

Surface Modification of Polythiophene and Poly(3-methyl thiophene) Films by Graft Copolymerization

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ABSTRACT: Polythiophene (PTH) and poly(3-methyl thiophene) (PMT) films were electrochemically polymerized in an electrolyte solution of boron fluoride–ethyl ether. Ozone-pretreated PTH and PMT films were subjected to UV-light-induced graft copolymerization with different monomers, including poly(ethylene glycol) monomethacrylate, acrylic acid, and glycidyl methacrylate. Surface grafting with the hydrophilic polymers gave rise to more hydrophilic PTH and PMT films. The structure and chemical composition of each copolymer surface were studied by X-ray photoelectron spectroscopy. The surface

grafting with the hydrophilic polymers resulted in a more hydrophilic PTH film. The dependence of the density of surface grafting and the conductivities of the grafted PTH and PMT films on the ozone pretreatment was also studied. A large amount of the grafted groups at the surface of the PTH and PMT films remained free for further surface modification and functionalization. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2582–2587, 2012

Key words: conducting polymers; graft copolymers; surface modification

INTRODUCTION

During recent years, there has been growing interest in electrically conducting polymers because of their potential applications for electronic devices,¹ biochemical sensors,² rechargeable batteries,³ and photovoltaics.⁴ Among these polymers, polythiophene (PTH) derivatives have attracted considerable attention because of their high magnetic, mechanical, and optical properties; electrical conductivity; and environmental stability.^{5–10}

In view of these applications, materials modifications, in particular, surface modifications, may be

required. Surface modifications with biocompatible polymeric materials for biochemical and biomedical applications have been well reported.^{11,12} It has also been demonstrated that surface modifications can be performed through graft copolymerization under mild conditions when the surfaces are pretreated with high-energy radiation, glow discharge, ozone exposure, or UV irradiation.^{13–15}

Functionalized conducting polymers constitute an interesting class of materials that can specifically interact with external physical or chemical quantities, depending on the nature of the functional group. There have been some reports about the surface functionalization of polyaniline and polypyrrole.^{16,17} However, to our knowledge, there have been few reports about the surface functionalization of PTH derivative films. Accordingly, it should be interesting to study surface modifications of conducting PTH derivative films because these films may provide an added advantage.

This study involved a preliminary investigation of the surface modifications of PTH and poly(3-methyl thiophene) (PMT) films by graft copolymerization with different monomers, including poly(ethylene glycol) monomethacrylate (PEGMA), acrylic acid (AAc), and glycidyl methacrylate (GMA). Graft copolymerization with the hydrophilic monomers readily resulted in a decrease in the water contact angle of the PTH film surface. The grafting of these polymers provided appropriate functional groups at the surface for the

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subsequent immobilization of protein and enzyme. The grafted PTH and PMT film surfaces were characterized with X-ray photoelectron spectroscopy (XPS). The efficiency of surface grafting copolymerization and its subsequent effects on the conductivity and the hydrophilicity of the film were also studied.

EXPERIMENTAL

Materials

Thiophene and 3-methyl thiophene were purchased from Aldrich (Milwaukee, WI) and were distilled under a nitrogen atmosphere just before use. Boron trifluoride–ethyl ether was freshly distilled before use. The monomers used for graft copolymerization, PEGMA (weight-average molecular weight \approx 360 g/mol), AAc, and GMA, were also obtained from Aldrich and were passed through inhibitor-removing columns. The other reagents were used without further purification unless otherwise mentioned.

Electrochemical synthesis of the PTH and PMT films

Electrochemical polymerizations were performed in a one-compartment, three-electrode cell with an Auto-lab-PGSTAT30 (Metrohm-Schmidt, Ltd., Utrecht, Netherlands) under the control of a computer at room temperature.¹⁸ The free-standing films were obtained with stainless steel plates (3 cm²) as the working electrode; these were polished with abrasive paper and diamond paste and then washed with acetone. A platinum wire gauge and an Ag/AgCl/0.1M KCl electrode were used as the counter electrode and the reference electrode, respectively. Thiophene or 3-methyl thiophene (0.1M) was added to the boron trifluoride–ethyl ether solution. The solution was deaerated by the bubbling of dry argon before each electrochemical experiment. The PTH or PMT film was electrochemically deposited by the application of a current of 1 mA/cm², and the film thickness was controlled by the amount of charge passed. The obtained PTH and PMT films were approximately 20 and 25 μ m in thickness, respectively. They were washed thoroughly with acetone and dried by pumping under reduced pressure.

Graft copolymerization

We generated ozone with an ozonizer (Azcozon RMU 16-04 EM, Langley, Canada) at 100 V by allowing oxygen to enter the ozonizer at a flow rate of 100 L/h. The mixture of generated ozone and oxygen was introduced into a U-shaped glass cell containing the polymer film.¹⁶

In the case of graft copolymerization with AAc or GMA, each PTH or PMT film was immersed in 20 mL

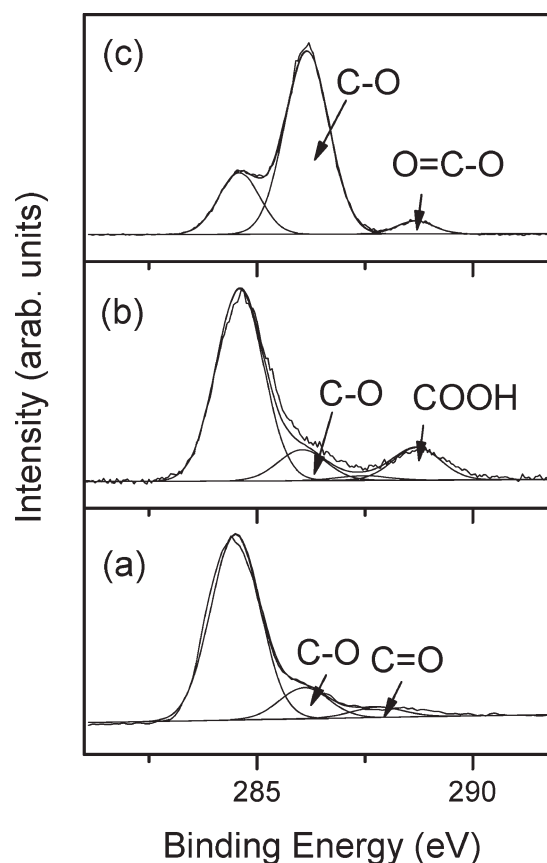


Figure 1 XPS C1s core-level spectra of the (a) pristine PTH film, (b) 20-s ozone-pretreated PTH film after the film was subjected to graft polymerization in a 6 vol % AAc solution, and (c) 20-s ozone-pretreated PTH film after the film was subjected to graft polymerization in a 5 vol % PEGMA solution.

of an acetone solution containing AAc or GMA of a predetermined concentration between 2 and 10 vol % in a Pyrex tube. Each reaction mixture was thoroughly degassed and sealed off under a nitrogen atmosphere. The tubes were then subjected to UV irradiation in a Riko rotary photochemical reactor (RH400-10W) for about 25 min at about 25°C. After each of the grafting experiments described previously, the PTH film was finally subjected to good washing with ethanol to remove the residual homopolymer. Similar procedures were used for grafting with PEGMA.

Characterization

XPS analysis of the films was performed on a Kratos AXIS HSi spectrometer with a monochromatized Al K α X-ray source (1486.6-eV photons).¹⁹ The pressure in the analysis chamber was maintained at 5.0×10^{-8} Torr or lower during each measurement. To compensate for the surface charging effect, all core-level spectra were referenced to the C1s hydrocarbon peak at 284.6 eV. In spectral deconvolution, the line width (full width at half-maximum) of the Gaussian peaks was maintained at a constant value

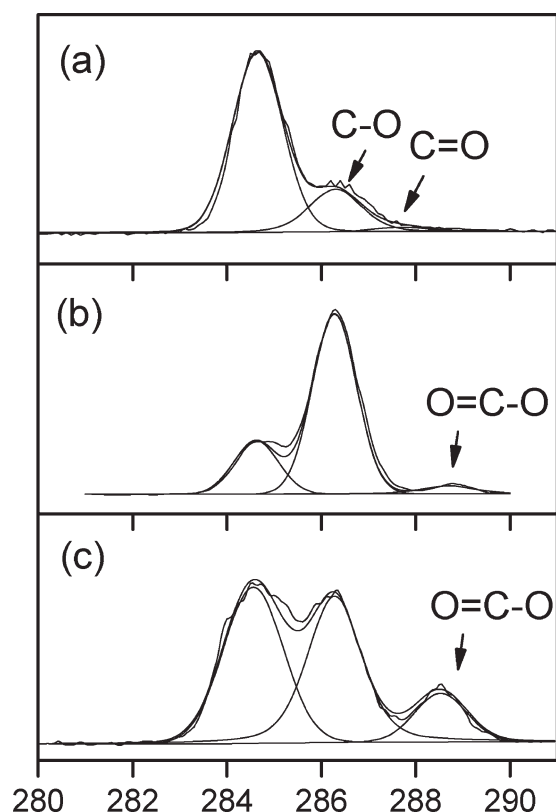


Figure 2 XPS C1s core-level spectra of the (a) pristine PMT film, (b) 20-s ozone-pretreated PMT film after the film was subjected to graft polymerization in a 5 vol % PEGMA solution, and (c) 20-s ozone-pretreated PMT film after the film was subjected to graft polymerization in a 6 vol % GMA solution.

for all components in a particular spectrum. The peak area ratios for the various elements were corrected with experimentally determined instrumental sensitivity factors. The conductivities of the films were measured by the four-point probe method. The static water contact angles of the pristine and grafted polymer film surfaces were measured with the sessile drop method with a 3- μ L water droplet in a telescopic goniometer [Rame-Hart model 100-00-(230), manufactured by the Rame-Hart, Inc., Mountain Lakes, NJ]. For each angle reported, at least three measurements from different surface locations were averaged. The angle reported was accurate to $\pm 3^\circ$.

RESULTS AND DISCUSSION

In this study, AAc and PEGMA were selected for the preparation of surface-grafted PTH films, whereas GMA and PEGMA were selected for the preparation of surface-grafted PMT films. AAc polymer with carboxylic groups can be used for the direct coupling of amino and for exploiting the carbodiimide chemistry.^{20,21} GMA polymer is a potential linker for biomolecules, and PEGMA polymer exhibits a good antifouling effect for lots of pro-

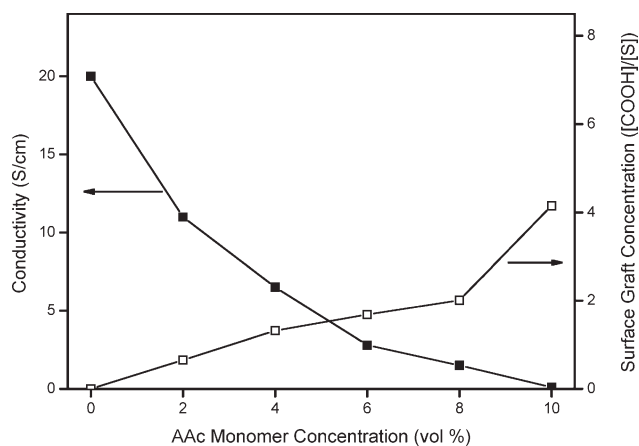


Figure 3 Effects of the AAc monomer concentration on the surface graft concentration of the AAc polymer and the conductivity of the 20-s ozone-pretreated PTH film.

teins.^{22,23} The success of the UV-induced surface graft copolymerization of different monomers on the PTH and PMT film surfaces could be ascertained by a comparison of the XPS C1s spectra of the films before and after the grafting process, as shown in Figures 1 and 2. The XPS C1s core-level spectrum of the pristine PTH or PMT indicated a small amount of oxidized C, primarily C—O (286.2 eV) and C=O (287.6 eV) [Fig. 1(a) or Fig. 2(a)],^{24,25} which may have resulted from the surface oxidation or charge-transfer complexing with oxygen. For the as-prepared PTH-AAc film, the appearance of a distinct peak at about 288.7 eV, attributable to the COOH species in Figure 1(b), as compared to those of the pristine PTH film, indicated the successful graft copolymerization of AAc. On the other hand, the C1s core-level spectrum of the PTH-PEGMA surface could be curve-fitted with three peak components having binding energies (BEs) at about 284.6, 286.2,

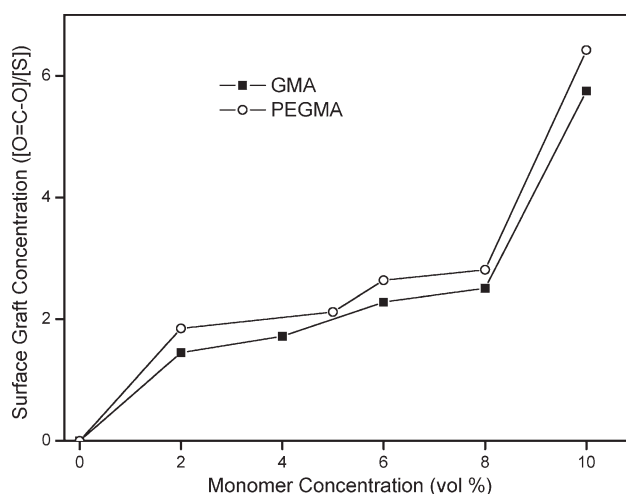


Figure 4 Effects of the GMA monomer and PEGMA monomer concentrations on the surface graft concentration of the corresponding polymers on the 20-s ozone-pretreated PMT film.

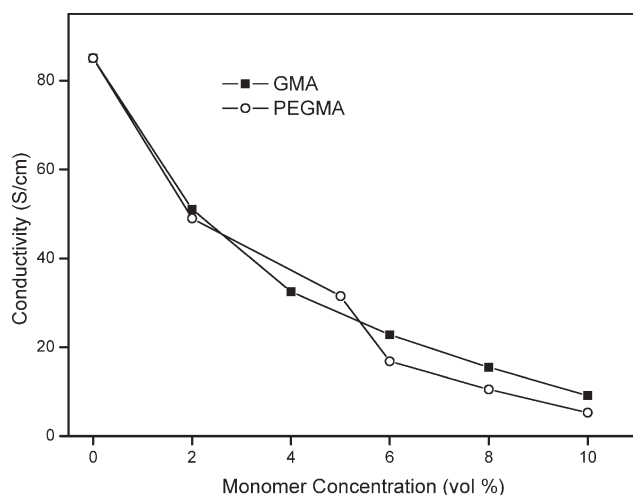


Figure 5 Effects of the GMA monomer and PEGMA monomer concentrations on the conductivity of the grafted PMT film (20-s ozone-pretreated film).

and 288.6 eV, attributable to the C–H, C–O, and O=C–O species, respectively. The C1s line shape thus confirmed that PEGMA was successfully graft copolymerized with the PTH surface. Moreover, the C1s core-level spectra of the as-prepared PMT–GMA and PMT–PEGMA films could also be curve-fitted into three peak components with BEs at about 284.6 eV for C–H species, 286.2 eV for C–O species, and 288.6 eV for O=C–O species, respectively.^{22,23} The C1s line shape thus confirmed that GMA and PEGMA were successfully graft copolymerized with the PMT surface.

The extent of surface grafting of AAc on the PTH film was estimated from the corrected area ratio of the C1s peak component, which was attributable to the carboxyl group of the AAc polymer, and the total S 2p area due to the PTH film. The ratio was expressed as $[\text{COOH}]/[\text{S}]$. Figure 3 shows the dependence of the surface graft concentration of the

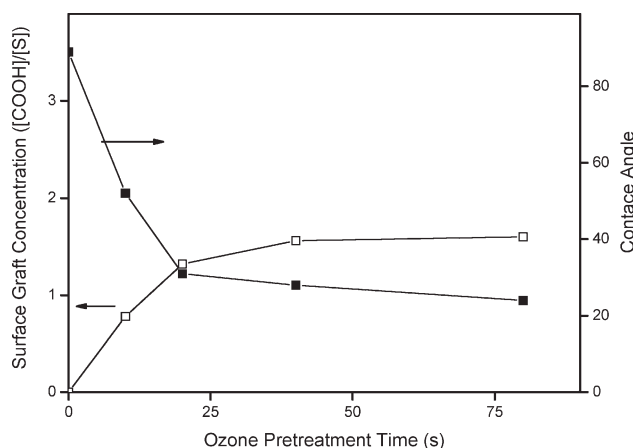


Figure 6 Surface graft concentration of the AAc polymer and corresponding water contact angle of the PTH film after graft polymerization in a 4 vol % AAc solution as a function of the ozone pretreatment time.

TABLE I
Surface Properties of the Various PTH Films with the Surface-Grafted PEGMA Polymer

Ozone pretreatment time (s)	Grafted density $[\text{O}=\text{C}-\text{O}]/[\text{S}]$	Contact angle ($^{\circ}$)
0	0.0	89
10	0.7	53
20	1.3	50
40	1.4	48
80	1.5	45

AAc polymer on the AAc monomer concentration. The surface graft concentration of the AAc polymer increased with increasing AAc monomer concentration. The extent of surface grafting of GMA and PEGMA on the PMT film was estimated from the corrected area ratio of the C1s peak component at 288.6 eV, attributable to the ester group of the GMA polymer and PEGMA polymer, and the total S 2p area due to the PMT film. The ratio was expressed as the $[\text{O}=\text{C}-\text{O}]/[\text{S}]$. Figure 4 shows the dependence of the surface graft concentration of the GMA polymer and the PEGMA polymer on the corresponding monomer concentration. The surface graft concentration of the polymer increased with increasing corresponding monomer concentration.

We expected that a lower electrical conductivity of the PMT film would result from the increase in the concentration of the monomer because of the non-conductive grafted polymer. However, the decrease in the conductivity of the grafted PTH and PMT films was not proportional to the increase in the surface graft concentration, as shown in Figures 3 and 5. In the range of monomer concentration from 4 to

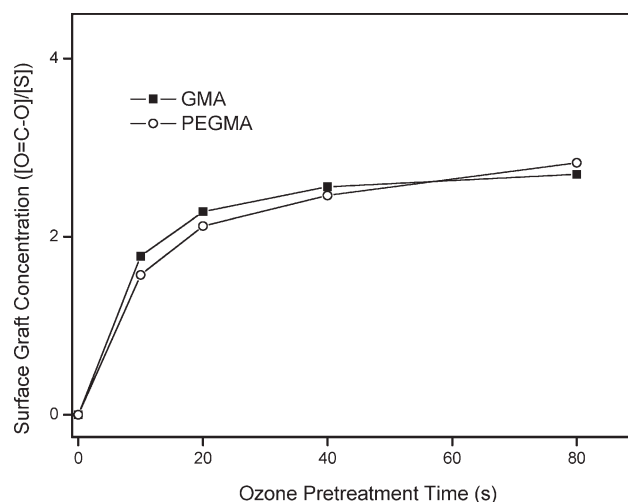


Figure 7 Surface graft concentration of the GMA polymer and the PEGMA polymer of the PMT film after graft polymerization in a 6 vol % GMA solution and in a 5 vol % PEGMA solution, respectively, as a function of the ozone pretreatment time.

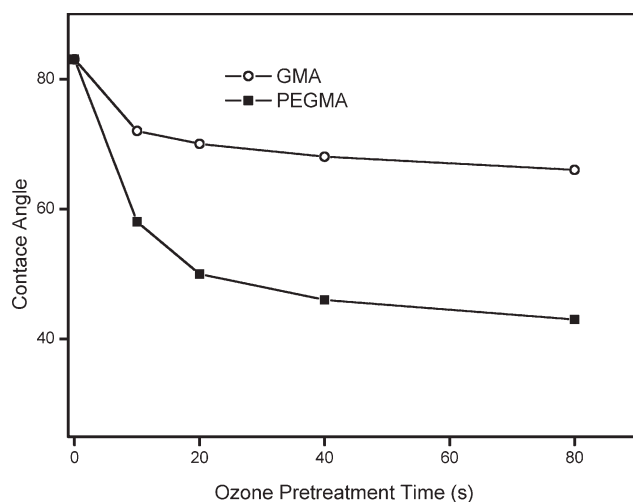


Figure 8 Static water contact angle of the grafted PMT film as a function of the ozone pretreatment time.

8 vol %, the surface graft concentration changed little, whereas the conductivity showed a gradual decrease. This could be ascribed to the fact that the grafted polymer may not have only existed on the film surface, but also a substantial amount of grafted polymer may have affected the molecular level of the sublayer of the PTH and PMT films because the conductivity measured by four-point probe was not the surface conductivity.¹⁷

The effect of the ozone pretreatment time on the properties of the grafted PTH and PMT films was also studied. The corresponding water contact angle of the AAc-grafted PTH and PMT films as a function of ozone pretreatment time is plotted in Figure 6. The water contact angles of the pristine PTH and PMT films showed that the surfaces of the pristine PTH and PMT films were highly hydrophobic because of the doping with anions of the supporting electrolyte during electrochemical polymerization.²⁶ The decrease in water contact angles from about 89° for the pristine ungrafted PTH film to as low as about 24° for the AAc-grafted surface indicated that surface grafting with the AAc polymer gave rise to a more hydrophilic PTH film. The surface graft concentration of the AAc polymer with the ozone pretreatment time is also shown in Figure 6. Table I summarizes the surface graft concentration and the water contact angle of the various PTH films with surface-grafted PEGMA polymer. An increase in hydrophilicity was observed upon graft copolymerization with hydrophilic PEGMA polymer. With the ozone pretreatment, $[O=C-O]/[S]$ ratios more than 1 were obtained for a number of PEGMA-grafted PTH films. Figures 7 and 8 show the surface graft concentration of GMA and PEGMA polymer and the dependence of the corresponding water contact angle of the grafted PMT films on the ozone pre-

treatment time, respectively. The decrease in water contact angles from about 83° for the pristine ungrafted PMT film to as low as about 44° for the PEGMA-grafted surface indicated that surface grafting with the PEGMA polymer gave rise to a more hydrophilic PTH film. The water contact angle of the GMA-grafted PMT films decreased also to 66°. With increasing ozone pretreatment time, $[O=C-O]/[S]$ ratios of more than 2 were obtained for the grafted PMT films.

CONCLUSIONS

The PTH and PMT films obtained by electrochemical synthesis could readily undergo surface graft copolymerization with AAc, GMA, and PEGMA monomers. We could vary the graft concentration by changing the monomer concentrations and ozone pretreatment times. XPS was used to investigate the structure and chemical composition of the grafted PTH and PMT films. Graft copolymerization with the hydrophilic monomers readily resulted in a decrease in the water contact angle of the pristine hydrophobic PTH and PMT films. Because a large amount of the grafted groups in the grafted polymer at the surface of PTH film remained free, we could use it for further surface modification and functionalization. Further work on this aspect is in progress in our laboratory.

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