

Preparing Polymer Brushes on Poly(vinylidene fluoride) Films by Free Radical Polymerization

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ABSTRACT: Grafting of polymer brushes on the poly(vinylidene fluoride) (PVDF) films was carried out by the surface-initiated free radical polymerization. Surface-initiators were immobilized on the PVDF films by surface hydroxylation and esterification of the surface-tethered hydroxyl groups with 4,4'-azobis(4-cyanopentanoic acid) (ACP). Homopolymer brushes of methyl methacrylate (MMA) were prepared by free radical polymerization from the azofunctionalized PVDF surface. The chemical composition and topography of the graft-functionalized PVDF surfaces were characterized by X-ray photoelectron spectroscopy (XPS),

attenuated total reflectance (ATR) FTIR spectroscopy, and atomic force microscopy (AFM). Kinetics study revealed an exponential increase in the graft concentration of polymer brushes with the reaction time, indicating that the chain growth from the surface was consistent with a chain polymerization. Water contact angles on PVDF films were reduced by surface grafting of MMA. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 857–862, 2006

Key words: poly(vinylidene fluoride); free radical polymerization; surface science; polymer brush

INTRODUCTION

Surface-initiated polymerization or surface graft polymerization has been investigated as an effective and versatile approach for imparting new functionalities, such as improved hydrophilicity, biocompatibility, conductivity, and lubricative and adhesive properties, to the existing polymers.^{1–3} Surface modification of fluoropolymers, for example poly(vinylidene fluoride) (PVDF), has been of particular interest, because the fluoropolymers are one of the most important families of engineering polymers. They are well-known for their physical and chemical resistance.^{4–6} In addition to numerous and versatile industrial applications, new developments of PVDF have been found in biotechnology^{7–10} and in the biomedical sectors (vascular sutures, regeneration templates).^{11–13} But the biomedical equipments could be polluted easily because of the low surface energy and hydrophobicity of PVDF. To improve surface hydrophilicity of PVDF, a large amount of work had been devoted to the surface modification of fluoropolymers by chemical,¹⁴ plasma,^{15–17} irradiation,¹⁸ corona discharge,¹⁹ flame,²⁰ and ozone treatment.²¹

In the present work, surface modifications of the PVDF film with polymer brushes from surface-initi-

ated free radical polymerization are reported. Surface hydroxylation is first generated on the PVDF surface by chemical treatment. Immobilization of initiators is carried out by esterification of surface-tethered hydroxyl group and 4,4'-azobis(4-cyanopentanoic acid) (ACP). Poly(methyl methacrylate) (PMMA) brushes are prepared by surface-initiated free radical polymerization of methyl methacrylate (MMA) from the azofunctionalized surface. The chemical composition and hydrophilic property of the pristine and functionalized PVDF surfaces are determined by X-ray photoelectron spectroscopy (XPS) and contact angle measurement.

EXPERIMENTAL

Materials

PVDF films having a thickness of 0.5 mm were obtained from Goodfellow Cambridge Limited of Huntingon (England). The PVDF films were sliced into rectangular strips of about 1×2 cm² in size. To remove the organic residues on the surface, the PVDF film was washed with acetone, methanol, and doubly distilled water in the order. The films were dried under reduced pressure at room temperature for about 24 h and then stored in a clean and dry box.

Lithium hydroxide monohydrate (LiOH(H₂O, 56%), sodium borohydride (NaBH₄, 99%), and diisobutylaluminum hydride (DIBAL-H, 1.0M solution in toluene) were purchased from Acros Organics (Geel, Belgium) and used as received. Methyl methacrylate

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(MMA) was distilled under reduced pressure and stored in an argon atmosphere at -10°C .

Surface characterization

Attenuated total reflectance (ATR) FTIR spectra of the surface functionalized films were obtained from a Shimadzu IRPrestige-21 spectrophotometer using a ZnSe prism with an incident angle of 60° . Each spectrum was collected by cumulating 160 scans at a resolution of 4 cm^{-1} . A contact angle measurement JC2000A was used to measure static water contact angles of the polymer films at 25°C and 60% relative humidity, using a sessile drop method. For each angle reported, at least five sample readings from different surface locations were averaged. The angles reported were reliable to $\pm 2^{\circ}$.

The chemical composition of the pristine and the functionalized PVDF surfaces was determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed on a Kratos AXIS Ultra spectrometer using a monochromatic Al $K\alpha$ X-ray source (1486.71 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The samples were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level signals were obtained at a photoelectron takeoff angle (α , measured with respect to the sample surface) of 90° . The X-ray source was run at a reduced power of 225 W (15 kV and 15 mA). The pressure in the analysis chamber was maintained at 10^{-8} Torr or lower during each measurement. All binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.8 eV. Surface elemental stoichiometries were determined from the spectral area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to within $\pm 10\%$. The elemental sensitivity factors were calibrated using stable binary compounds of well-established stoichiometries.

The topography of the pristine and graft-polymerized PVDF surfaces was studied by atomic force microscopy (AFM), using an AJ-III AFM from the Shanghai AJ Nano-Science Development Co. In each case, an area of $5 \times 5\ \mu\text{m}^2$ was scanned using the tapping mode. The drive frequency was $330 \pm 50\text{ kHz}$ and the voltage was between 3 and 4.0 V. The drive amplitude was about 300 mV and the scan rate was 0.5–1.0 Hz. An arithmetic mean of the surface roughness (R_a) was calculated from the roughness profile determined by AFM.

The thickness of the polymer films grafted on the PVDF substrates was determined by ellipsometry. The measurements were carried out on a variable angle spectroscopic ellipsometer (M-2000, J. A. Woollam Inc., Lincoln, NE) at incident angles of 60° and 65° in the wavelength range 370–1000 nm. The refractive index of the dried films at all wavelengths was as-

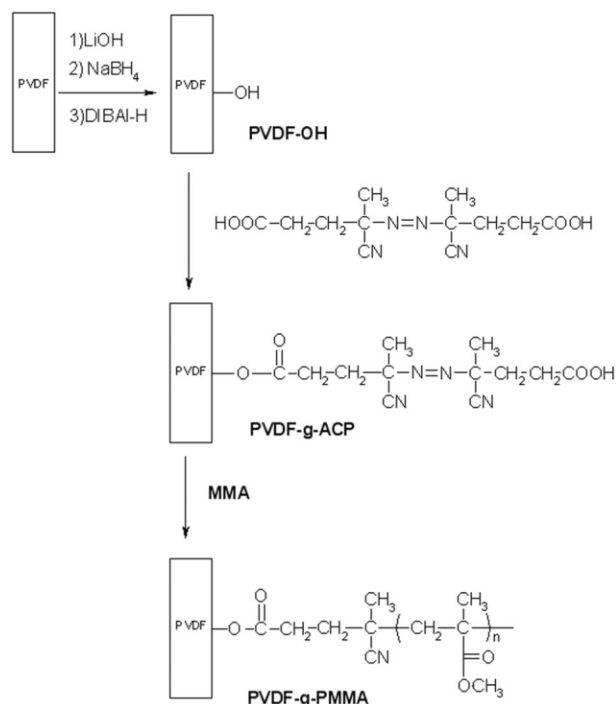


Figure 1 Schematic diagram illustrating the processes of hydroxylation of PVDF surface, formation of the azo-functionalized PVDF surface, and surface grafting polymer brushes from the azo-functionalized PVDF surface via free radical polymerization.

sumed to be 1.5. All measurements were conducted in the dry air at room temperature. For each sample, thickness measurements were made on at least three different surface locations. Each thickness reported was reliable to $\pm 1\text{ nm}$. Data were recorded and processed using the WVASE32 software package.

Surface hydroxylation of PVDF film

The surface hydroxylation of PVDF films was carried out by treatment of PVDF films with aqueous LiOH, followed by successive reductions with NaBH₄ and DIBAL-H, according to the literature (Fig. 1).²²

Immobilization of the azo initiator on the hydroxylated PVDF surface

To a mixture solution of 3 mL pyridine and 7 mL triethylamine was added the hydroxylated PVDF substrates, followed by addition of triphenylphosphor, ACP, and toluenesulfonic acid. The reaction mixture was gently stirred at 30°C for 24 h. The so-modified PVDF substrates (PVDF-g-ACP) were removed and washed with acetone and doubly distilled water. The substrates were then dried by pumping under reduced pressure for about 10 h.

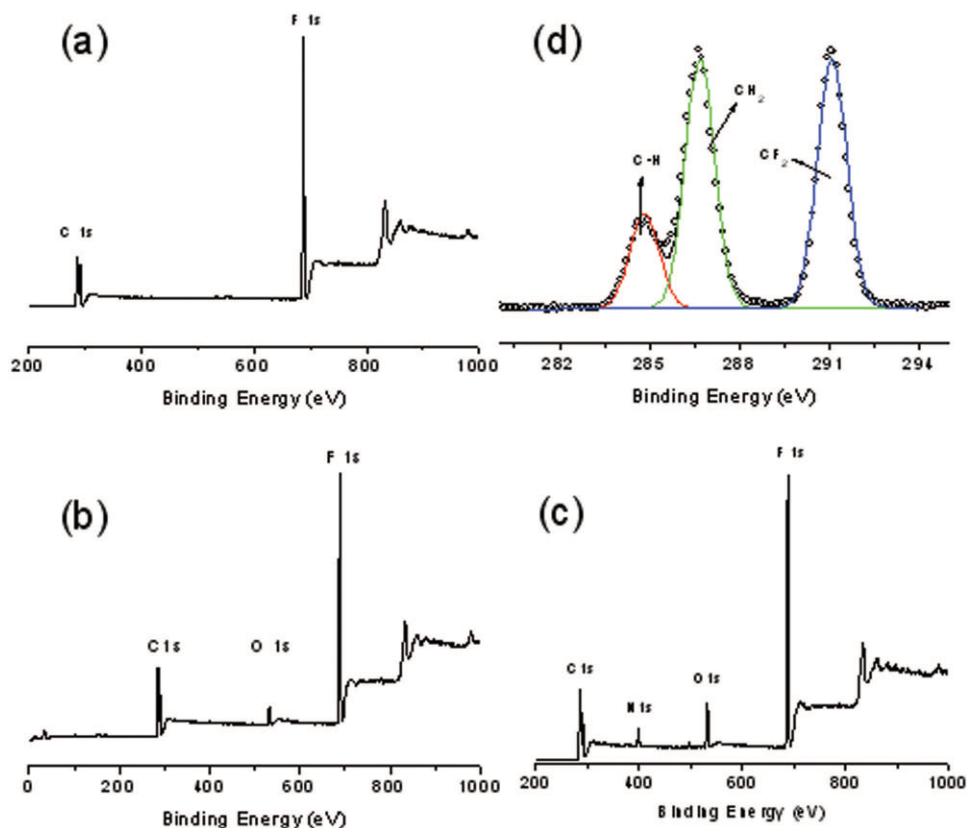


Figure 2 XPS wide-scan spectra of (a) the pristine PVDF surface, (b) the PVDF-OH surface, (c) the PVDF-g-ACP surface, and (d) C 1s core-level spectra of the pristine PVDF surface. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Surface-initiated free radical polymerization

For the preparation of poly(methyl methacrylate) (PMMA) brushes on the PVDF-g-ACP surface, MMA (2 mL, 18.6 mmol) was added to 8 mL toluene. While the solution was degassed with argon for 20 min, the PVDF-g-ACP substrate was added to the solution. The reaction flask was sealed and kept in an 80°C oil bath for a predetermined period of time. After the reaction, the PVDF substrate with surface-grafted PMMA (the PVDF-g-PMMA surface) was removed from the solution and washed thoroughly with excess tetrahydrofuran and distilled water for several times, respectively. The so-modified substrate was dried until the weight kept unchanged.

RESULTS AND DISCUSSION

Surface hydroxylation of PVDF substrates

The surface of PVDF film was selectively modified by wet chemistry, according to the procedures.²² The detailed investigation for each step of hydroxylation treatment was presented in a previous paper.²³ For the pristine PVDF surface, the wide-scan spectrum comprises predominately two peaks at the BEs of about

286 and 688 eV, attributable to the C 1s and F 1s signals [Fig. 2(a)], while the wide-scan spectrum of the hydroxylated PVDF surface comprises not only C 1s and F 1s but also O 1s signal [Fig. 2(b)]. The hydroxyl coverage on the treated PVDF films was further estimated by radiolabeling experiments.²³ The experimental radioactivity was converted to hydroxyl units per surface area (nm^2). About 0.72 units/ nm^2 of hydroxyl coverage on the treated PVDF surface was obtained.

Immobilization of the azo initiator on the hydroxylated PVDF surface

To prepare the polymer brush on the PVDF surface, a uniform and dense layer of initiators immobilized on the PVDF surface is indispensable. Coupling of the azo monolayers to the PVDF surface, as initiator of free radical polymerization, was performed using the well-established esterification of the surface-tethered hydroxyl groups with ACP. The peak at 402 eV, attributable to N 1s, was observed in the XPS wide-scan spectrum of the PVDF-g-ACP surface, besides the peaks at 286, 531, and 688 eV, attributable to C 1s, O 1s, and F 1s, respectively, [Fig. 2(c)]. The persistence of

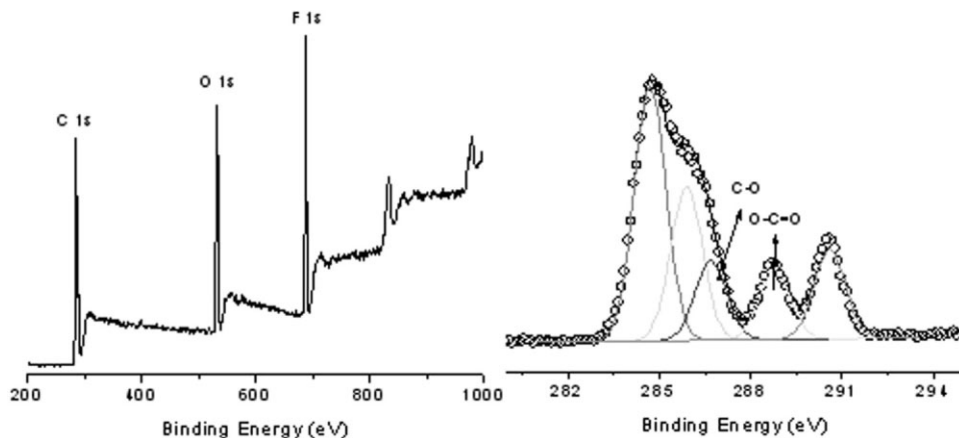


Figure 3 XPS wide-scan and C 1s core-level spectra of the PVDF-g-PMMA surface.

very strong F signals in the wide scan spectrum of the PVDF-g-ACP surface provides additional evidence to the fact that the thickness of monolayer is much less than the sampling depth of the XPS technique (about 7.5 nm in an organic matrix). The azo monolayers formed on the PVDF films were determined quantitatively by reaction with 2,2-diphenyl-1-picrylhydrazyl (DPPH). Three pieces of the PVDF-g-ACP films each of 2 cm² were immersed in 5 mL of a 0.1 mM deaerated toluene solution of DPPH. The reaction mixture was kept at 80°C for 24 h to decompose the azo formed on the PVDF film surface. The DPPH molecules consumed during reaction with the azo were deduced from the difference in transmittance of the reaction mixture at 520 nm, before and after the thermal decomposition of the azo, and the absorption calibration curve of the DPPH solutions. The calibration curve was obtained by measurement of the transmittance of six DPPH solutions in the concentration range of 0.05–0.1 mM. The azo coverage on the PVDF-g-ACP surface was estimated to be about 0.68 units/nm². In comparison to hydroxyl coverage on the hydroxylated PVDF surface, almost all hydroxyl groups were reacted with ACP to form azo monolayers on the PVDF surface. When the PVDF-g-ACP film was kept in the same DPPH solution at room temperature, or below the decomposition temperature of the azo groups, in a control experiment, no significant change in DPPH concentration was observed after the same period of time. These results, together with the appearance of nitrogen species on the PVDF surface (see XPS data), confirm the formation of the azo groups on the PVDF-g-ACP surface and their subsequent decomposition into radicals at an elevated temperature.

Surface-initiated free radical polymerization

The polymer brushes can be prepared from PVDF-g-ACP surface via free radical polymerization of vinyl

monomer. Therefore, the physicochemical properties of the PVDF surface can be tuned by the choice of a variety of vinyl monomers. As the model monomer, MMA was selected. The C 1s core-level spectrum of the pristine PVDF surface consists of two peak components of about equal integral area with BE at 286.4 eV for the CH₂ species and at 290.9 eV for the CF₂ species (Fig. 2 days). The presence of grafted polymer on the PVDF surface is ascertained by XPS analysis. The results are shown in Figure 3. The XPS wide-scan spectrum of PVDF-g-PMMA surface consists of peaks at 286, 531, and 688 eV, attributable to C 1s, O 1s, and F 1s, respectively. The C 1s core-level spectra of the PVDF-g-PMMA surface can be curve-fitted with five peak components having BEs at about 284.8, 286.2, 286.6, 288.9, and 290.9 eV, attributable to the Neutral C, CH₂, C—O, O—C=O, and CF₂ species, respectively. The [C—O] : [O—C=O] ratios of the PVDF-g-PMMA surface, obtained from XPS analysis, are in fairly good agreement with the respective theoretical ratios. In addition, the CF₂ peak component associated with the PVDF substrate persists in the curve-fitted C 1s core-level spectra of the PVDF-g-PMMA surface, but presents a lower area in comparison to the CH₂ component. The graft concentration of the PMMA brushes grown on the PVDF surface can be derived from the O—C=O peak component to the CF₂ peak component. With the increase of graft polymerization time, the [O—C=O] : [CF₂] ratio of PVDF-g-PMMA surface increases, until CF₂ peak component can not be determined by XPS. This result suggests that thickness of the grafted polymer layer is gained gradually until thickness of graft layer is beyond the probing depth of the XPS technique.

The presence of PMMA brushes on the PVDF surface is ascertained also by ATR FTIR spectra. The ATR FTIR spectra of the PVDF-g-PMMA surface reveal the appearance of the absorption band at 1730 cm⁻¹, attributable to the stretching of ester carbonyl group, as

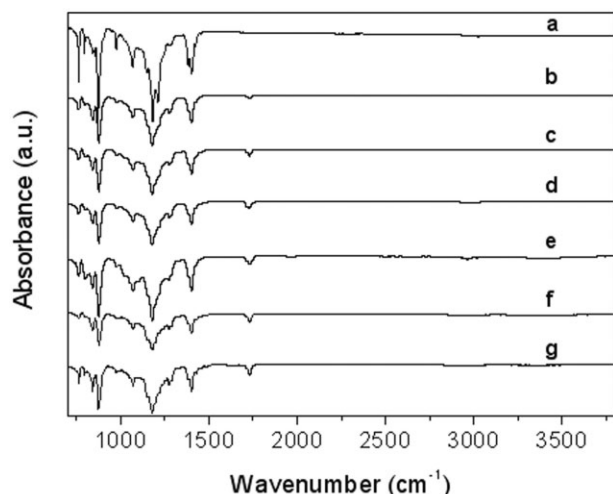


Figure 4 ATR FTIR spectra of (a) the pristine PVDF surface and the PVDF-g-ACP surface subjected to free radical polymerization of MMA for (b) 1 h, (c) 4 h, (d) 8 h, (e) 12 h, (f) 17 h, and (g) 22 h. Reaction conditions: [MMA] = 1.8M; solvent, toluene; temperature, 80°C.

shown in Figure 4. The variations in graft concentration (polymerization time) are reflected in the changes in ratio of the intensity of the absorption band at 1730 cm^{-1} to that of the absorption band at 1400 cm^{-1} .

The variation in water contact angle for the PVDF surfaces with PMMA brushes indicates that the hydrophilicity of the PVDF surface can be easily tuned, according to polymerization time. The contact angle of the pristine PVDF surface is about 93°. When grafted with a PMMA layer, the PVDF surface becomes more hydrophilic and the contact angle decreases with increase of graft concentration (relative to reaction time), as shown in Figure 5.

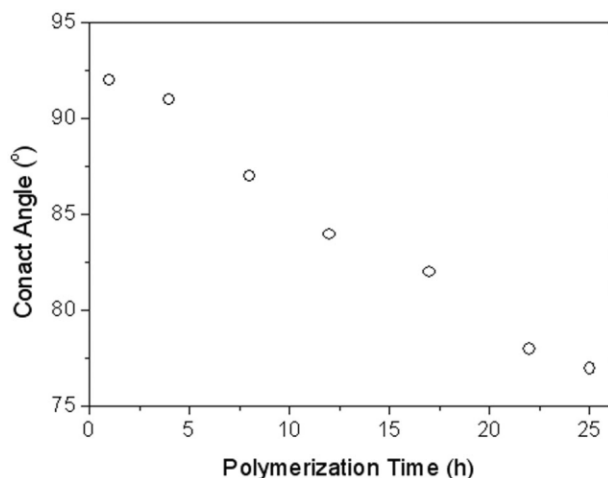


Figure 5 The dependence of water contact angles of the PVDF-g-PMMA surface on graft polymerization time of surface-initiated free radical polymerization.

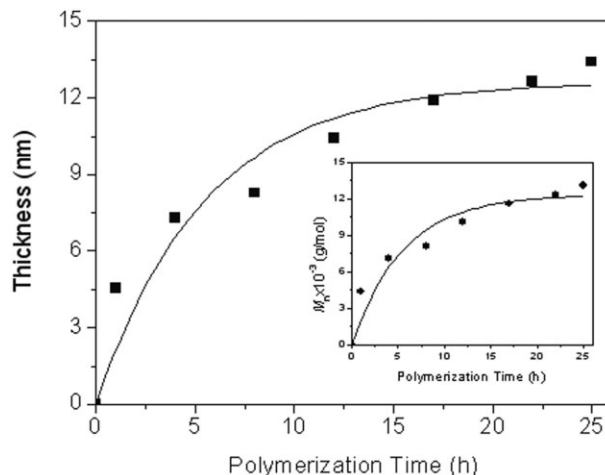


Figure 6 Dependence of the thickness of the PMMA layer on reaction time (insert: dependence of the M_n of polymer brushes on reaction time).

The ellipsometry measurements indicate a large increase in film thickness after the growth of the PMMA layer on the PVDF surface. Control experiments, under the conditions similar to that for surface graft polymerization, are directly carried on the pristine PVDF surface. No increase in thickness on all the control surface was discernible. The results confirm that the increase in thickness observed is the result of graft polymerization from the azo functionalized PVDF surface. As shown in Figure 6, an exponential increase in thickness of the grafted PMMA layer on the PVDF-g-ACP surface with the polymerization time is observed. These results indicate that the process of surface-initiated free radical polymerization of MMA is in good agreement with the kinetics of chain polymerization. The number-average molecular weight (M_n) of the polymer brushes were calculated from the product of thickness and the initiator coverage on the PVDF surface. For simplicity, the density of the corresponding bulk polymer is used as the density of the grafted polymer film (1.1 g/cm^3 for PMMA). The M_n of the polymer brushes on PVDF surface exhibited an exponential increase with increase in reaction time (inserted figure in Fig. 6). These results indicate that the kinetics of surface-initiated graft polymerization is consistent with that of free radical polymerization.

The changes in topography of the PVDF surfaces after modification by surface-initiated free radical polymerization were studied by AFM. Representative AFM images of the pristine PVDF, PVDF-g-PMMA (PMMA thickness of 10.4 nm), and PVDF-g-PMMA (PMMA thickness of 12.6 nm) surfaces are shown in Figure 7. The root-mean-square surface roughness (R_a) of the pristine PVDF surface is only about 16.8 nm. After surface-initiated free radical

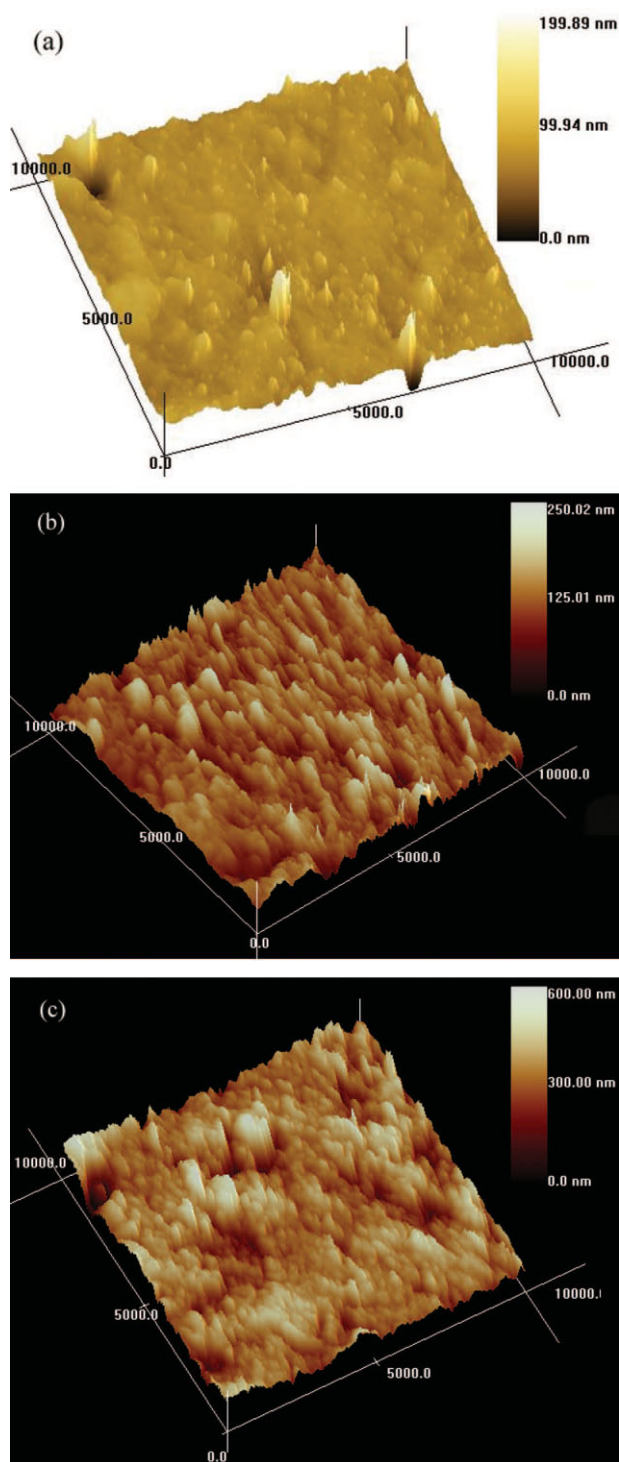


Figure 7 AFM images of (a) the pristine PVDF surface, (b) PVDF-g-PMMA surface (PMMA thickness of 10.4 nm), and (c) PVDF-g-PMMA surface (PMMA thickness of 12.6 nm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymerization, the R_a value increases to about 27.6 and 43.4 nm for PMMA thickness of 10.4 and 12.6 nm, respectively. These results suggest that the sur-

face-initiated free radical polymerization has given rise to nonuniform molecular weight distribution of polymer brushes and a dense coverage of PMMA on the PVDF surface. As is also shown in Figure 7(b,c), the grafted PMMA chains exist as a distinctive overlayer on the PVDF surface. The formation of the nanosized islands probably has resulted from the nanoscaled phase aggregation of the grafted polymer after the surface has been dried.

CONCLUSIONS

Grafting of PMMA brushes was carried out via free radical polymerization of MMA on the PVDF surfaces. Prior to the surface initiated polymerization, the PVDF surface was hydroxylated with LiOH, NaBH_4 , and DIBAL-H. The azo initiator was immobilized by esterification of the surface-tethered hydroxyl group with 4,4'-azobis(4-cyanopentanoic acid). The XPS and ATR FTIR analysis of the modified surface indicated the formation of polymer brushes on the PVDF surface. The polymer brushes covalently tethered to the PVDF surface have imparted new functionalities directly onto the fluoropolymer surfaces.

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