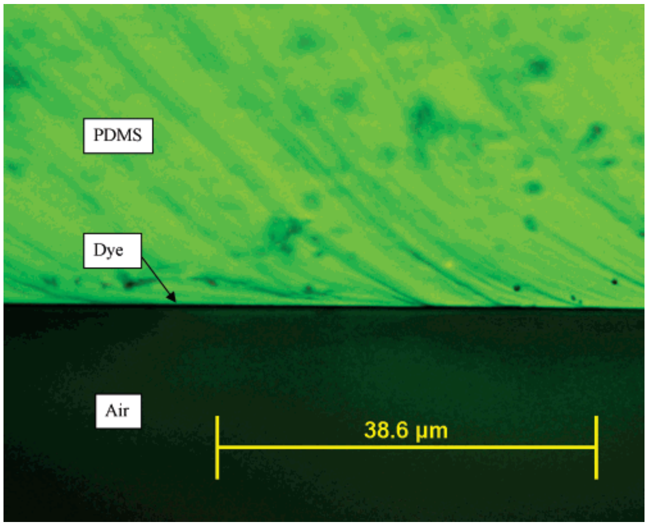


Figure 1. Optical microscopy image of cross-section of PDMS film. The edge between the PDMS matrix and the air is evidenced by the physically adsorbed dye.

Wettability of Modified Surfaces. Contact angle measurements are presented in Table 1. The advancing water contact angle of PDMS is 114°, and the receding angle is 98°. After modification by different monomers, both the advancing and receding angles were greatly decreased, which suggests that the hydrophilic polymer is attached on the polymer surface. For example, for the AA-coated surface, the advancing and receding angles

Table 1. Water Contact Angles for Modified PDMS Substrates (degrees)[a]

sample description [b]	θ_a	θ_r
PDMS	114	98
PDMS-*g*-PAA	74	62
PDMS-*g*-PAM	77	68
PDMS-*g*-DMA	90	79
PDMS-*g*-PHEMA	93	80
PDMS-*g*-PHEA	87	76

[a] Measurement of contact angles represents the average of 5 measurements; contact angles are within 2°. PDMS films were grafted with monomers (10%, w/w, relative to solvent) by reaction at 80 °C for 3 h. [b] PDMS = poly(dimethylsiloxane), PAA = poly(acrylic acid), PAM = poly(acrylamide), PDMA = poly(*N*,*N*-dimethylacrylamide), PHEMA = poly(2-hydroxyethyl methacrylate), PHEA = poly(2-hydroxyethyl acrylate).

Table 2. XPS Atomic Compositions of Surface Grafted PDMS[a]

sample description	C/O	C/N
PDMS-*g*-PAM[b]	1.85	10.61
PDMS-*g*-PAM[c]	1.57	59.50
PDMS-*g*-PAA[d]	1.56	[e]
PDMS-*g*-PHEA[f]	1.83	[e]
PDMS-*g*-PHEMA[g]	1.76	[e]

[a] XPS spectra are not shown but are available as Supporting Information. All reactions were performed at 80° for 3 h. [b] PDMS films were grafted using 10% acrylamide (w/w, relative to solvent). [c] PDMS films were grafted using 10% acrylamide (w/w, relative to solvent). [d] PDMS films were grafted using 10% acrylic acid (w/w, relative to solvent). [e] No nitrogen observed in the XPS spectrum. [f] PDMS films were grafted using 10% 2-hydroxyethyl acrylate (w/w, relative to solvent). [g] PDMS films were grafted using 10% 2-hydroxy methacrylate (w/w, relative to solvent).

are 74° and 61°, respectively. For the HEA-coated surface, the advancing and receding angles are 87° and 76°, respectively.

ATR−IR Spectroscopy. Surface characterization of the modified PDMS samples was carried out by ATR−IR. Figure 2 shows the spectra of several PDMA samples. It is known that there are no absorption peaks in the range of 1500−1800 cm^{-1} for PDMS. However, for the polymer-modified PDMS surfaces, strong absorbance peaks were observed at 1700 cm^{-1}, which correspond to the carbonyl groups of the attached monomer. For the HEA- and HEMA-modified surfaces, absorption bands were observed at 1730 cm^{-1} that are characteristic of the ester carbonyl group, which confirms the presence of the PHEA and PHEMA on the surface of modified PDMS samples. For the DMA- and AM-modified surface, peaks observed at 1650−1660 cm^{-1} correspond to the amide carbonyl group. For the AA-coated surface, an absorbance peak at 1715 cm^{-1} corresponds to the carboxyl absorption band.[17] These results are consistent with the supposition that the hydrophilic monomer was successfully grafted onto the polymer surface.

XPS Analysis. To further investigate surface grafting, XPS spectra were measured with different polymer-modified surfaces (Table 2). For the HEA-modified surface, the elements of O, C, Si were observed, indicating that the PDMS was not completely covered relative to the penetration depth of the XPS sample. For the AM-coated surface, the nitrogen peak appeared at a 400-eV binding energy, owing to the contribution from the NH structure of the grafted AM polymers. For the lightly coated AM with only 2% of AM, the content of N is 0.8%; however, for the 10% AM-coated polymer, the content of N is 4.9% (the XPS spectra of all the grafted surfaces are available as Supporting Information). Because we do not know the grafting density, it is difficult to compare these values for % N to PAM brushes in the literature. We are presently working on a better quantification of the grafting density. These results are consistent with covalent grafting to the PDMS surface. For the 10% AM-coated surface, the dry thickness of the grafted layer is 17 nm (by ellipsometry), and the grafting yield is around 26 μm/cm^2. The thickness and the grafting density are similar to the data of plasma-induced polymerization of AM as reported in the literature.[18]

Measurement of Conversion. Conversion of monomers during the polymerization is demonstrated in Figure 3. Monomer was polymerized rapidly within 1 h. As time increases, the reaction rate slows down. For the HEA-coated surface, the conversion is 15% in 1 h, while the conversion is 25% after 4 h of reaction. For the DMA-coated surface, the conversion is even lower.

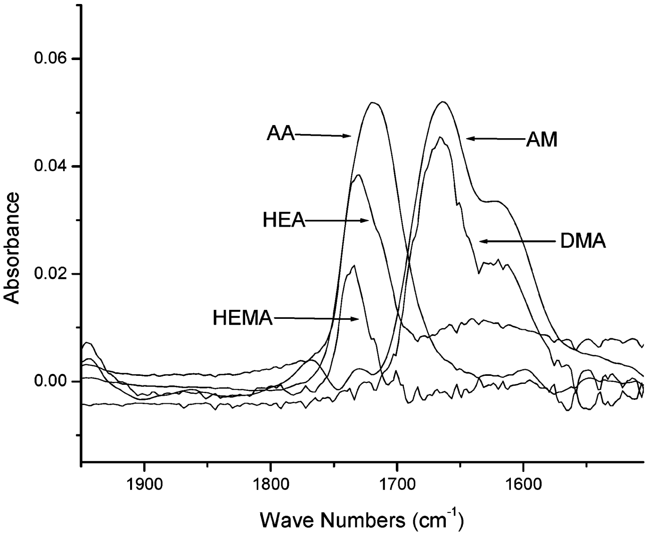


Figure 2. Measurement of the ATR−IR of grafted and unmodified PDMS. PDMS films were grafted with monomers (10%, w/w, relative to monomer) by reaction at 80 °C for 3 h; PAA = poly(acrylic acid), PAM = poly(acrylamide), PDMA = poly(*N*,*N*-dimethylacrylamide), PHEMA = poly(2-hydroxyethyl methacrylate), PHEA = poly(2-hydroxyethyl acrylate).

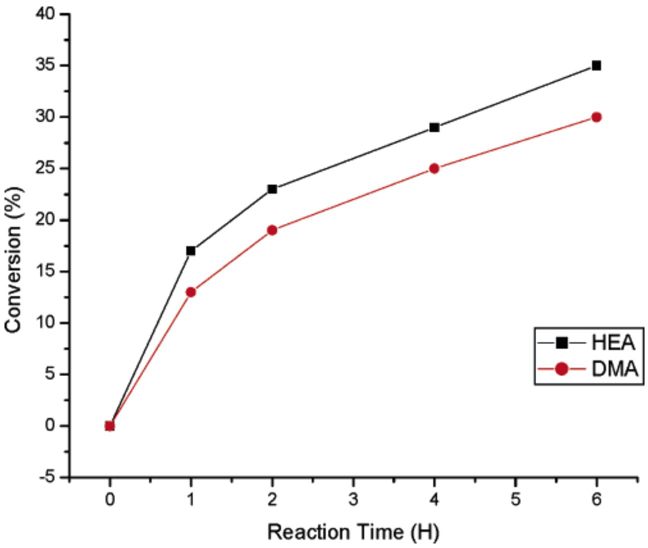


Figure 3. Effect of reaction time on the conversion of the monomers. The concentration of monomers was 10% (w/w, relative to solvent); HEA = 2-hydroxyethylacrylate, DMA = *N*,*N*-dimethylacrylamide.

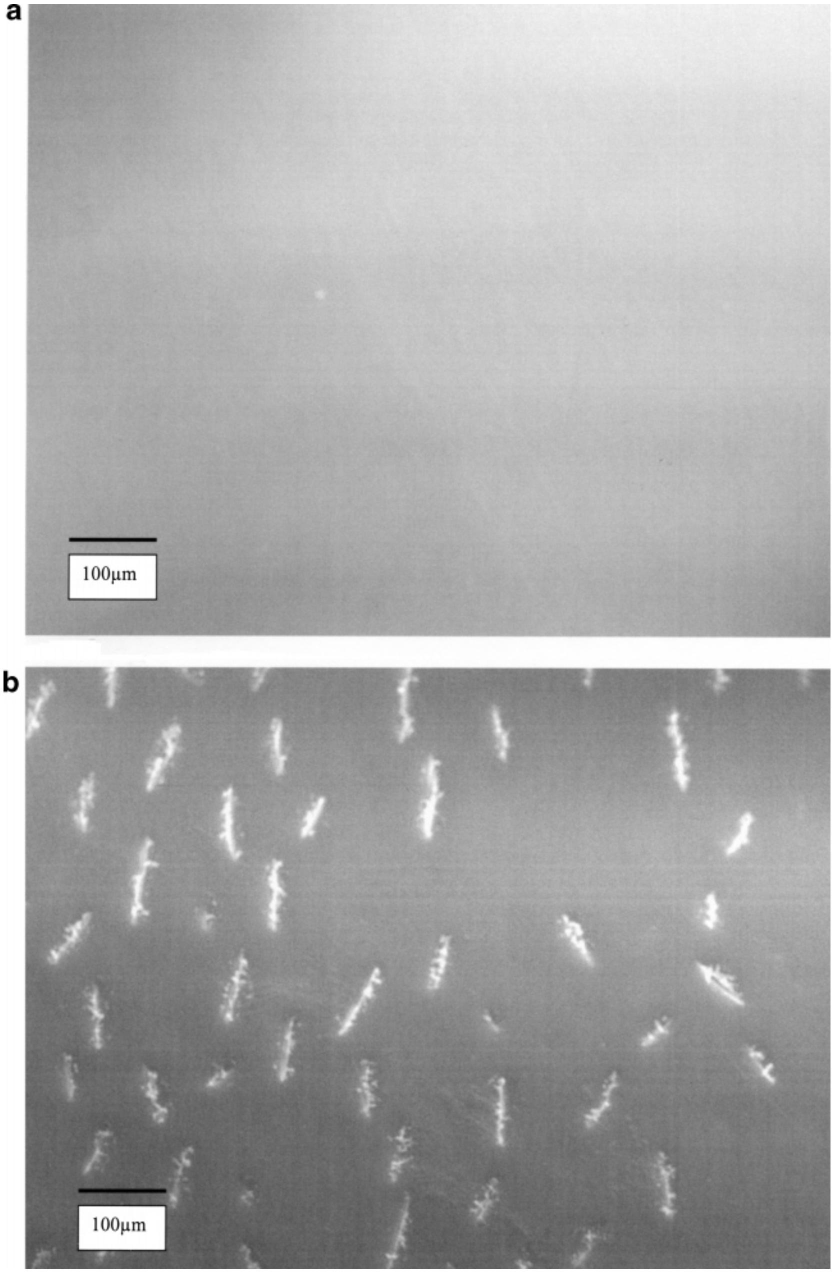


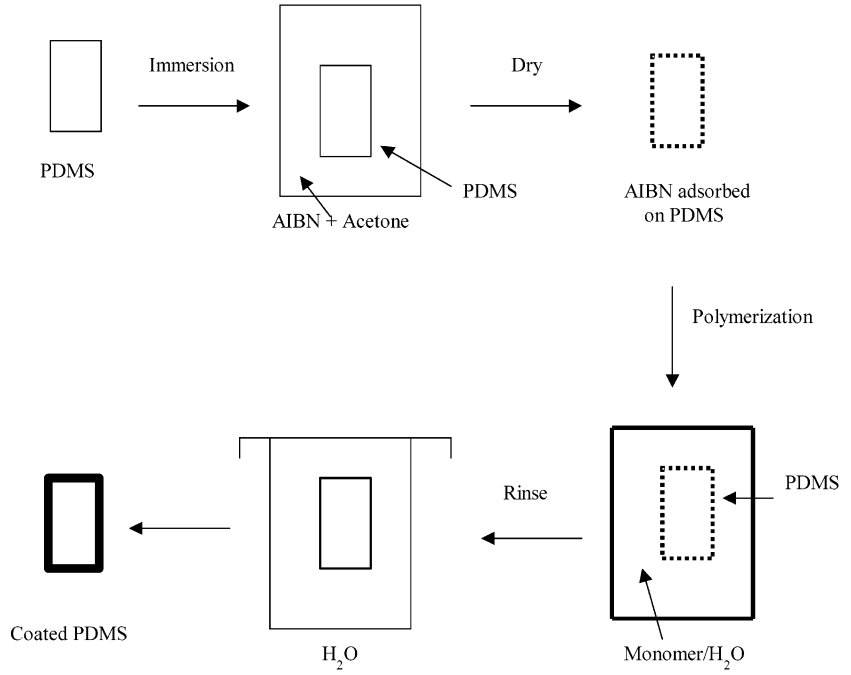
Figure 4. (a) SEM picture of uncoated PDMS surface. (b) SEM picture of polyacrylamide-coated surface. PDMS films were grafted with 10% acrylamide (w/w, relative to solvent) by reaction at 80 °C for 3 h.

Morphology Study of the Surface. Figures 4a and b illustrate the morphology change during the surface coating via SEM. We observed that the surface of uncoated PDMS is relatively smooth. However, for the AM-coated PDMS film, we observed that "islands" indicated a rougher surface where we speculate that the "islands" correspond to grafted polymers. The high glass transition temperature of PAM may produce polymer aggregates on the PDMS surface. The results are consistent with the visual observation of a "cloudy" surface.

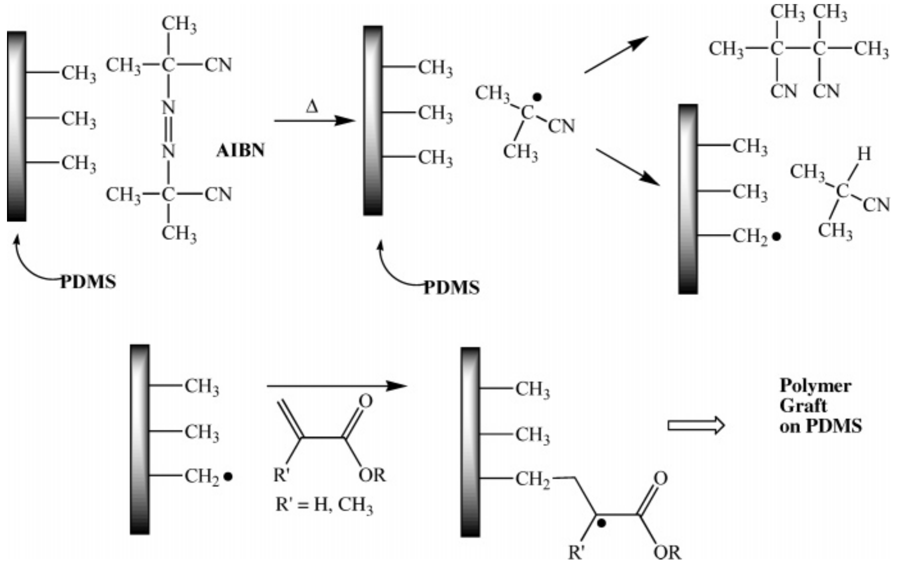
Mechanism of the Free Radical Graft Polymerization. AIBN is widely used as a free radical for solution polymerization because it can be readily dissolved in organic solvents and decomposed at moderate temperatures such as 65 °C.[19] In our study, AIBN was selected for surface graft polymerization because it is hydrophobic and, as such, will be readily adsorbed onto a PDMS surface. When the PDMS having the physically absorbed initiator was immersed into a hydrophilic acrylate monomer/H_2O solution, the AIBN remained partitioned to the polymer surface. As the reaction temperature was increased, the AIBN decomposed into an isobutyronitrile radical. There are three possible reactions for the isobutyronitrile radical: (1) bimolecular termination, (2) extraction of hydrogen from methyl groups on the PDMS surface, or (3) initiation of a free radical polymerization in the aqueous phase. Energetically, the extraction of the hydrogen from the methyl group of polymer is unfavorable. However at the interphase of solid and liquid solution, the reaction of the hydrophobic radicals and the methyl group of the PDMS are enhanced by the lack of diffusion of the AIBN-formed radicals into the aqueous environment.

From Schemes 1 and 2, we depict that the polymer attached to the PDMS surface arises from two possible contributions. One possible pathway is that the monomers are initiated by the radicals from the methyl

Scheme 1. Free Radical Surface Graft Polymerization onto a PDMS Surface



Scheme 2. Possible Mechanism of Surface Grafted Free Radical Polymerization



radical of PDMS. Another possible pathway is oligomer chain transfer to the polymer surface. To examine this point further, AIBN was blended with H_2O, and the cloudy solution was heated to 80 °C. As the temperature increased, the cloudy solution became slowly clear, presumably because of the decomposed isobutyronitrile radicals, which have a relatively higher solubility in water than that of AIBN. One piece of PDMS and 10% HEA (w/w) was added to the mixture solution. After 3 h, the reaction was stopped, and the PDMS film was washed exhaustively by deionized water. The ATR–IR indicated that the absorbance peak of the polymer is weaker than that of a polymer formed by a preabsorbed initiator. These results indicate that it is possible that some chain transfer occurs to PDMS during graft polymerization. However, we believe the major contribution of polymer grafting arises from radical abstraction from PDMS by an isobutyronitrile radical.

Conclusions

We have demonstrated an experimentally simple method to "covalently" attach hydrophilic monomers onto a hydrophobic polymer surface that involves the following steps: (1) physisorbed attachment of AIBN onto the polymer surface, and (2) graft polymerization of the monomers onto the polymer surface. Using this technology, various kinds of hydrophilic monomers can be covalently attached onto the polymer surfaces. Perhaps, most significantly, functional monomers can be easily grafted onto the inside wall of a tube or other interior surfaces. The surface polymerization can be performed without limitation of more complicated procedures such as high-energy reactors or intense light sources. Even though the surface-modified polymer was extracted by hot water for over one week, the grafting density and water contact angles did not change with time, consistent with a stable, covalently attached film.

Acknowledgment. The authors thank Wayne Jennings (MATNET, CWRU) for XPS assistance.

Supporting Information Available: XPS spectra of polyacrylamide-coated PDMS, PDMS films grafted with 10% acrylamide; XPS spectra of polyacrylamide-coated PDMS, PDMS films grafted with 2% acrylamide; XPS spectra of poly(acrylic acid)-coated PDMS; XPS spectra of poly(2-hydroxyethyl acrylate)-coated PDMS; XPS spectra of poly(2-hydroxyethyl methacrylate)-coated PDMS. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0479060