

Graft Polymerization of Methacrylic Acid onto Polytetrafluoroethylene Initiated by Alkylolithium/ Electron-Donating Solvents

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Received 20 October 2003; accepted 14 April 2004

DOI 10.1002/app.20926

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Graft polymerization of methacrylic acid (MAA) onto polytetrafluoroethylene (PTFE), initiated by the mixed solution of alkylolithium/hexamethylphosphoramide (HMPA) at low temperature, was studied. Using electron spin resonance (ESR), nuclear magnetic resonance, X-ray photoelectron and vibrational (infrared) spectroscopies, the chemical structure of the grafted poly(methacrylic acid) (PMAA) onto the PTFE (PTFE-g-PMAA) was investigated. The grafted PMAA was found to be located deeper than 2.5 nm from the surface of the PTFE. The molecular motion of the PTFE-g-PMAA was also studied by means of the tem-

perature-dependent ESR spectra of the spin-labeled PTFE-g-PMAA. The results suggested that the molecular motion of the grafted PMAA chain was mainly controlled by that of the principal PTFE chain, and the evaluated activation energy was lower for the grafted PMAA chain (e.g., 6.5 kJ/mol at temperature range below 295 K) than that for the PMAA homopolymer (13.2 kJ/mol). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 923–931, 2004

Key words: polytetrafluoroethylene (PTFE); NMR; ESR; graft copolymers; spin label

INTRODUCTION

Polytetrafluoroethylene (PTFE) has been widely used in the electronics, chemical, and medical industries, because of its excellent properties such as high chemical inertness, low surface energy, high thermal stability, low dielectric constant, and low dielectric loss,^{1–3} or biological inertness in the human body.⁴ Numerous attempts have been made to introduce polar groups such as hydroxyl group or carboxyl group into PTFE to enhance its adhesiveness to other materials, or to improve its biocompatibility, especially in biomedical applications.⁵

The objective of the present study was to develop a new surface activation reaction of PTFE that can be followed by covalent binding of proteins or peptides, to enhance the biocompatibility of PTFE. Because PTFE is highly resistant against most chemical substances, somewhat complex reaction conditions and complicated equipment are required for the elimination of fluorine atoms. Physical processes such as radiation grafting,^{6,7} UV excimer laser treatment,⁸ ion-beam irradiation,⁹ or treatment by plasma¹⁰ require somewhat expensive

equipment and have difficulties in controlling the reaction. As chemical treatments, defluorination with alkali metal,¹¹ lithium–amalgam,¹² aromatic radical anions such as naphthalene radical anion¹³ or benzoin dianion,¹⁴ or alkylolithium with a catalytic amount of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) at 423 K,¹⁵ have been studied. In these chemical reactions, a dark brown colored carbonaceous layer is simultaneously formed on the modified PTFE surface upon reduction of the C—F bonds because the reduction reaction may be very fast. The rapid reaction makes it difficult to control the number of carbon radicals formed on the PTFE surface after defluorination; the radicals can initiate the following graft polymerization. To date little is known about the graft polymerization initiated by the radical species formed during the defluorination reaction of PTFE.

In our previous study, a spectroscopic study was carried out for defluorination of PTFE using an alkylolithium (RLi)/electron-donating solvent (ED-S) system.¹⁶ It was found that an electron from a radical species, which was generated in the RLi/ED-S solution, was transferred onto PTFE molecule so as to eliminate fluorine atoms from the PTFE and to form carbon-centered radicals on the PTFE. No carbonaceous layer was formed on the defluorinated surface, and the crystallinity and the molecular weight were not altered by the defluorination reaction.

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The present study aimed to develop graft polymerization of methacrylic acid (MAA) onto PTFE initiated by the RLi/ED-S system. The amino groups of proteins or peptides can easily be bonded to the carboxyl groups of the grafted poly(methacrylic acid) (PMAA). The graft polymerization was studied using electron spin resonance (ESR), nuclear magnetic resonance (NMR), X-ray photoelectron, ultraviolet-visible (UV-vis), and vibrational [infrared (IR)] spectroscopies. The molecular motion of the grafted PMAA chain were also studied by the temperature-dependent ESR spectra of the spin-labeled PMAA chain grafted onto the PTFE.

EXPERIMENTAL

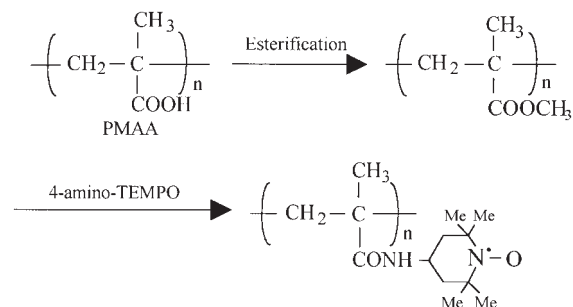
Materials

The following reagents were used as received: PTFE powder (F-104, average particle size = 560 μm ; Daikin Industries, Osaka, Japan), PTFE film (Asahi Glass Co., Tokyo, Japan), *tert*-butyllithium (*t*-BuLi, 1.7M solution in pentane; Aldrich, Milwaukee, WI), hexamethylphosphoramide (HMPA, Aldrich), 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO, Wako Pure Chemicals, Osaka, Japan), methyl alcohol (methanol), 1,2-dichloroethane, sulfuric acid, and sodium methoxide. Methacrylic acid (MAA, Wako Pure Chemicals) was used after distillation. Tetrahydrofuran (THF) was distilled over sodium metal to remove any dissolved water.

Graft polymerization of MAA onto PTFE

Sample preparations

To a *t*-BuLi solution was added HMPA at a 1 : 1M ratio, then the mixed solution (5 mmol of *t*-BuLi and 5 mmol of HMPA) was added to PTFE powder (50 mg) under an argon atmosphere at 273 K. The mixture was kept for 0.5 h at the same temperature, after which the solvent was removed from the mixture and the remaining PTFE was washed three times with THF at 273 K. MAA was then added to the washed PTFE, and the mixture was kept at 353 K for 8 h. The mixture was next washed with distilled water at 330 K for 24 h to remove any water-soluble residues, then washed with ethanol for 24 h, and finally washed with acetone for 24 h to remove any organic residues. These prepared samples were subjected to NMR and IR absorption measurements. For XPS measurement, the PTFE film was used instead of the PTFE powder. Furthermore, to obtain information on the chemical structure of the PTFE that reacted with *t*-BuLi/HMPA, the sample of the PTFE that had reacted with the *t*-BuLi/HMPA mixture before addition of MAA was also subjected to the ESR NMR, XPS, UV-vis, and IR absorption measurements.



Scheme 1 Reaction scheme for spin-labeling of the PMAA chain.

Spectroscopies

For the ESR spectra measurement, all samples were prepared in Spectrosil ESR sample tubes and directly subjected to ESR measurement using a JEOL RE-1 spectrometer (JEOL, Tokyo, Japan) at 77 K and then at elevated temperatures.

For the NMR, XPS, UV-vis, and IR absorption spectra measurements, all the samples were washed with distilled water at 330 K for 24 h to remove any water-soluble residues, then washed with ethanol for 24 h, and finally washed with acetone for 24 h to remove any organic residues as mentioned above. The samples prepared in this manner were subjected to ¹³C-CP-MAS-NMR measurements, using a Bruker AMX-400 spectrometer (Bruker Instruments, Billerica, MA); XPS measurement, using a Perkin-Elmer Physical Electronics 5100 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT); and UV-vis absorption measurement using a Hitachi U-3400 spectrophotometer (Hitachi, Tokyo, Japan). The IR spectrum was obtained by the KBr powder method using a Perkin-Elmer Spectrum 2000 spectrometer.

To verify the generation of LiF on the reacted PTFE as the fluorine elimination product, the reacted PTFE, before washing with water, was subjected to a ⁷Li-CP-MAS-NMR measurement using an AMX 400 spectrometer with LiCl as the internal standard.

Spin-labeling of the grafted poly(methacrylic acid) and ESR measurement

The carboxyl group of the grafted PMAA was labeled with 4-amino-TEMPO according to the method^{17,18} shown in Scheme 1.

First, the methyl ester of the PMAA grafted on the PTFE was synthesized according to the following procedures. Sulfuric acid (0.2 mL) was added to the mixture of the grafted PMAA on the PTFE (1 g), methanol (5 mL), and 1,2-dichloroethane (15 mL); then the whole mixture was refluxed for 12 h, after which the reacted sample was washed with 1,2-dichloroethane. Next, 4-amino-TEMPO was reacted with the methyl

ester of the PMAA grafted onto the PTFE. That is, to 1 g of the methyl ester of the PMAA grafted on the PTFE, 0.67 g of sodium methoxide, 8 mL of methanol, and 0.0067 g of 4-amino-TEMPO were added, and the mixture was stirred for 24 h at room temperature. The reacted sample was then washed with methanol. Thus the grafted PMAA was spin-labeled with 4-amino-TEMPO and subjected to the ESR measurement.

RESULTS AND DISCUSSION

Generation of carbon-centered radicals on PTFE

The carbon-centered radicals on PTFE initiated graft polymerization of MAA. Here we start with briefly summarizing the generation of the radicals on PTFE¹⁶ before discussing the graft polymerization.

When the PTFE powder was reacted with the mixed solution of *t*-BuLi/HMPA, the color of the PTFE varied from its original white to dark brown. The ESR spectrum of the reacted PTFE gave a broad triplet with an isotropic hyperfine (*hf*) splitting of 23.0 G at 77 K, and each of the triplet lines was further split into 10 *hf* lines with a smaller splitting of 1.6 G at 300 K. The triplets can be attributed to two equivalent β -fluorine atoms of PTFE, and the 10 *hf* lines to the nine γ -hydrogen atoms of the *tert*-butyl (*t*-Bu) group [C(CH₃)₃]. Thus the formation of the carbon-centered radicals on the PTFE was identified.

The ⁷Li-MAS-NMR spectrum of the reacted PTFE, before washing with water, gave a ⁷Li resonance absorption peak at -0.30 ppm, whose chemical shift was attributed to the ⁷Li atom of LiF.¹⁹ Thus we could confirm the fluoride ion (F⁻) elimination from PTFE that was followed by the reaction with Li⁺ from *t*-BuLi to yield the LiF.¹²

The ¹³C-CP-MAS-NMR spectra gave a broad singlet at 142 ppm and two sharp peaks at 27.2 and 37.5 ppm. The latter two signals were attributed to the C(CH₃)₃ carbons from *t*-BuLi and a broad singlet was attributed to CF₂ carbon of PTFE.²⁰ Consistent with the ESR results, the ¹³C-NMR spectra also suggested the transference of *tert*-butyl (*t*-Bu) group [C(CH₃)₃] from the *t*-BuLi onto the defluorinated carbon.

The UV-vis absorption spectra of the reacted PTFE gave a broad absorption band in the 200–400 nm range that is characteristic of the π - π^* transition of C=C bonds.²¹ The IR spectra for the reacted PTFE gave an absorption around 1720 cm⁻¹ and the absorption could be attributed to the C=C stretching vibrational absorption of the monofluorinated olefin,¹⁴ consistent with the UV-vis spectra. Thus the conjugated C=C bond formation by the fluorine elimination reaction from PTFE was confirmed.

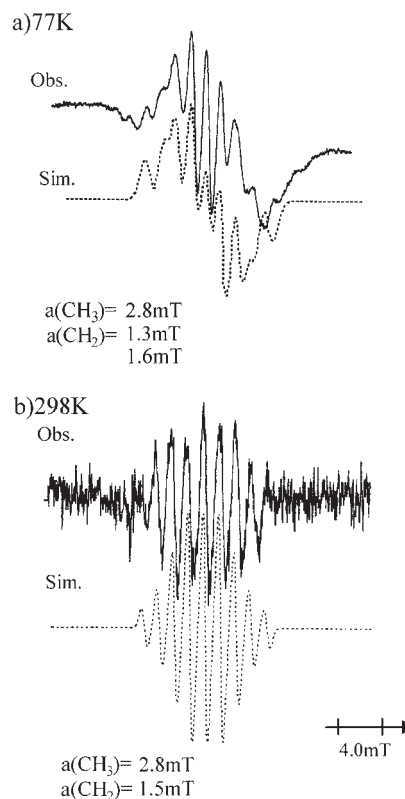
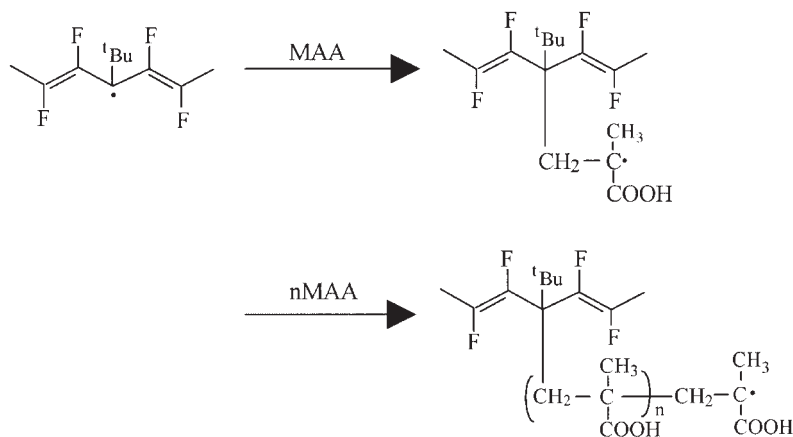


Figure 1 ESR spectra of the mixed solution of methacrylic acid and PTFE, which were reacted with *t*-BuLi/HMPA, observed at (a) 77 K and (b) 298 K. The spectra were simulated using the isotropic ¹H-*hf* splittings given in the figure.

Evidence for graft polymerization of MAA onto PTFE

Figure 1 shows the ESR spectra of the mixed solution of methacrylic acid with the PTFE that reacted with *t*-BuLi/HMPA solution at 77 and 298 K. The spectra consist of the following hyperfine (*hf*) splittings: $a(\text{CH}_3) = 2.8 \text{ mT}$ (3H), $a(\beta\text{-H}) = 1.3 \text{ mT}$ (1H), and $a(\beta\text{-H}) = 1.6 \text{ mT}$ (1H) for the spectrum at 77 K; and $a(\text{CH}_3) = 2.8 \text{ mT}$ (3H) and $a(\beta\text{-H}) = 1.5 \text{ mT}$ (2H) at 298 K. The *hf* values are in fairly good agreement with those of the propagating radical of PMAA.^{22,23} This result clearly shows that the carbon-centered radicals generated on PTFE react with methacrylic acid monomers to generate the propagating radicals of graft polymerization, a possible reaction scheme of which is presented in (Scheme 2).

The formation of PMMA grafted onto PTFE was confirmed by ¹³C-NMR and IR absorption spectra. After washing the samples with distilled water at 330 K for 24 h to remove any water-soluble residues, they were then washed with ethanol for 24 h, and finally washed with acetone for 24 h to remove any organic residues. The ¹³C-CP-MAS-NMR spectra of the PMAA homopolymer (*h*-PMAA) and the PTFE-*g*-PMAA (*t*-BuLi/HMPA/PTFE/MAA) are shown in



Scheme 2 Possible graft polymerization scheme of methacrylic acid initiated by the carbon-centered radicals generated on PTFE by t -BuLi/HMPA treatment.

Figure 2. In the spectrum of the h -PMAA, signals appeared at 11.3, 39.1, 48.9, and 180.3 ppm, and the chemical shifts were attributed to the carbons in the CH_3 , CH_2 , C, and COOH groups of the h -PMAA. For the PTFE- g -PMAA, the same peaks as in the h -PMAA were identified in addition to the peak at 142 ppm, attributed to the carbon of CF_2 . Figure 3 shows the IR spectra of the h -PMAA and the PTFE- g -PMAA. In the

h -PMAA spectrum, the absorption peaks at 1689 cm^{-1} as the $\text{C}=\text{O}$ stretching vibration, $3500\text{--}2500\text{ cm}^{-1}$ as the $\text{O}-\text{H}$ stretching vibration, and $1550\text{--}1350\text{ cm}^{-1}$ as the deformation vibration of $\text{C}-\text{H}$ and $\text{O}-\text{H}$ were identified. For the PTFE- g -PMAA, the same peaks as in the h -PMAA were identified in addition to the peaks attributed to PTFE: 1243 , 1231 , and 1152 cm^{-1} as the stretching vibration of $\text{C}-\text{F}$, and at $510\text{--}640\text{ cm}^{-1}$

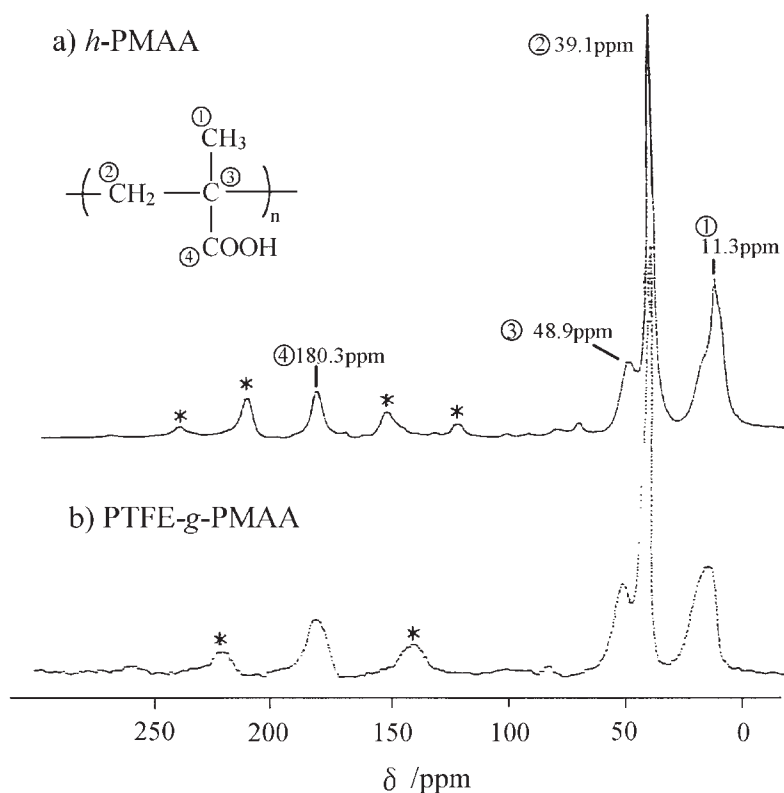


Figure 2 ^{13}C -CP-MAS-NMR spectra of (a) poly(methacrylic acid) homopolymer (h -PMAA) and (b) PTFE- g -PMAA (t -BuLi/HMPA/PTFE/MAA). The attribution of the chemical shifts is given in the figure. The peaks labeled with * are side-band signals.

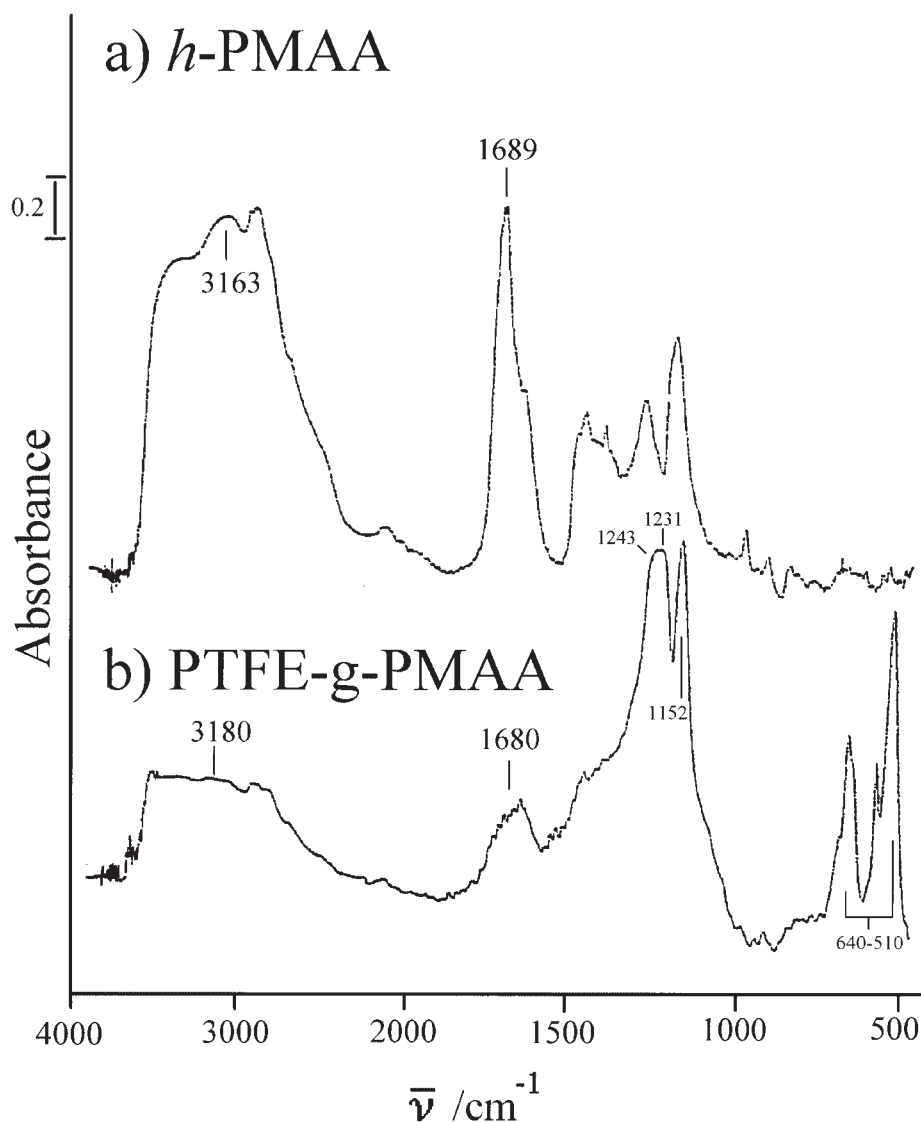


Figure 3 IR absorption spectra of (a) poly(methacrylic acid) homopolymer (*h*-PMAA) and (b) PTFE-*g*-PMAA.

as the deformation vibration. Thus, based on both the ^{13}C -CP-MAS-NMR and IR studies, we could successfully confirm the formation of PMAA grafted onto PTFE (PTFE-*g*-PMAA).

The grafting amount (wt %) was evaluated by thermogravimetry (TG), whose weight loss over the temperature range from 580 to 670 K resulted from the decomposition of PMAA. The amount of PMAA grafted onto PTFE was 0.75, 1.0, 1.5, 1.8, and 2.0 wt % for the reaction times of 0.15, 0.5, 2, 6, and 8 h, respectively, as shown in Figure 4; and the longer reaction time did not increase the amount of PMMA. This means that the radical polymerization reaction was terminated within 8 h. Based on the number of carbon-centered radicals on PTFE (1.9×10^{17}) by ESR, the average molecular weight for the reaction time of 8 h was estimated to be 67,000.

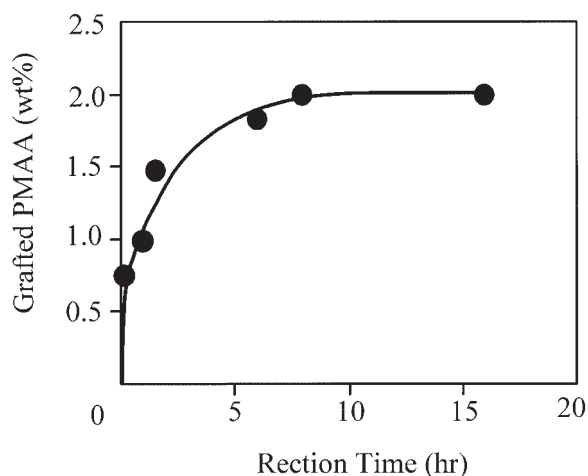
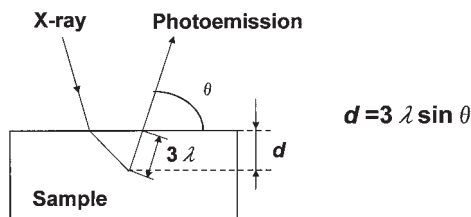


Figure 4 Amount of PMAA grafted on PTFE (%) (from TG) was plotted against reaction time (h).



Scheme 3 Dependency of photoemission angle (θ) on depth (d).

Crystallinity and molecular weight change of PTFE

The crystallinity of the PTFE was evaluated using a differential scanning calorimeter (DSC). The heat of fusion for the PTFE crystal was 18.8 and 18.6 J/g for the PTFE before and after the graft polymerization, respectively. It is well known that the crystallinity of the PTFE is dependent on the molecular weight, as shown in Suwa's equation.²⁴ Thus the results suggest that the crystallinity and the molecular weight of the PTFE were not altered by the graft polymerization.

Depth profiling by XPS

To obtain further information about the chemical structure of the grafted PMAA, angle-resolved XPS measurements were carried out. The depth profile of the average elemental composition can be obtained by changing the photoemission angle θ , with respect to the sample surface (Scheme 3).

The photoelectron signal intensity I , arising from a particular element, is given by

$$I \propto \int c(z) \exp(-z/\lambda) dz$$

where $c(z)$ is the function describing the variation of the concentration of the element in question with depth z and λ is the inelastic mean free path of the photoelectrons in the material.²⁵ When the distribution of the element in the material is homogeneous, $c(z)$ is constant, and 95.0% of the total photoelectron signal intensity will arise from the sample surface region down to depths of 3λ .²⁶ When the photoemission angle is varied, as illustrated in Scheme 3, the associated depth d is described as $d = 3\lambda \sin \theta$, and thus the depth increases with the increasing photoemission angle θ .

For organic materials, λ is described as a function of the density ρ (kg/m³) and energy of photoelectron E (eV), by Sear and Dench,²⁷ as follows:

$$\lambda(\text{nm}) = \frac{49}{10^{-3}\rho E^2} + \frac{0.11E^{0.5}}{10^{-3}\rho}$$

The experimental value of E for pure PTFE was 294 eV; the value is attributed to the CF₂ carbon of the original PTFE. The depths obtained with $\theta = 90^\circ$ ($\sin \theta = 1$) were calculated to be 2.5 and 3.0–5.1 nm for pure PTFE (with a density of 2.2 g/cm³) and pure PMAA (1.1–1.4 g/cm³), respectively. The density of the present PTFE-g-PMAA samples must be between 1.1 and 2.2; accordingly, the angle of $\theta = 90^\circ$ corresponds to the depth between 2.5 and 5.1 nm. In Figure 5, the ratios of fluorines to carbons (F/C ratio) are plotted as a function of $\sin \theta$ for the PTFE-g-PMAA samples (grafted amount 2.0 wt %). The F/C value was not greater than 2.0 (the ideal value of pure PTFE) at $\theta = 90^\circ$, as shown in Figure 5. This result suggests that the PMAA is located deeper than at least 2.5 nm from the surface of the PTFE. On the other hand, the O/C value was less than 0.5 (the ideal value of pure PMAA) at all angles observed. The result is consistent with the result obtained from the F/C value; a mixture of PMAA and PTFE is located at the surface area.

Molecular motion of grafted PMAA chains

To obtain further information about molecular structure and molecular motion of the grafted PMAA chains on the PTFE, ESR measurements were carried out for the PTFE-g-PMAA that was spin-labeled with nitroxide radical. The carboxyl group of the grafted PMAA was coupled with 4-amino-TEMPO according to the reaction formula shown in Scheme 1.^{17,18} To make a comparison, the homopolymer of the PMAA (*h*-PMAA) was also spin-labeled with the same nitroxide radical of 4-amino-TEMPO. The ESR spectrum of nitroxide radical gives rise to an anisotropic triplet ascribed to the dipole interaction between electron spin and ¹⁴N nucleus spin ($I = 1$) (i.e., hyperfine

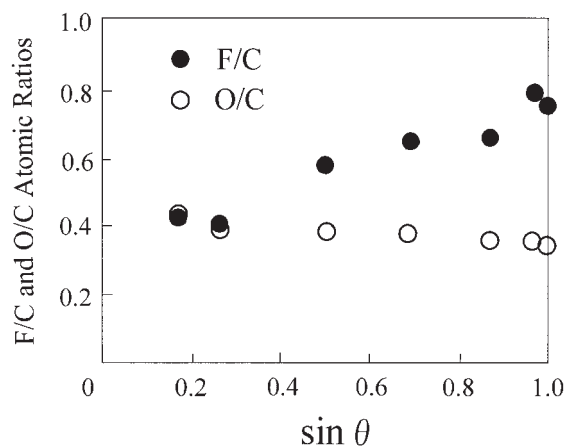
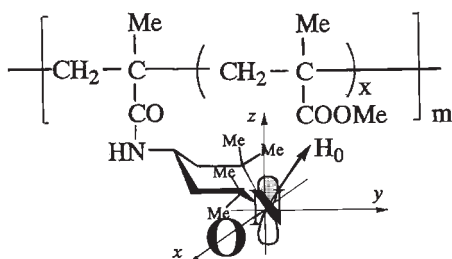


Figure 5 Depth profile (from XPS) of F/C and O/C atom ratios for the PTFE-g-PMAA sheet as a function of the take-off angle, $\sin \theta$.



Scheme 4 Schematic illustration of nitroxide radical with three-dimensional molecular axes.

anisotropy) together with g -tensor anisotropy (Scheme 4).

In the motional narrowing region where the rotational correlation time τ_c is less than 10^{-9} s, the anisotropic interactions are averaged to zero so that the ESR spectrum becomes isotropic. On the other hand, in the slow motional region of $10^{-9} < \tau_c < 10^{-6}$ s, the ESR spectra remain anisotropic, but the ESR lineshapes depend strongly on the value of τ_c or the diffusion rate.

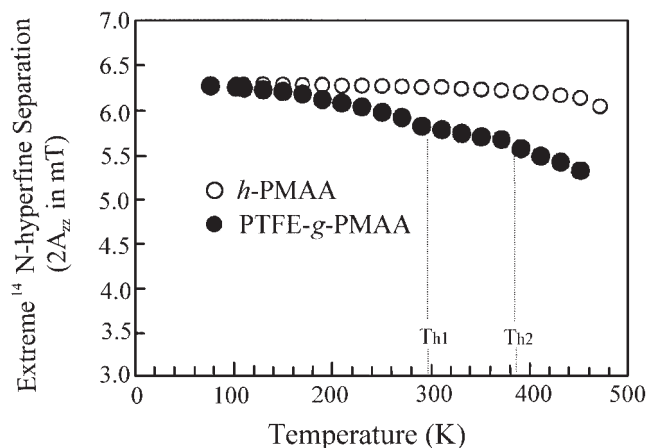


Figure 7 Temperature dependency of the extreme¹⁴N hyperfine separation ($2A_{zz}$) for PTFE-g-PMAA and *h*-PMAA.

The ESR spectra are shown in Figure 6(a) for the labeled PTFE-g-PMAA and in Figure 6(b) for the labeled *h*-PMAA. The extreme ¹⁴N hyperfine separations ($2A_{zz}$) for both PTFE-g-PMAA and *h*-PMAA

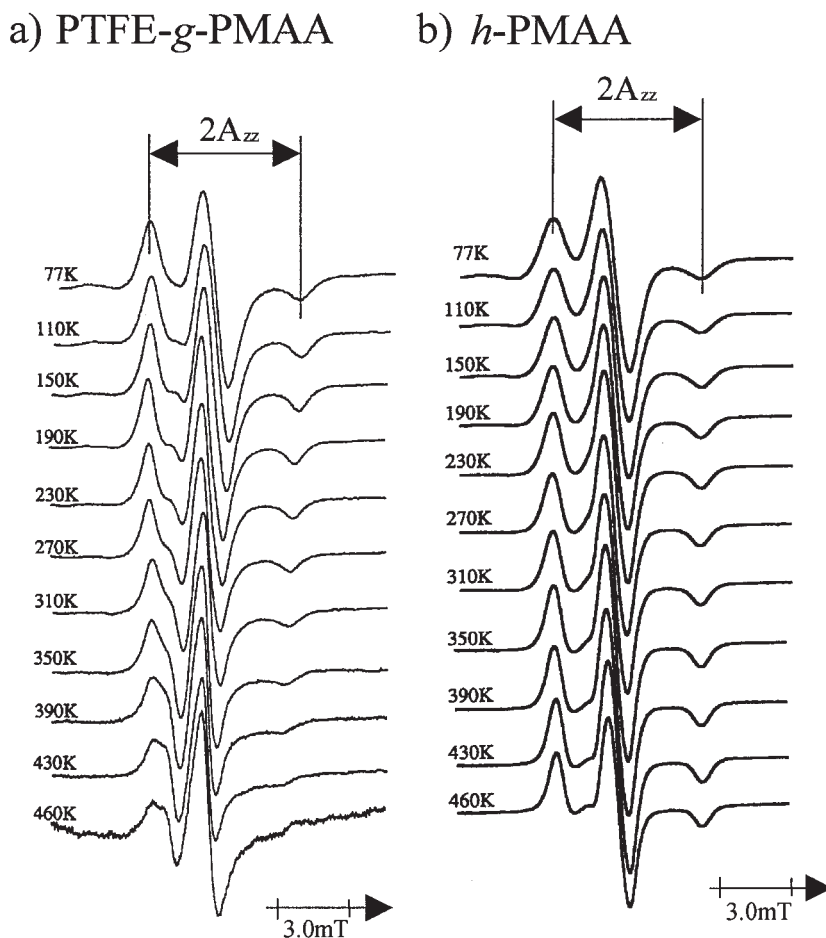


Figure 6 (a) Temperature-dependent ESR spectra of spin-labeled PMAA copolymer chains grafted onto PTFE (PTFE-g-PMAA). (b) The spectra of spin-labeled PMAA homopolymer (*h*-PMAA) are shown for comparison.

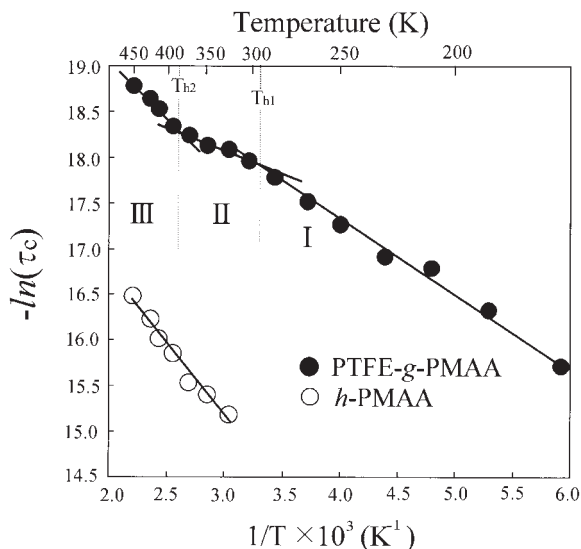


Figure 8 Arrhenius plots of the rotational correlation time for PTFE-g-PMMA and *h*-PMMA.

were plotted as a function of temperature (Fig. 7). At temperatures below 140 K, both of the PTFE-g-PMMA and the *h*-PMMA gave the same hyperfine separation of $2A_{zz}$, which corresponds to the rigid-limit value of $2A_{zz}$. The $2A_{zz}$ value of the PTFE-g-PMMA gradually decreases with increasing temperature above 140 K, whereas that of *h*-PMMA remains almost constant below about 400 K. This result suggests the higher molecular motion for the PTFE-g-PMMA than for the *h*-PMMA. The result can be explained in terms of the lower density of the PMMA chains in the PTFE-g-PMMA than that in the *h*-PMMA. That is, the surface of the PTFE-g-PMMA cannot be completely covered with the grafted PMMA molecules; therefore, the intermolecular interaction is expected to be lower for the PTFE-g-PMMA than for the *h*-PMMA. Also, the temperature dependency of the extreme separation for the PTFE-g-PMMA has two turning points at about 295 K (indicated as T_{h1} in Fig. 7) and about 385 K (indicated as T_{h2} in Fig. 7), which may correspond to the transition points for PTFE conformational changes at 292 K^{28,29} and 395 K.³⁰ Thus, we conclude that the molecular motion of the PTFE-g-PMMA is mainly controlled by that of the principal PTFE chain. We note that the glass-transition temperature (T_g) of the *h*-PMMA is 510 K, and is much higher than the transition points of the PTFE.

To obtain further quantitative information on molecular motion, the rotational correlation time (τ_c) of the PTFE-g-PMMA chains was estimated using a Brownian rotational diffusion model developed by Freed et al.³¹ Based on such a process, the τ_c for such slower rotational diffusion of the nitroxide radical can be approximately calculated using the “*S*” parameter, defined as^{32,33}

$$S = A'_{zz}/A_{zz}$$

where A_{zz} is one-half the extreme separation of the ESR spectra for the rigid limit value that corresponds to the state at which the rotation is completely restricted, and A'_{zz} is the one for slow motional tumbling value. Using the “*S*” parameter, τ_c can be experimentally described by the expression^{32,33}

$$\tau_c = c(1 - S)^d$$

where the values of c and d are experimentally obtained and are dependent on the type of rotational model, intrinsic linewidth, and hyperfine parameters of the ESR spectra. Appropriate values of c and d are given as 5.4×10^{-10} and -1.36 , respectively when the rotational model is the Brownian rotational diffusion model and, the Lorentzian linewidth is 0.3 mT and $A_{zz} = 3.2$ mT.^{32,33}

The τ_c values thus obtained for PTFE-g-PMMA and *h*-PMMA were plotted versus $1/T$, according to the following Arrhenius type of equation (Fig. 8):

$$-\ln(\tau_c) = E_a/kT - \ln(t_0)$$

where E_a is the activation energy for rotational diffusion and k is the Boltzmann constant. From Figure 8, values of E_a were evaluated to be 6.5, 4.9, and 11.0 kJ/mol for the PTFE-g-PMMA (2.0 wt %) in the temperature ranges I ($T \leq \sim 295$ K), II ($\sim 295 \leq T \leq \sim 385$ K), and III ($\sim 385 \text{ K} \leq T$), respectively. On the other hand, a higher activation energy of $E_a = 13.2$ kJ/mol was evaluated for the *h*-PMMA. The lower activation energy evaluated for the PTFE-g-PMMA may be attributable to the lower intramolecular interaction arising from the low density of the grafted PMMA chains on the PTFE. Thus we conclude that the grafted PMMA chain can have a higher degree of freedom for the rotational motion compared with *h*-PMMA (bulk PMMA).

CONCLUSIONS

We summarize the present study as follows.

1. The carbon-centered radicals were generated on PTFE by the reaction of the mixed solution of alkyllithium/HMPA with the PTFE (ESR).
2. The graft polymerization of MAA was initiated by the carbon-centered radicals generated on the PTFE (ESR, ¹³C-NMR, IR).
3. The crystallinity and the molecular weight of the PTFE did not change as a result of graft polymerization (DSC).
4. The grafted PMMA was located deeper than at least 2.5 nm (XPS).

5. The molecular motion of the grafted PMAA chain was controlled by those of the principal PTFE chain (ESR).
6. The rotational correlation time (τ_c) was evaluated using the "S" parameter defined by Freed,^{32,33} and the associated activation energies were estimated to be 6.5 kJ/mol for the PTFE-g-PMAA (2.0%) in the temperature range below about 295 K and 13.2 kJ/mol for the *h*-PMAA, respectively (ESR).
7. The lower activation energy for the PTFE-g-PMAA may be attributable to lower intramolecular interaction arising from the low density of the grafted PMMA chains to the PTFE (ESR).

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