

# Surface Functionalization of Poly(tetrafluoroethylene) Films via Consecutive Graft Copolymerization with Glycidyl Methacrylate and Aniline

Yongjun Chen, E. T. Kang,\* and K. G. Neoh

Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 119260

K. L. Tan

Department of Physics, National University of Singapore, Kent Ridge, Singapore 119260

Received: January 11, 2000; In Final Form: July 3, 2000

Chemical modification of argon-plasma-pretreated poly(tetrafluoroethylene) (PTFE) film by UV-induced surface graft copolymerization with glycidyl methacrylate (GMA), followed by epoxide-ring-opening reaction with aniline (An), and finally oxidative graft polymerization with aniline had been carried out to render the PTFE surface conductive. The surface composition and microstructure of the graft-copolymerized PTFE films were studied by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), respectively. The graft concentration of the GMA polymer and An polymer increased with increasing concentration of the respective monomer used for graft polymerization. Ethanol, when used as a solvent, catalyzed the coupling reaction of epoxide with An and should be of more than 40 vol % in concentration to achieve the optimum effect. The physicochemical characteristics of the polyaniline (PANI) chains grafted onto PTFE film surface were grossly similar to those of the PANI homopolymer. The surface resistance of the aniline graft-polymerized PTFE film was reduced to the order of about  $10^4 \Omega/\text{square}$ , in comparison to the value of  $10^{16} \Omega/\text{square}$  for the pristine PTFE film.

## Introduction

With the rapid advances in and broad implementation of computer and telecommunication technologies, there is an increasing interest in the shielding of electromagnetic interference (EMI), especially in the radio and microwave frequency ranges.<sup>1</sup> The usual approach is to physically coat the electronic devices or molded plastic surfaces with a layer of electrically conductive compounds or conductive polymer films. This method may have certain limitations, since most of the coatings do not remain permanently on the surface. Thus, a more viable method is to covalently bond a conductive film to the surface of the substrate, creating a “permanently” conductive surface. Covalent bonding methods involve chemical reactions between the coating layer and the surface molecules of the substrate. Chemical modification is also a convenient and effective means to render the existing substrate surface with improved physicochemical properties, and biocompatibility.<sup>2,3</sup> Among the techniques available, surface modification via grafting and graft copolymerization are some of the most promising techniques, as they allow the molecular re-design of most substrate surfaces to impart new and specific functionalities.<sup>4–10</sup> Youngblood and McCarthy<sup>7</sup> and Chen et al.<sup>8</sup> have prepared ultra-hydrophobic polymer surfaces using plasma sputtering of poly(tetrafluoroethylene) and plasma polymerization of fluorine-containing monomers. On the other hand, Zhao and Brittain<sup>9</sup> have demonstrated the chemisorption of silane monolayers on modified fluoropolymer surfaces. The same authors have also reported on the synthesis of polystyrene brushes on silicate substrates via carbocationic polymerization from self-assembled mono-

layers.<sup>10</sup> Accordingly, it should be useful to extend the surface graft copolymerization technique to the covalent bonding of conductive polymers to the surfaces of conventional polymer dielectrics.

Among the conductive polymers, polyaniline (PANI) has been of particular interest because of its environmental stability, controllable electrical conductivity and interesting redox properties associated with the chain nitrogen.<sup>11</sup> PANI also exhibits crystallinity and solution- or counterion-induced processability.<sup>12</sup> Furthermore, the electrical properties of polyaniline (PANI) can be substantially improved through secondary doping.<sup>13</sup> Polyaniline has potential applications not only in the areas of corrosion protection of metals,<sup>14</sup> light-emitting devices,<sup>15</sup> control of electromagnetic reaction (EMR), and the dissipation of electrostatic charges,<sup>16,17</sup> but also as biocompatible materials<sup>18</sup> and materials for catalysts, electrodes, and sensors.<sup>19–22</sup> The microwave-sensitive properties of polyaniline make it also a very promising material for electromagnetic shielding,<sup>23</sup> radar microwave absorbing,<sup>24</sup> and plastics welding.<sup>25</sup>

Poly(tetrafluoroethylene) (PTFE), on the other hand, has many desirable properties, such as thermal stability, low dielectric constant, and chemical inertness which make it ideal as a dielectric material for microelectronics applications.<sup>26–28</sup> For these applications, extensive work has been done to overcome the surface inertness of PTFE. These efforts have included the modification of the fluoropolymer surfaces by wet chemical, gas plasma, UV laser, and electron beam treatments.<sup>29</sup>

In this study, we report on a process for the covalent bonding of the polyaniline chains onto the surfaces of poly(tetrafluoroethylene) (PTFE) films. The method involves initial surface modification of the Ar-plasma-pretreated PTFE film via UV-induced graft copolymerization with glycidyl methacrylate

\* Author to whom correspondence should be addressed. Fax: (65) 779-1936. E-mail: cheket@nus.edu.sg.

(GMA). The epoxide functional groups of the grafted GMA polymer chains on the PTFE surface are subsequently reacted with aniline. The PTFE surface with the covalently coupled aniline is then subjected to oxidative graft polymerization with aniline. The covalently grafted aniline polymer can readily impart electrical conductivity onto the surface of the highly insulating PTFE substrate.

### Experimental Section

**Materials.** The poly(tetrafluoroethylene) (PTFE) film of 0.1 mm thickness was purchased from Goodfellow Ltd. of Cambridge, U.K. The surfaces of the PTFE films were cleaned ultrasonically with acetone and then soaked in acetone for 24 h before use. The glycidyl methacrylate (GMA) and aniline (An) monomers were obtained from Aldrich Chemical Co., of Milwaukee, and were used as received. The solvents, such as 1,4-dioxane, acetone, ethanol, *N*-methylpyrrolidinone (NMP), and other chemicals were of reagent grade. They were also obtained from Aldrich Chemical Co. and were used without further purification.

**Plasma Pretreatment and Surface Graft Copolymerization.** A cylindrical quartz glow discharge cell, model SP-100, manufactured by Anatech Ltd, was used for the plasma pretreatment of the PTFE substrate. The glow discharge was generated at a frequency of 40 kHz and a plasma power of 35 W. The pressure in the quartz cell was maintained at  $\sim 0.58$  Torr of argon while the polymer films were exposed to the glow discharge for 0 to 100 s. The Ar-plasma-pretreated PTFE films were exposed to air for about 10 min to facilitate the formation of surface peroxides and hydroperoxides species for the subsequent UV-induced surface graft copolymerization process.<sup>30</sup>

The surface modification of PTFE film by graft copolymerization with GMA and aniline was carried out in three steps. The first step involved the UV-induced graft copolymerization of GMA on the Ar-plasma-pretreated PTFE substrate. The second step involved the coupling reaction between the epoxide groups of the graft-copolymerized GMA and aniline. The last step involved the surface oxidative polymerization of aniline with the covalently immobilized aniline on the GMA graft-copolymerized PTFE surface.

The UV-induced surface graft copolymerization with GMA was carried out in a Riko Rotary Model RH 400-10W photochemical reactor, manufactured by Riko Denki Kogyo of Chiba, Japan. The reactor was equipped with a 1000 W high-pressure Hg lamp and a constant-temperature water bath. All UV-induced graft copolymerization was carried out at constant temperature of 28 °C. The Ar-plasma-pretreated PTFE film was immersed in 1,4-dioxane solution GMA in a Pyrex tube. Each reaction mixture was thoroughly degassed before being sealed under a nitrogen atmosphere. It was then subjected to UV irradiation for 30–120 min. After each grafting experiment, the PTFE film was washed with copious amounts of 1,4-dioxane to remove the residual monomer and adsorbed homopolymer. The GMA graft-copolymerized PTFE (GMA-*g*-PTFE) substrate was then dried under reduced pressure. The epoxide-ring-opening reaction with the aniline (An) monomer was carried out in ethanol solution, containing the GMA-*g*-PTFE film and An. The reaction temperature was varied in the range of 25–70 °C and the reaction time in the range of 2–10 h. The An concentration, on the other hand, was varied between 20 and 100 vol %. After the covalent coupling of An to the epoxide group, the film was washed thoroughly with copious amounts of NMP to remove the unreacted An monomer. The An

immobilized GMA-*g*-PTFE film (An-GMA-*g*-PTFE) was then dried under reduced pressure.

The oxidative polymerization of aniline with the aniline moiety on the An-GMA-*g*-PTFE surface was carried out in 0.5 M aqueous solution of H<sub>2</sub>SO<sub>4</sub>, containing the An-GMA-*g*-PTFE film, 0.01 to 0.2 M of aniline, and the corresponding amount of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> oxidant to achieve an aniline monomer-to-oxidant molar ratio of 1:1. The reaction was allowed to be processed at 0 °C for 5 h. The method was thus similar to that reported in the literature for the oxidative homopolymerization of aniline to produce the conductive emeraldine (EM) salt.<sup>22,31</sup> The grafted EM salt on the PTFE surface was converted to the neutral EM base form by treatment with a large excess of 0.5 M NaOH solution. The surface neutralized film was subsequently immersed in a large volume of NMP (a good solvent for EM base) for at least 24 h with continuous stirring to remove the adhered and physically adsorbed EM base polymer before being dried under reduced pressure. During the washing process, the NMP solvent was changed every 8 h.

### Characterization of the Surface-Modified PTFE Surface.

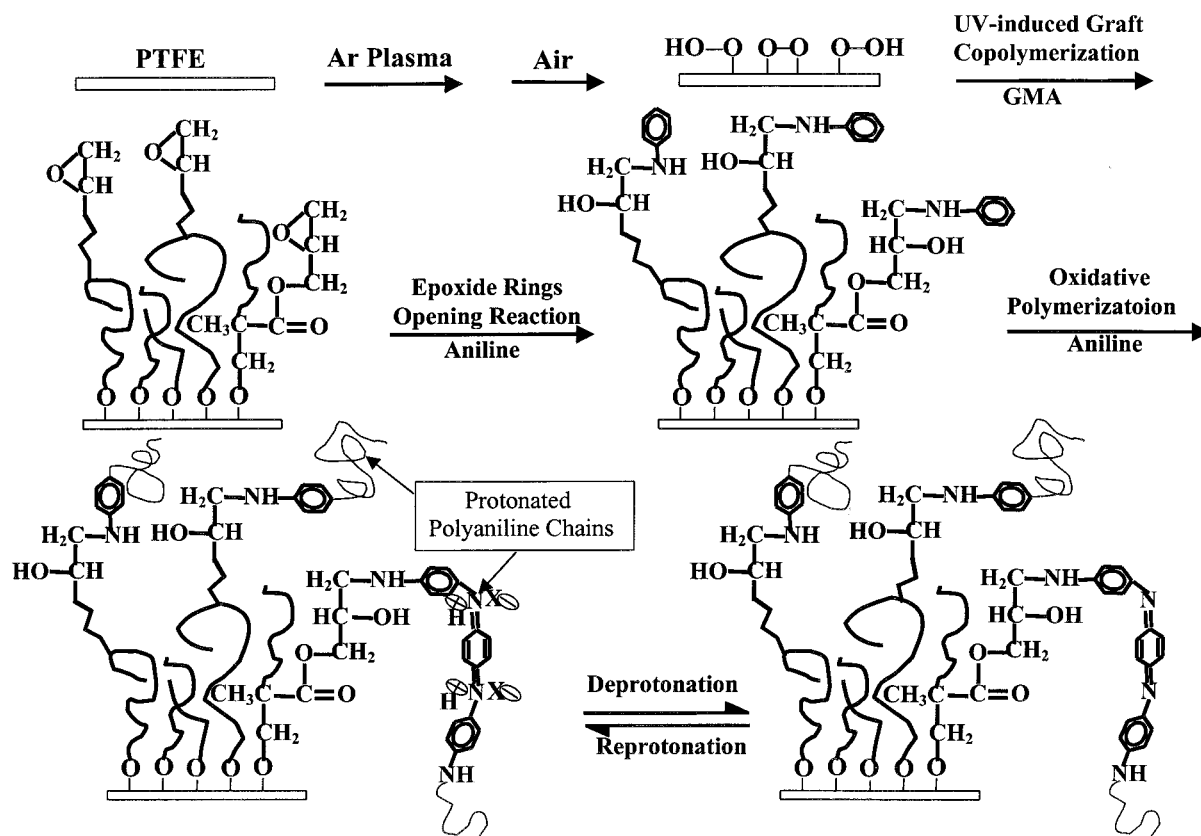
The graft-modified PTFE films were characterized by atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS), and conductivity measurements. The surface morphologies of the pure and modified PTFE films were examined in a Nanoscope IIIa atomic force microscope (AFM) using the tapping mode at a scan size of 5  $\mu$ m and a scan rate of 1 kHz. The average roughness (*R<sub>a</sub>*) of the film surface was evaluated directly from the AFM image.

XPS measurements were made on a VG ESCALAB MkII spectrometer with a Mg K $\alpha$  X-ray source (1253.6 eV photons). The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). The EM films were mounted on the standard VG sample studs by means of double-sided adhesive tapes. The core-level spectra were obtained at the photoelectron takeoff angle ( $\alpha$ , with respect to sample surface) of 75°. The pressure in the analysis chamber was maintained at  $10^{-8}$  Torr or lower during each measurement. To compensate for surface charging effects, all binding energies (BEs) were referenced to the C 1s neutral carbon peak at 284.6 eV. In peak synthesis, the line width (full width at half-maximum or fwhm) of Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to within >5%. The elemental sensitivity factors were calibrated using binary compounds of the well-defined stoichiometries.

The UV–visible absorption spectra were measured on an UV–vis–NIR scanning spectrophotometer (Shimadzu UV-3101 PC). The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of the surface graft-copolymerized films were measured on a Shimadzu Model 8101 FTIR. The surface resistance of the graft-modified PTFE films was measured by the two-probe method, using a Hioki Model 3265 digital electrometer. For each resistance value reported, at least three sample measurements were averaged.

### Results and Discussion

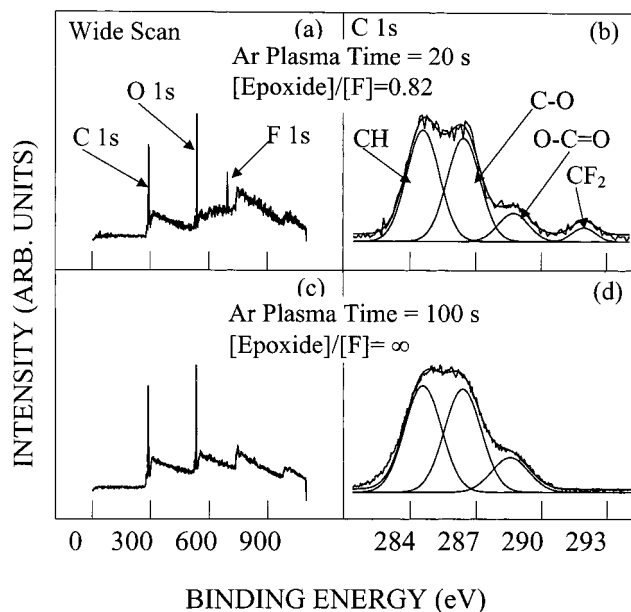
The processes of surface modification of PTFE by argon plasma treatment, UV-induced graft copolymerization with GMA, reactive coupling of the epoxide functional group of the grafted GMA polymer with aniline, and finally oxidative graft polymerization of aniline with the surface-bonded aniline moieties are shown schematically in Figure 1. Each process is described in detail below.



**Figure 1.** Schematic representations of the surface modification processes and the surface structures of the PTFE substrates with grafted GMA and aniline polymers.

**UV-Induced Surface Graft Copolymerization of the Ar-Plasma-Pretreated PTFE Film with GMA: The GMA-g-PTFE Surface.** The effect of Ar plasma pretreatment under similar experimental conditions on the surface composition of the PTFE film has been reported earlier.<sup>32</sup> The glow discharge causes the breakage of C–F bonds, resulting in the abstraction of fluorine atoms from the surface. The subsequent exposure of the Ar-plasma-pretreated surface to air causes oxygen to be incorporated onto the PTFE surfaces, leading to surface oxidation and the formation of peroxide and hydroperoxide species. The peroxide and hydroperoxide species can readily initiate the surface free radical polymerization in a mechanism generally proposed for the UV-induced surface graft copolymerization.<sup>30,32</sup>

Figure 2 shows the respective wide scan and C 1s core-level spectra of the 20 s (parts a and b) and 100 s (parts c and d) argon-plasma-pretreated PTFE films after the UV-induced graft copolymerization in 20 vol % GMA solution for 1 h. The presence of surface-grafted GMA polymer can be deduced from the three C 1s peak components with binding energies similar to those of the GMA homopolymer,<sup>33</sup> viz., 284.6 eV for the C–H species, 286.2 eV for the CO species, and 288.7 eV for the COO species. The graft concentration can be defined in this case as the [epoxide]/[F] ratio and derived from the COO spectral component to F 1s spectral area ratio, as each GMA molecule has one COO species and one epoxide unit. From Figure 2, it can be deduced that the graft concentration increases with increasing Ar plasma pretreatment time of the PTFE film. Increasing the Ar-plasma-pretreatment time results in more activated sites on the PTFE surface. The increase in active sites, in turn, leads to the formation of more peroxide and hydroperoxide species, upon exposure to air, for the subsequent UV-induced graft copolymerization. For PTFE surface with the low Ar-plasma-treatment time of 20 s, the underlying PTFE substrate



**Figure 2.** Wide scan and C 1s core-level spectra of the 20 s (parts a and b) and 100 s (parts c and d) Ar-plasma-pretreated PTFE film after the UV-induced graft copolymerization in 20 vol % GMA solution for 1 h.

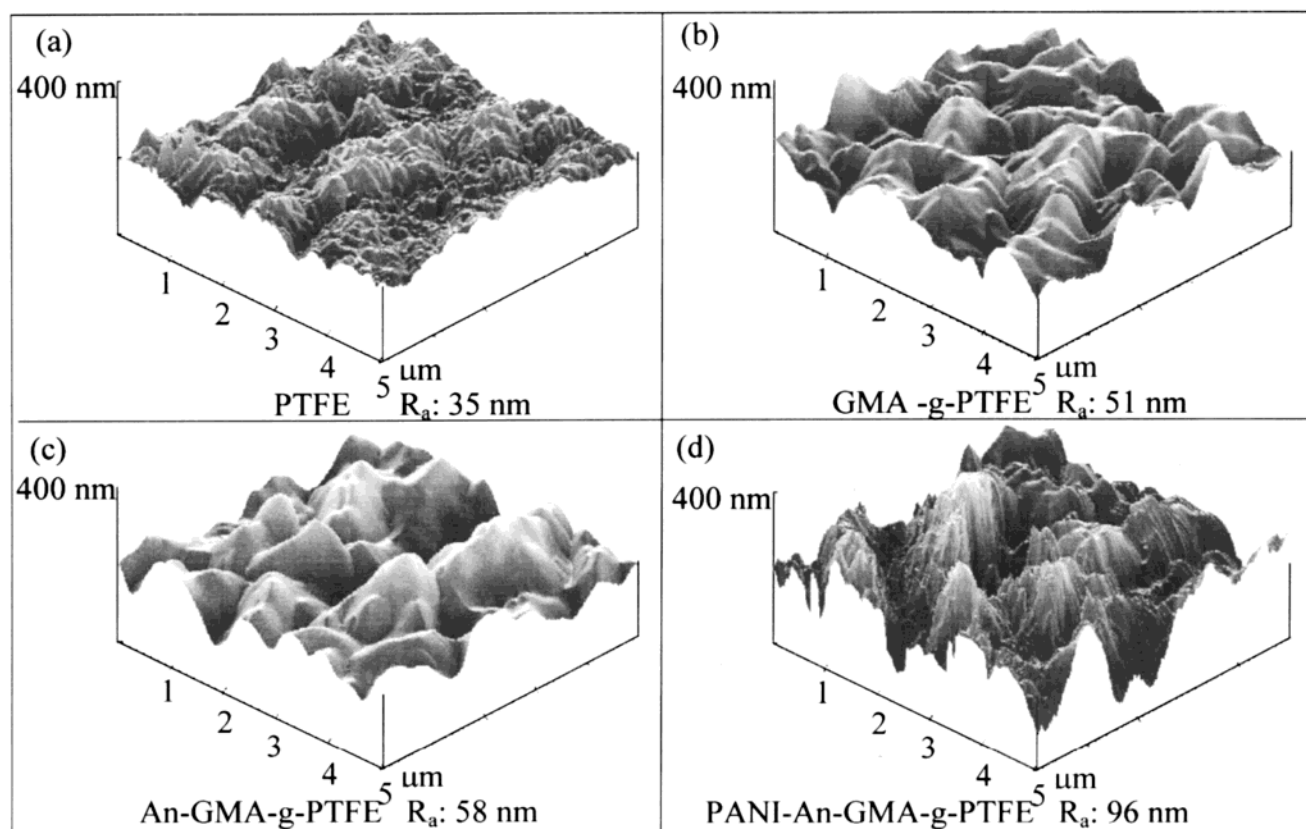
is still discernible, as indicated by the persistence of the CF<sub>2</sub> component signal at the BE of 291.4 eV<sup>32</sup> (Figure 2, parts a and b). At the Ar-plasma-pretreatment time of 100 s, the PTFE surface is completely covered by the grafted GMA polymer, as shown in Figure 2, parts c and d, to beyond the probing depth of the XPS technique (~7.5 nm in an organic matrix<sup>34</sup>). Furthermore, the CH:CO:COO peak area ratio for this surface with a high graft concentration of the GMA polymer is about



**TABLE 1: Effect of Plasma Pretreatment Time, GMA Monomer Concentration, and UV Graft Copolymerization Time on the Graft Copolymerization PTFE Film with GMA**

plasma time (s) <sup>a</sup>	[epoxide]/[F] <sup>b</sup>	GMA monomer concentrated (vol %) <sup>c</sup>	[epoxide]/[F]	UV graft copolymerization time (h) <sup>d</sup>	[epoxide]/[F]
0	0	10	0.5	0.5	0.9
20	0.8	20	7.5	0.8	24.8
40	4.8	30	35	1.2	∞
60	7.5	40	∞		
80	8.5				
100	∞				

<sup>a</sup> Graft copolymerization conditions: UV graft copolymerization time = 1 h, GMA concentration = 20 vol %. <sup>b</sup> Based on the corrected area ratios of the COO component at 288.7 eV in the C 1s spectrum and the F 1s spectrum. <sup>c</sup> Graft copolymerization conditions: plasma time = 60 s, UV graft copolymerization time = 1 h. <sup>d</sup> Graft copolymerization conditions: plasma time = 60 s, GMA monomer concentration = 30 vol %.



**Figure 3.** The three-dimensional AFM images of (a) a pristine PTFE film, (b) a GMA-g-PTFE film with complete GMA polymer coverage, (c) an An-GMA-g-PTFE film with a [N]/[C] of 0.07, and (d) a PANI-An-GMA-g-PTFE film with a [N]/[C] ratio of 0.10.

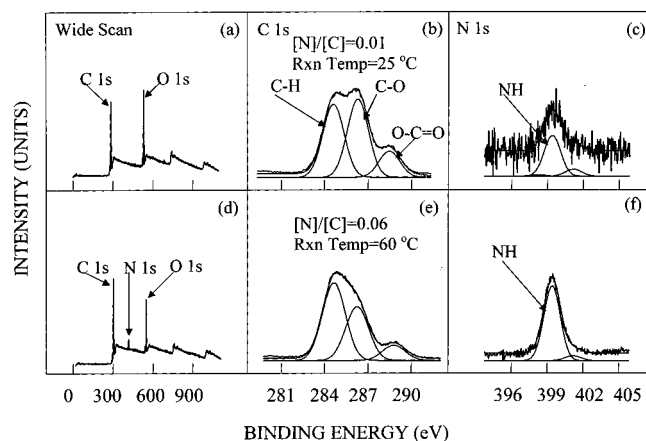
3:3:1, which is equivalent to the theoretical ratio of 3:3:1 dictated by the chemical structure of the GMA polymer. The effect of Ar-plasma-pretreatment time of the PTFE substrate on the graft concentration of GMA polymer is summarized in Table 1.

Table 1 also shows the effect of GMA monomer concentration on the graft concentration of the GMA polymer on the 60 s Ar-plasma-pretreated PTFE film. The UV graft copolymerization time was kept at 1 h. The data in Table 1 indicate that the graft concentration, expressed as the [epoxide]/[F] ratio, increases with increasing monomer concentration. Complete coverage of the PTFE surface can be achieved with a GMA monomer concentration of less than 40 vol %. As to the effect of UV graft copolymerization time on the graft concentration of the GMA polymer on the 60 s Ar-plasma-pretreated PTFE film, the data in Table 1 suggests that the PTFE film surface has been completely covered by the GMA polymer at UV graft copolymerization above 1.2 h.

Based on the observed effects of Ar-plasma-pretreatment time, monomer concentration, and UV graft copolymerization time on the graft concentration, the optimum conditions chosen

for this study to achieve the complete coverage of PTFE surface with GMA polymer are 80 s of Ar-plasma-pretreatment time, 20 vol % GMA monomer concentration, and 2 h of UV-induced graft copolymerization time. Under this set of optimum conditions, the surface morphology of the PTFE film revealing the complete coverage by the grafted GMA polymer is shown in the AFM image of Figure 3b. The average surface roughness ( $R_a$ ) of this GMA-g-PTFE surface, as derived from the AFM micrograph, is about 51 nm, in comparison to that of 35 nm for the pristine PTFE film (Figure 3a). The increase in surface roughness further confirms the presence of grafted GMA polymer on the PTFE surface. The wide scan and C 1s core-level spectra of this graft-modified surface are grossly similar to those shown in Figure 2, parts c and d, for the PTFE surface with complete GMA polymer coverage.

**Reactive Coupling of An with the Epoxide Moiety of the Grafted GMA Polymer: The An-GMA-g-PTFE Surface.** The GMA graft-copolymerized PTFE surface can be further functionalized through reactions with amines, including the less reactive aromatic amine, such as aniline (An). The reaction is



**Figure 4.** Wide scan, C 1s and N 1s core-level spectra of a GMA-g-PTFE film after reaction with aniline in 20 vol % ethanol solution of aniline for 4 h at 25 °C (parts a–c) and at 60 °C (parts d–f).

allowed to proceed in ethanol since alcohols can act as catalysts in the ring-opening reaction of the epoxides.<sup>35</sup> Figure 4 shows the respective wide scan, C 1s and N 1s spectra of the GMA-g-PTFE films with complete surface coverage by the GMA polymer after reactive coupling with An in 20 vol % ethanol solution of An for 4 h at 25 °C (parts a–c), and 60 °C (parts d–f). The extent of reaction can be expressed as the [N]/[C] molar ratio, determined from the corrected spectral area ratio of the C 1s and N 1s core-level spectra. If the GMA-g-PTFE surface was completely covered by aniline to beyond the probing depth of the XPS technique, the [N]/[C] ratio should approach the value of about 0.17 since every aniline unit had one nitrogen atom and six carbon atoms. The XPS results in Figure 4 indicate that the coupling reaction is greatly affected by the reaction temperature. The [N]/[C] molar ratio increases from 0.01 to 0.06 when the reaction temperature is increased from 25 to 60 °C. Thus, for reaction carried out at near room temperature, the coupling reaction does not proceed to a significant extent. At the elevated temperature of 60 °C, the nitrogen signal in the wide scan spectrum of Figure 4d is fairly strong. Furthermore, when aniline reacts with the epoxide group on the GMA-g-PTFE surface, the covering of the substrate surface by aniline leads to a decrease in the relative signal intensities of the CO and COO species, as shown in Figure 4e. Furthermore, the N 1s core-level spectra in Figure 4, parts c and f, suggest that the reaction between the epoxide groups and aniline involves only the primary amine. The coupled amine functional groups probably do not undergo further reaction with the epoxide groups as the N 1s core-level spectra are dominated by the NH peak component at the BE of 399.4 eV.<sup>36</sup> The phenomenon probably has resulted from the presence of high concentration (higher than 20 vol %) of aniline, which contains primary amine, in the reaction solution mixture and the fact that the reactivity of the primary amine toward the epoxide is higher than that of the secondary amine.

The effect of temperature, aniline concentration, and reaction time on the extent of the coupling reaction between the epoxide groups of the GMA polymer and aniline is summarized in Table 2. Thus, the extent of the reaction, expressed as the [N]/[C] ratio, increases with increasing temperature. At temperatures above 60 °C, the effect of temperature on the extent of the reaction diminishes. Furthermore, as the boiling point of ethanol is only about 78 °C, the highest reaction temperature chosen for the coupling reaction in this study is 70 °C. For coupling reaction carried out at the temperature of 50 °C for 4 h on the GMA-g-PTFE surface with complete GMA polymer coverage,

**TABLE 2: Effect of Temperature, Aniline Monomer Concentration, and Reaction Time on the Coupling Reaction between GMA and Aniline<sup>a</sup>**

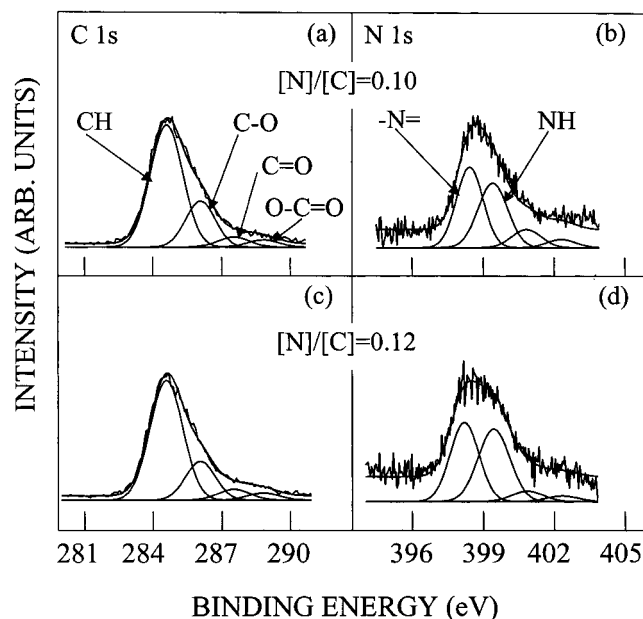
temperature (°C) <sup>b</sup>	aniline monomer concentration (vol %) <sup>c</sup>		coupling reaction time (h) <sup>d</sup>		
	[N]/[C]		[N]/[C]		[N]/[C]
25	0.01	35	0.05	2	0.06
40	0.03	50	0.05	4	0.06
50	0.05	60	0.06	6	0.07
60	0.06	80	0.04	8	0.07
70	0.07	100	0.03	10	0.07

<sup>a</sup> Coupling reaction of aniline with the epoxide groups of GMA on the GMA-g-PTFE surface having complete GMA polymer coverage. The extent of coupling reaction, expressed as [N]/[C] mole ratio, was determined from the curve-fitted N 1s and C 1s core-level spectral area ratio. <sup>b</sup> Other reaction conditions: aniline monomer concentration = 20 vol %, coupling reaction time = 4 h. <sup>c</sup> Other reaction conditions: temperature = 50 °C, coupling reaction time = 4 h. <sup>d</sup> Other reaction conditions: temperature = 60 °C, aniline concentration = 60 vol %.

the [N]/[C] ratio does not change appreciably when the aniline concentration is increased from 20 to 60 vol %. On the other hand, however, when the aniline concentration is increased to above 60 vol %, the [N]/[C] ratio begins to decrease. This phenomena may be associated with the fact that the alcohol solvent is known to promote the ring-opening reaction of the epoxides.<sup>35</sup> The solvent effect becomes less important at ethanol concentration below 40 vol %. The effect of reaction time on the extent of the coupling reaction was also shown in Table 2. The reaction was carried out at the temperature of 60 °C and the aniline concentration of 60 vol % on a GMA-g-PTFE surface with complete GMA polymer coverage. The extent of reaction, expressed as the [N]/[C] ratio, increases with increasing reaction time. However, at reaction time above 6 h, the [N]/[C] ratio does not seem to increase further. This result indicates that the reaction is not limited by the rate of diffusion of aniline to the epoxide groups of the GMA polymer and all the epoxide functional groups probably have been consumed.

Based on the observed effects of the experimental variables on the extent of the coupling reaction between the epoxide groups of the grafted GMA polymer and aniline, the set of optimum conditions for achieving the maximum extent of reaction appears to be 60 °C for the reaction temperature, 60 vol % for the aniline concentration, and 6 h for the reaction time. Based on the above reaction conditions, the extent of the coupling reaction, expressed as the [N]/[C] ratio, is about 0.07. This ratio is about half of the theoretical ratio required for the complete coverage of the GMA-g-PTFE surface by aniline to beyond the probing depth of the XPS technique. The lack of complete coverage by aniline must have resulted, at least in part, from the fact that the coupled aniline units are probably distributed along the grafted GMA chains. The surface morphology of the so-modified PTFE film (An-GMA-g-PTFE) is shown in the AFM micrograph of Figure 3c. The average surface roughness ( $R_a$ ) is about 58 nm, which is higher than that of the original GMA-g-PTFE surface. The increase in  $R_a$  is consistent with the presence of the coupled aniline units on the grafted GMA chains. The above An-GMA-g-PTFE film with a [N]/[C] ratio of 0.07 is used in the final oxidative graft polymerization of aniline.

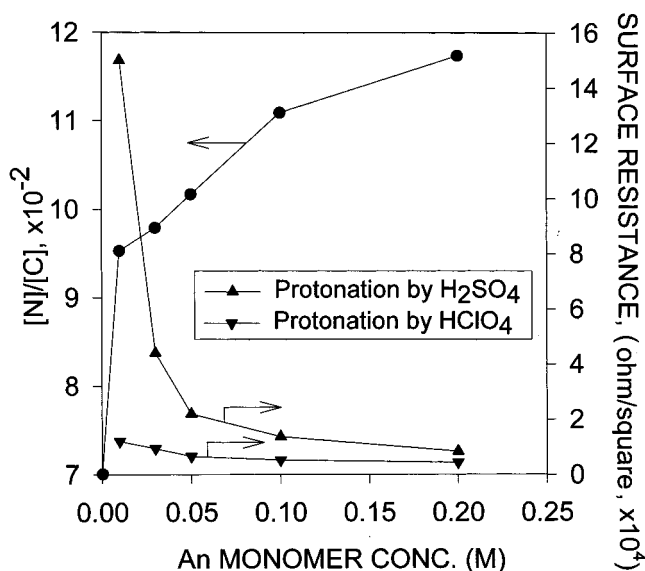
**Oxidative Graft Polymerization of Aniline onto the An-GMA-g-PTFE Film: The PANI-An-GMA-g-PTFE Surface.** Oxidative graft polymerization of aniline was carried out on the An-GMA-g-PTFE film which had a [N]/[C] ratio of about 0.07. The high surface concentration of the immobilized aniline units will help to promote the subsequent oxidative graft



**Figure 5.** C 1s and N 1s core-level spectra of an An-GMA-g-PTFE film after oxidative graft polymerization with aniline in 0.03 M aniline solution (parts a and b) and in 0.2 M aniline solution (parts c and d). The spectra were obtained after the films had been deprotonated in 0.5 M NaOH.

polymerization of aniline. Figure 5 shows the C 1s and N 1s core-level spectra of the An-GMA-g-PTFE film after the oxidative graft polymerization in 0.5 M  $\text{H}_2\text{SO}_4$  containing (parts a and b) 0.03 M aniline, and (parts c and d) 0.2 M aniline, followed by deprotonation of the surface-grafted polyaniline (PANI) salt with 0.5 M NaOH to convert the PANI salt to its neutral emeraldine (EM) base form. The reaction conditions are similar to those used for the oxidative polymerization of aniline during the preparation of the PANI homopolymer.<sup>22,31</sup> The graft concentration can also be expressed as the  $[\text{N}]/[\text{C}]$  mole ratio. The N 1s core-level spectra in Figure 5, parts b and d, also show the presence of the quinonoid imine ( $=\text{N}-$  structure), benzenoid amine ( $-\text{NH}-$  structure) and positively charged nitrogen ( $\text{N}^+$  structure), which correspond, respectively, to peak components with bonding energies (BEs) at about 398.2, 399.4, and  $>400$  eV.<sup>36</sup> Furthermore, the presence of almost equal amounts of imine and amine nitrogen in the N 1s core-level spectra is consistent with the intrinsic redox state ( $[\text{N}]/[\text{NH}]$  ratio) of the EM base form of PANI.<sup>37</sup> The residual high BE tail in the N 1s spectra probably has originated from the surface oxidation products or weakly charge-transferred complex oxygen.<sup>31</sup>

Figure 6 shows the increase in the graft concentration of PANI with increasing aniline concentration. When the aniline concentration is above 0.10 M, the increase in graft concentration becomes moderate. The PANI graft concentration on the An-GMA-g-PTFE surface for oxidative graft polymerization carried out in 0.20 M aniline can reach about 0.12 or about two-thirds of that of the aniline homopolymer which has a  $[\text{N}]/[\text{C}]$  ratio of 0.17. The  $[\text{N}]/[\text{C}]$  ratio of 0.12 for the aniline graft polymerized surface suggests an aniline/GMA molar ratio of about 3, as each GMA unit also contributes 7 carbon atoms to the copolymer structure at the surface. The significantly enhanced  $[\text{N}]/[\text{C}]$  ratio over that of the An-GMA-g-PTFE film, which has a  $[\text{N}]/[\text{C}]$  of 0.07, confirms the oxidative graft polymerization of aniline onto the An-GMA-g-PTFE surface. The process is shown schematically in Figure 1. The presence of grafted PANI (in EM base form) on the PTFE surface is

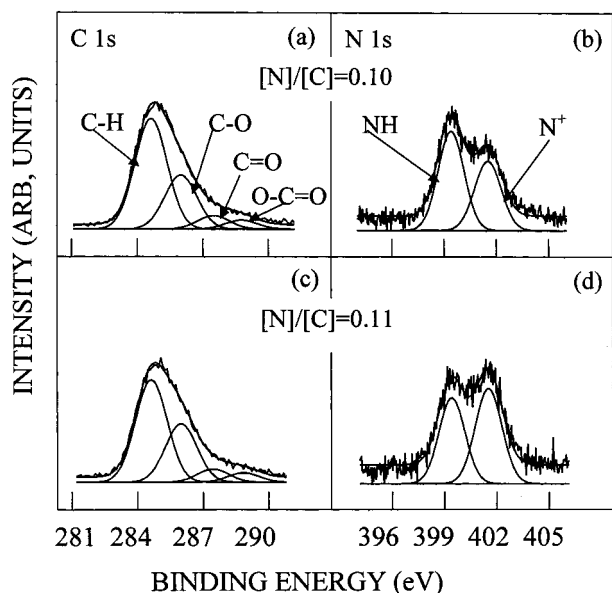


**Figure 6.** Effect of aniline monomer concentration used during the oxidative graft polymerization on the PANI graft concentration, expressed as the  $[\text{N}]/[\text{C}]$  ratio, and on the surface resistance of the corresponding PTFE films after reprotonation by 1 M  $\text{H}_2\text{SO}_4$  and 1 M  $\text{HClO}_4$ .

further confirmed by the UV-visible absorption spectrum of the PANI-An-GMA-g-PTFE film. Although somewhat obscured by the opacity of the PTFE film, the absorption spectrum exhibits two broad absorption maxima, one centered at around 330 nm and the other at around 600 nm. The two absorption peaks are attributable, respectively, to the  $\pi-\pi^*$  transition of the benzenoid rings and the exciton-like absorption of the quinonoid rings.<sup>37</sup> Finally, the presence of surface-grafted PANI is also confirmed by the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The appearance of the absorption bands of about equal intensities at 1595 and 1503  $\text{cm}^{-1}$ , attributable to the quinonoid unit and benzenoid unit, respectively, suggests the presence of PANI in its 50% intrinsically oxidized EM base form.<sup>37</sup>

To investigate the surface conductivity of the aniline graft polymerized An-GMA-g-PTFE surface (the PANI-An-GMA-g-PTFE surface), acid reprotonation has been carried out to convert the insulating EM base polymer into the conductive EM salt form of PANI. Two types of inorganic acid,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$ , were used to examine the protonation behavior of the surface-modified PTFE. The respective C 1s and N 1s core-level spectra of the PANI-An-GMA-g-PTFE surface ( $[\text{N}]/[\text{C}] = 0.10$ ) after reprotonation for 1 h in 1 M  $\text{H}_2\text{SO}_4$  solutions are shown in Figure 7, parts a and b. The corresponding C 1s and N 1s spectra of the surface after reprotonation in 1 M  $\text{HClO}_4$  are shown in Figure 7, parts c and d. Comparison of the N 1s core-level spectra in Figure 7, parts b and d, to that of the undoped (deprotonated) PANI-An-GMA-g-PTFE surface (Figure 5b) suggests that the surface-modified PTFE films can be effectively reprotonated by  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$ , as indicated by the disappearance of the  $-\text{N}=$  component and the appearance of the corresponding proportion of the positively charged nitrogen in both spectra, as protonation occurs preferentially at the imine units.<sup>38</sup> The reprotonation of the PANI-An-GMA-g-PTFE surface is also indicated by the change in the color of the film from blue (insulating state) to green (conductive state). The UV-visible absorption spectrum of the corresponding film reveals the appearance of a characteristic polaron peak at about 430 nm and a localized polaron absorption band (broad) between





**Figure 7.** C 1s and N 1s core-level spectra of a PANI-An-GMA-g-PTFE film with a [N]/[C] ratio of 0.10 after reprotonation in 1 M  $\text{H}_2\text{SO}_4$  (parts a and b), and a PANI-An-GMA-g-PTFE film with a [N]/[C] ratio of 0.11 after reprotonation in 1 M  $\text{HClO}_4$  (parts c and d).

800 and 1000 nm. The absorption spectrum is thus not unlike that of the protonated EM base polymer.<sup>37</sup>

The successfully grafting of the PANI chains and the preservation of their deprotonation–reprotonation behavior are further confirmed by the effect of aniline concentration on the extent of oxidative graft polymerization and on the resulting surface resistance of the modified PTFE films after reprotonation by 1 M  $\text{H}_2\text{SO}_4$  and 1 M  $\text{HClO}_4$ , (Figure 6). Generally, the surface resistance decreases with increasing aniline concentration, consistent with the effect of aniline monomer concentration on the graft concentration. The surface resistance of the PANI-An-GMA-g-PTFE film reprotonated by 1 M  $\text{H}_2\text{SO}_4$  is slightly higher than that of the corresponding surface reprotonated by 1 M  $\text{HClO}_4$ . Thus,  $\text{HClO}_4$  appears to be a more effective dopant than  $\text{H}_2\text{SO}_4$ . At the aniline concentration of 0.2 M used for the oxidative graft copolymerization, the surface resistance is about  $5 \times 10^3 \Omega/\text{square}$ , in comparison to the surface resistance of  $10^{16} \Omega/\text{square}$  for the pristine PTFE<sup>39</sup> and the bulk conductivity of 1–100 S/cm for the protonated PANI films.<sup>40</sup> The relation between surface resistance ( $R_s$ ) and bulk resistivity ( $\rho$ ) is given by  $R_s = \rho/t$ , where  $t$  is the thickness of the grafted PANI film. Thus, using 7.5 nm (the probing depth of the XPS technique<sup>34</sup>) as the thickness of the grafted aniline polymer layer, the bulk resistivity is in the order of  $10^{-2} \text{ ohm cm}$ , which is equivalent to a bulk conductivity value ( $\sigma$ ) in the order of  $10^2 \text{ S/cm}$ , as  $\sigma = 1/\rho$ . The preservation of equivalent bulk conductivity of PANI after graft polymerization on the PTFE film makes the present surface modification technique potentially valuable for antistatic applications and in shielding of electromagnetic interference (EMI). Furthermore, the surface resistance of the PANI-An-GMA-g-PTFE film can be changed by varying the protonation level<sup>37</sup> since the surface of the grafted PANI is not unlike that of the PANI homopolymer. When the surface composition is measured by XPS, the graft concentration, or the [N]/[C] ratio, is lower than that of polyaniline homopolymer. Nevertheless, the chemical states and physical properties of the PANI-An-GMA-g-PTFE surface are not unlike that of the aniline homopolymer, as shown by the data in Figures 5–7. Thus, the grafted PANI chains must have intermixed with the grafted GMA polymer chains on the PTFE surface.

The surface morphology of PANI-An-GMA-g-PTFE film is revealed by the AFM image shown in Figure 3d. This particular surface has a graft concentration, or [N]/[C] ratio, of 0.10. The average surface roughness ( $R_a$ ) is about 96 nm which is much higher than that of the original An-GMA-g-PTFE surface shown in Figure 3c. This increase in  $R_a$  value is due to the oxidative graft polymerization of aniline on the surface of the An-GMA-g-PTFE film of Figure 3c. Furthermore, this increase in  $R_a$  value is also larger than that which resulted from the graft copolymerization of GMA onto the Ar-plasma-pretreated PTFE surface (compare Figure 3, parts a and b). During the oxidative graft polymerization of An, steric hindrance of the rigid benzenoid and quinonoid units of the grafted PANI chains must have contributed to the high surface roughness.

Finally, it is appropriate to emphasize that the surface graft polymerized aniline chains are covalently tethered on the PTFE surface. The grafted PANI chains cannot be removed by extraction with organic solvents. The present surface modification approach differs from the earlier works which involve coating or physical adsorption of the conductive PANI on the surface-modified PTFE substrates.<sup>29,41,42</sup> The covalent bonding of the aniline polymer as a result of surface molecular design and the low surface resistance of the resulting PTFE film make the present method a viable and promising approach to the preparation of surface-conductive molecular and polymeric composites.

## Conclusion

Argon-plasma-pretreated PTFE films were subjected to surface modification via UV-induced graft copolymerization with GMA (the GMA-g-PTFE surface). The epoxide groups of the grafted GMA chains were reactively coupled with aniline (the An-GMA-g-PTFE surface) and then subjected to oxidative graft polymerization with aniline (the PANI-An-GMA-g-PTFE surface). The composition and microstructure of the graft-polymerized surfaces were characterized by XPS and AFM measurements, respectively. In general, the graft concentration of the GMA polymer increased with increasing Ar-plasma-pretreatment time, GMA concentration, and UV graft copolymerization time. The extent of the coupling reaction between the epoxide ring in the grafted GMA chain and aniline increased with increasing temperature and reaction time. The ethanol solvent for the epoxide-ring-opening reaction also served as the catalyst and must be present in more than 40 vol % to achieve the optimum effect. When the GMA surface graft-copolymerized and aniline-coupled PTFE films were oxidatively polymerized with aniline, the graft concentration increased with increasing aniline concentration. The intrinsic oxidation states, protonation/deprotonation behavior, and electrical conductivity of the aniline polymer were preserved in PANI grafted on the PTFE surface. The optimum surface resistance of the PANI-An-GMA-g-PTFE films was in the order of  $10^4 \Omega/\text{square}$ , in comparison to  $10^{16} \Omega/\text{square}$  for the pristine PTFE.

## References and Notes

- Joo, J.; Epstein, A. J. *Appl. Phys. Lett.* **1994**, 65 (18), 2278.
- Clark, D. T.; Dilks, A.; Shuttleworth, D. In *Polymer Surfaces*; Clark, D. T., Feast, W. J., Eds.; Wiley: New York, 1978; Chapter 9, p 185.
- Penn, L. S.; Wang, H. *Polym. Adv. Tech.* **1994**, 5, 809.
- Uyama, Y.; Kato, K.; Ikada, Y. *Adv. Polym. Sci.* **1998**, 137, 1.
- Kang, E. T.; Neoh, K. G.; Tan, K. L.; Uyama, Y.; Morikawa, N.; Ikada, Y. *Macromolecules* **1992**, 25, 1959.
- Ranby, B. *Polym. Eng. Sci.* **1998**, 38, 1229.
- Youngblood, J. P.; McCarthy, T. J. *Macromolecules* **1999**, 32, 6800.
- Chen, W.; Fadeev, A. Y.; Hsieh, M. C.; Oner, D.; Youngblood, J. P.; McCarthy, T. J. *Langmuir* **1999**, 15, 3395.

- (9) Zhao, B.; Brittain, W. J. *Macromolecules* **1999**, *32*, 796.
- (10) Zhao, B.; Brittain, W. J. *Macromolecules* **2000**, *33*, 342.
- (11) Tan, K. L.; Kang, E. T.; Neoh, K. G. *Polym. Adv. Technol.* **1994**, *5*, 171.
- (12) Angelopoulos, M.; Asturius, G. E.; Ermer, S. P.; Ray, A.; Scherr, E. M.; MacDiarmid, A. G.; Akhtar, M.; Kiss, Z.; Epstein, A. J. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 151.
- (13) MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1994**, *65*, 103.
- (14) Ahmad, N.; MacDiarmid, A. G. *Synth. Met.* **1996**, *78*, 103.
- (15) Chen, S. A.; Chuang, K. R.; Chao, C. L.; Lee, H. T. *Synth. Met.* **1996**, *82*, 207.
- (16) Trivedi, D. C.; Dhawan, S. K. In *Polymer Science Contemporary Themes*; Sivaram, S., Ed.; Tata McGraw-Hill: New Delhi, 1991; Vol. 2, p 746.
- (17) Joo, J.; Wu, C. Y.; Benatar, A., Jr.; Faisst, C. F.; Zegarski, J.; MacDiarmid, A. G. In *Intrinsically Conducting Polymers: An Emerging Technology*; Aldissi, M., Ed.; Kluwer Press: Norwell, MA, 1993; p 165.
- (18) Chen, Y. J.; Kang, E. T.; Neoh, K. G.; Wang, P.; Tan, K. L. *Synth. Met.* **2000**, *110*, 47.
- (19) Heeger, A. J.; Yang, Y.; Westerweele, E.; Zhang, C.; Cao, Y.; Smith, P. In *The Polymeric Materials Encyclopedia. Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press Inc., Boca Raton, FL, 1996; p 5500.
- (20) MacDiarmid, A. G.; Yang, L. S.; Huang, W. S.; Humphrey, B. D. *Synth. Met.* **1987**, *18*, 393.
- (21) Huang, S. W.; Neoh, K. G.; Shih, C. W.; Lim, D. S.; Kang, E. T.; Tan, K. L. *Synth. Met.* **1998**, *96*, 117.
- (22) Chen, Y. J.; Kang, E. T.; Neoh, K. G.; Tan, K. L. *Europ. Polym. J.*, in press.
- (23) Shacklett, L. *Polym. Prepr.* **1994**, *35*, 248.
- (24) Olmedo, L.; Hourquebie, P.; Jousse, F. In *Handbook of Organic Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons Ltd.: New York, 1997; Vol. 3, p 367.
- (25) Wu, C. Y.; Benatar, A. *Polym. Eng. Sci.* **1997**, *37*, 738.
- (26) Park, J. M.; Matienzo, L. J.; Spencer, D. F. *J. Adhes. Sci. Technol.* **1991**, *5*, 153.
- (27) Granneman, E. H. A. *Thin Solid Films* **1993**, *228*, 1.
- (28) Silvain, J. F.; Ehrhardt, J. J.; Picco, A.; Lutgen, P. *ACS Symp. Ser.* **1990**, *440*, 453.
- (29) Van Dyke, L. S.; Brumlik, C. J.; Liang, W.; Lei, J.; Martin, C. R.; Yu, Z.; Li, L.; Collins, G. J. *Synth. Met.* **1994**, *62*, 75.
- (30) Suzuki, M.; Kishida, A.; Iwata, H.; Ikada, Y. *Macromolecules* **1986**, *19*, 1804.
- (31) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Adv. Polym. Sci.* **1993**, *106*, 135.
- (32) Wu, S. Y.; Kang, E. T.; Neoh, K. G.; Tan, K. L. *Macromolecules* **1999**, *32*, 186.
- (33) Wang, T.; Kang, E. T.; Neoh, K. G.; Tan, K. L.; Cui, C. Q.; Lim, T. B. *J. Adhes. Sci. Technol.* **1997**, *11*, 679.
- (34) Tan, K. L.; Woon, L. L.; Wong, H. K.; Kang, E. T.; Neoh, K. G. *Macromolecules* **1993**, *29*, 2832.
- (35) Rozenberg, B. A. *Adv. Polym. Sci.* **1986**, *75*, 73.
- (36) Kang, E. T.; Neoh, K. G.; Tan, T. C.; Khor, S. H.; Tan, K. L. *Macromolecules* **1990**, *23*, 2918.
- (37) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog. Polym. Sci.* **1998**, *23*, 277.
- (38) Ray, A.; Asturias, G. E.; Kershner, D. L.; Richter, A. F.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1989**, *29*, E141.
- (39) *Goodfellow Catalogue, (Metals, Alloys, Compounds, Ceramics, Polymers, Composites)*; Goodfellow Cambridge Ltd.: Cambridge, U.K., 1996/1997; p 447.
- (40) Trivedi, D. C. In *Handbook of Organic Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons Ltd., New York, 1997; Vol. 2, p 505.
- (41) Pun, M. Y.; Neoh, K. G.; Kang, E. T.; Loh, F. C.; Tan, K. L. *J. Appl. Polym. Sci.* **1995**, *56*, 355.
- (42) Kang, E. T.; Tan, K. L.; Kato, K.; Uyama, Y.; Ikada, Y. *Macromolecules* **1996**, *29*, 6872.