Fabrication of High-Density Polymer Brush on Polymer Substrate by Surface-Initiated Living Radical Polymerization

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ABSTRACT: A well-defined, high-density poly(2-hydroxyethyl methacrylate) (PHEMA) brush was fabricated on the surface of a poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) film by surface-initiated living radical polymerization (LRP). First, a sufficient amount of peroxides as initiating moieties were successfully introduced on the film surface without causing etching by the O_2-plasma treatment. Subsequently, the polymerization mediated by reversible addition−fragmentation chain transfer (RAFT) was carried out at a mild temperature in a nonsolvent for FEP to minimize the swelling of the FEP film surface and avoid the growth of chains from deep inside of the film. The contact angle and ESCA measurements indicated that the boundary intermixing layer between FEP and PHEMA layers was reasonably thin (≤10 nm), meaning that the PHEMA brush was grown nearly regioselectively from the surface of the FEP film. The graft density was estimated to be about 0.3 chains/nm^2, which is almost the same as the one achievable by the RAFT technique on inorganic substrates with a hard surface. This graft density is much higher than the ones obtainable by conventional techniques.

Introduction

Living radical polymerization (LRP), as applied to surface-initiated graft polymerization,[1−15] has the overwhelming advantage over other surface grafting techniques in that it allows grafting of homo- and copolymers of controlled structures with an extremely high graft density. On inorganic substrates, the graft density reached as high as 0.7 chains/nm^2 for common polymers[15,11] such as poly(methyl methacrylate) (PMMA) and polystyrene. This density is about 1 order of magnitude higher than those of the semi-dilute brushes obtainable by other techniques, and the graft systems in this density regime may be termed concentrated or high-density brushes. Even in a dry state, such a high-density PMMA brush is necessarily anisotropic because its dry thickness reaches about 40% of the full length of the graft chain or the chain end-to-end distance in all trans conformations. Therefore, its dry-state properties such as glass transition temperature,[13] compression resistance,[14] and miscibility with untethered molecules[11] are quite different from those of semi-dilute brushes. The equilibrium thickness of the high-density brush swollen by a good solvent is surprisingly large, as large as 80−90% of the full length of the graft chains, meaning that the chains themselves are extended that much.[9,10] This highly anisotropic structure of the swollen brush brings about extremely strong resistance against compression and remarkable size-exclusion properties.[11] By taking advantage of unprecedented properties of high-density polymer brushes, one may create novel materials with smart surfaces. Recently, we found that a high-density poly(2-hydroxyethyl methacrylate) (PHEMA) brush formed on an inorganic substrate exhibits much better biocompatibility than a comparable semi-dilute brush.[12]

While surface-initiated LRP has been first established on inorganic solid surfaces,[1−15] there have been an increasing number of attempts for its application to organic polymer substrates. These include fibers,[16,17] films,[18−21] porous membranes,[22−24] particles,[25−28] lanterns,[29,30] and monoliths[31−33] composed of cellulose,[17,18] hydrocarbon polymers such as polyethylene and polystyrene,[19,20,22,23,25−29,31−33] polyester,[21] and fluorocarbon polymers.[24,30] Most studies focused on the control in molecular weight and polydispersity of the graft polymer. On the other hand, little attention has been paid to graft density, although high-density grafting provides fascinating surface properties unpredictable, in many cases, from those which low- to moderate-density grafting does, as mentioned above.

The prerequisites to fabricate a well-defined, high-density brush on a polymer substrate are: (1) the introduction of the initiating moiety on the surface with a sufficiently high density, (2) the optimization of LRP conditions to have fast initiation and uniform chain growth, and (3) the proper choice of the polymerization media to prevent the surfaces of polymer substrates from swelling. The last requirement is specific to polymer substrates, namely, in a swollen substrate, chains can grow from its deep inside, forming a thick boundary (coexisting) layer of graft and substrate polymers (Scheme 1a). In some cases, the thickness of the boundary layer reaches an order of micrometers.[19,30] Such graft systems, even if the graft density may be high, are poorly defined in both the structure and properties.

In this paper, we report the successful preparation of a well-defined, high-density polymer brush on a polymer substrate (Scheme 1b). 2-Hydroxyethyl methacrylate (HEMA) was graft-polymerized from the sur-

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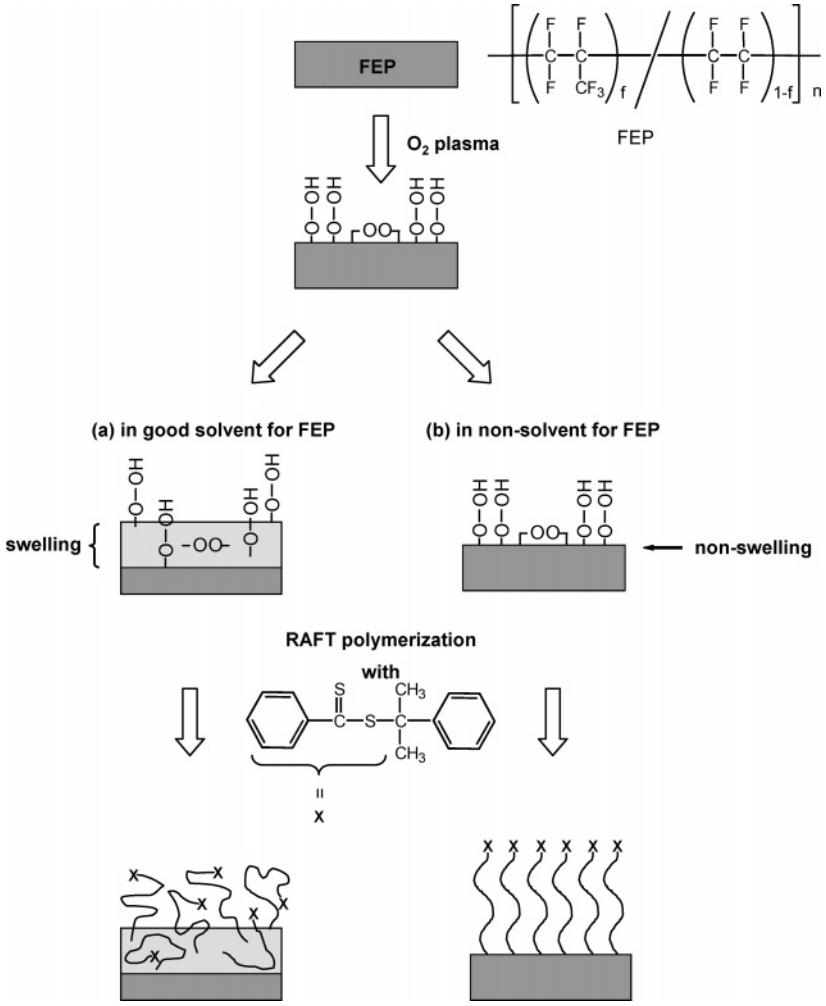
Scheme 1. Schematic Illustration of the Graft Polymerization on the FEP Film in (a) Good and (b) Non-solvents for FEP



face of poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) film by reversible addition−fragmentation chain transfer (RAFT)-mediated LRP.[34,35] The surface-initiated LRP of HEMA has so far been carried out on inorganic surfaces[36,37] but not on polymer substrates. The combination of the polar monomer with the nonpolar substrate suppressed the swelling of the film surface. Among various techniques, including chemical reaction and high-energy-beam irradiation,[38] we chose O_2-plasma irradiation (Scheme 1) to introduce initiating moieties on the surface of the polymer film. The plasma treatment is a powerful and effective method to introduce initiating moieties (peroxides) selectively on the surface (within a depth less than 10 nm, typically[39]) of an inert film without reactive functional groups. Because the plasma technique is applicable to a variety of polymer substrates with various shapes and RAFT polymerization is applicable to versatile monomers, this procedure can be an effective route to novel polymeric materials functionalized with high-density polymer brushes.

Experimental Section

Materials. HEMA (99%, Nacalai Tesque, Japan) was purified as follows:[40] an aqueous solution of HEMA (25 vol % HEMA) was washed with hexane (4 × 200 mL). To this solution, NaCl was added to salt HEMA out of the aqueous phase. The HEMA phase was dried over Na_2SO_4 and then distilled under reduced pressure. Cumyl dithiobenzoate was prepared according to the CSIRO group.[34,35] Methanol (99.9%, Wako Pure Chemical, Japan), 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V70) (99.9%, Wako), *N*,*N*-dimethylaniline (98%, Nacalai), and 1,1-diphenyl-2-picrylhydrazyl (DPPH) (98%, Wako) were used as received. The FEP film (100 μm thickness; Daikin, Japan) was washed by ultrasonication in acetone for 30 min and dried under reduced pressure at room temperature overnight.

Plasma Treatment. The O_2-plasma treatment was made by a BP-1U bell-jar-type plasma reactor (Samco, Kyoto, Japan) with two parallel plate electrodes. The applied frequency was 13.56 MHz. The O_2 pressure was kept 60 Pa (the gas flow rate was 0.4 mL/min), and the electronic power was 40 W. The FEP films were placed on the ground electrode, and plasma was exposed to one side of the film. After the plasma treatment, the film was stored at room temperature in air for 30 min and then subjected to the determination of the peroxide concentration and the graft polymerization (see below). After the graft polymerization, we confirmed by attenuated total reflection infrared (ATR−IR) spectroscopy that the graft polymer was homogeneously distributed on the one side of the film with no graft polymer on the other side.

Determination of Peroxide Concentration. The peroxide concentration on the film surface was determined by the radical-scavenging method.[41,42] Namely, the plasma-treated film (6 × 6 cm^2) was folded, placed in a glass tube (1 cm diameter), and immersed in a toluene solution (2 mL) of DPPH (0.2 mM). After being degassed and sealed under vacuum, the glass tube was heated at either 40 or 80 °C to decompose the peroxides, and the formed radicals were scavenged by DPPH. The peroxide concentration was estimated by following the

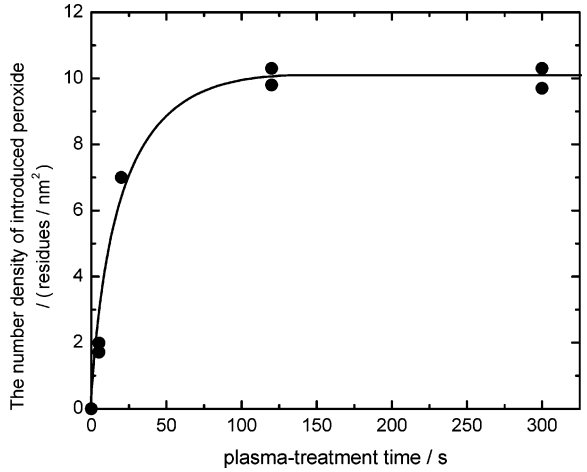


Figure 1. Plot of the number density of introduced peroxide vs plasma-treatment time. For the determination of the number density, see the text.

decrease of DPPH concentration by electron spin resonance (ESR). The experiment was duplicated. The duplicated data agreed within 10% (Figure 1), suggesting good quality of the data.

Graft polymerization. The plasma-treated FEP film (1 × 2 cm^2) immersed in a methanol solution of HEMA (4 M), cumyl dithiobenzoate (1 mM), V70 (0.1 mM), and *N*,*N*-dimethylaniline (0.5 M) in a glass tube (1 cm diameter) was degassed, sealed under vacuum, and heated at either 40 or 80 °C. After polymerization, the solution was diluted with *N*,*N*-dimethylformamide (DMF) to a known concentration and analyzed by gel permeation chromatography (GPC). The conversion was determined from the GPC peak area. The film was rinsed in a Soxhlet apparatus with methanol for 6 h to remove physisorbed free polymer and impurities.

Measurements. The ESR spectra were recorded at room temperature on a Bruker EMX spectrometer (Karlsruhe, Germany) equipped with a cavity of the type ER4119ST. The measurement was performed with 100-kHz magnetic field modulations at microwave output of 0.5 mW.

The GPC analysis was made on a Tosoh HLC-802 UR high-speed liquid chromatograph (Tokyo, Japan) equipped with two Shodex gel columns LF804 (300 × 8.0 mm; bead size = 6 μm; pore size = 20−2000 Å) (Tokyo). DMF was used as eluent (40 °C). The column system was calibrated with Tosoh standard poly(ethylene glycol)s (PEGs). Sample detection and quantification were made with a Tosoh differential refractometer RI-802. Sample detection was also made with a multi-angle laser light scattering (MALLS) detector, a Wyatt Technology DAWN EOS (Santa Barbara, CA), equipped with a Ga−As laser (λ = 690 nm). The refractive index increment dn/dc was determined to be 0.075 mL g^{-1} by a Wyatt Technology OPTILAB DSP differential refractometer (λ = 690 nm).

The graft amount was estimated from ATR-IR absorption spectra recorded on a BioRad FTS 6000 Fourier transform spectrometer (Hercules, CA) equipped with a ZnSe ATR prism. The PHEMA layers of known thickness, spin-coated on the FEP films, were used for the calibration of the PHEMA thickness vs absorbance. The thickness of the spin-coated PHEMA layer was determined by a compensator-rotating ellipsometer (M-2000U, J. A. Woolam, Loncoln, Germany) equipped with a D_2-QTH lamp. The polarizer angle was 45° and the incident angles were 60°, 65°, and 70°. For conversion between the thickness and the weight, the bulk density of PHEMA of 1.15 g/cm^3 was used.

Electron spectroscopy for chemical analysis (ESCA) was performed on a Shimadzu ESCA 750 spectrometer (Kyoto, Japan) using a nonmonochromatic Mg Kα photon source with a takeoff angle of 15°. The anode voltage was 10 kV, the anode current was 20 mA, and the pressure in the chamber was 10^{-6} Pa.

Topographic images of the graft surface were obtained by an atomic force microscope (AFM) (SPI3600, Seiko Instruments, Tokyo) with an aluminum-coated cantilever (OMCL-AC160TS, Olympus, Tokyo; spring constant 42 N/m). Contact angles (θ) were measured at room temperature with a contact angle meter CA-X (Kyowa Interface Science, Saitama, Japan). The measurement was made on at least five different spots for each sample, and the results were averaged.

Results and Discussion

Introduction of Peroxide. We introduced peroxides on the FEP film by the O_2-plasma treatment, as shown in Scheme 1. To form a high-density PHEMA brush on the FEP film, peroxides should be introduced with a sufficiently high density. To optimize the plasma-treatment time, we determined the concentration of the introduced peroxide as a function of the treatment time by using the radical-scavenging method. Namely, the plasma-treated film was immersed in a toluene solution containing the radical scavenger DPPH and heated for 6 h at 80 °C. The radicals formed by thermal decomposition of the peroxides were scavenged by DPPH. We followed the decay of the DPPH concentration by ESR and, assuming that all the formed radicals were scavenged by DPPH, we calculated the amount of decomposed peroxides, which would be approximately equal to that of the introduced peroxides after a sufficiently long time because the initiation efficiency of the peroxides is typically 0.9−1.0.[44] The DPPH concentration did not decrease after 6 h, meaning that 6 h was long enough for all the peroxide molecules to decompose. Figure 1 shows the plot of the amount (number density) of peroxides vs the plasma-treatment time (the experiment was duplicated). The number density increased with increasing plasma-treatment time up to 120 s and then reached a constant value of about 10 peroxides/nm^2.[41−43] As indicated in Scheme 1, the introduced peroxides can either be hydroperoxides (C−O−O−H) or dialkylperoxides (C−O−O−C) or both.[38] The former would afford one initiating radical immobilized on the surface, and the latter, two. Therefore, the number density of the initiating moiety should be between 5 and 10 residues/nm^2, which was high enough to achieve high-density brushes, such as obtained in this work (see below).

We used the 60, 80, and 120 s plasma-treated films for graft polymerization. They had peroxides in sufficiently high densities. In addition, the AFM studies revealed that their surfaces exhibited no morphology change before and after the plasma treatment; the root-mean-square roughness was about 6 nm in 1 × 1 μm^2 before *and* after the treatment, suggesting successful introduction of initiating moieties without significant surface etching. A longer plasma treatment (e.g., 300 s) made the film surface frailer and easier to swell because of etching.

For the 120-s treated sample, we examined the decomposition rate of the peroxides at 40 °C (the polymerization temperature). It took about 4 h to have a decomposition of 0.3 peroxides/nm^2, namely, the average first-order decomposition rate constant k_d was about 2 × 10^{-6} s^{-1}. This meant that some 4 h was necessary to have 0.3 initiating sites/nm^2, which was too long to meet the requirement of fast initiation for living polymerization. Therefore, we added *N*,*N*-dimethylaniline to accelerate the decomposition of the peroxides via a redox process. Although we could not determine k_d in the presence of *N*,*N*-dimethylaniline

because of the degradation of DPPH by *N,N*-dimethylaniline, we confirmed that we had a sufficiently fast initiation, as shown below.

Graft Polymerization. We carried out the graft polymerization of HEMA from the plasma-treaded FEP film in the presence of cumyl dithiobenzoate (1 mM) as a free RAFT agent, V70 (0.1 mM) as a conventional radical initiator, and *N,N*-dimethylaniline as an accelerator of the decomposition of the peroxides on the film. The polymerization was carried out at a mild temperature, 40 °C, in aqueous methanol (50 vol %), a nonsolvent for FEP, to prevent the FEP film from swelling.

The RAFT process[34−35,46] (Scheme 2), i.e., a degenerative or exchange chain transfer process, is the key reaction of this polymerization. It involves the addition of the propagating radical P• to the dormant species P′-X (X = dithiobenzoate in this work) to form the intermediate radical P-(X•)-P′ followed by the fragmentation into P′• and P-X. A number of such exchange transfer reactions will give approximately uniform growth of all polymer chains, providing a low-polydispersity polymer. In the present system, the initiating radical formed on the FEP surface will, after incorporating some monomers, take the dithiobenzoate group from the free RAFT agent. A part of the free RAFT agent will consequently lose the dithiobenzoate group. However, because the concentration of the peroxide (10^{-3} mM) is negligibly small compared with that of the feed RAFT agent (1 mM), most of the free chains will also possess a dithiobenzoate group and grow in a controlled manner. The RAFT reaction can occur among the free and graft chains.

The first-order plot of the monomer concentration was almost linear in the examined time range (≤5 h), and the conversion reached about 25% at 5 h for all polymerization runs. Because free polymers simultaneously produced in the solution are a good index in M_n and M_w/M_n for graft polymers,[8] we collected free polymers and analyzed them by GPC. Figure 2 shows the plots of the M_n and M_w/M_n for the free polymer (filled symbols) vs conversion, where PEG was used for calibration. The M_n (filled symbols) obtained by PEG calibration deviated from the theoretical line (solid line). The absolute values of M_n (open symbols) obtained by GPC-MALLS for selected samples reasonably agreed with the theoretical ones (the GPC-MALLS molecular weights (M_n in particular) were presumably overestimated by 10−20%, because a low-molecular-weight region was not taken into calculation because of a too-weak MALLS signal). Thus, we may adopt the theoretical M_n in the following discussion. The M_w/M_n (Figure 2) decreased with an increase in conversion up to about 15% and then stayed at a low value of about 1.3. In addition, we observed a linear increase of the graft layer thickness with an increase of the theoretical M_n, as discussed below. These results suggest that a controlled polymerization has occurred in the graft phase as well as in the solution phase.

Because the graft chains in a high-density brush are highly stretched in a good solvent with their chain ends

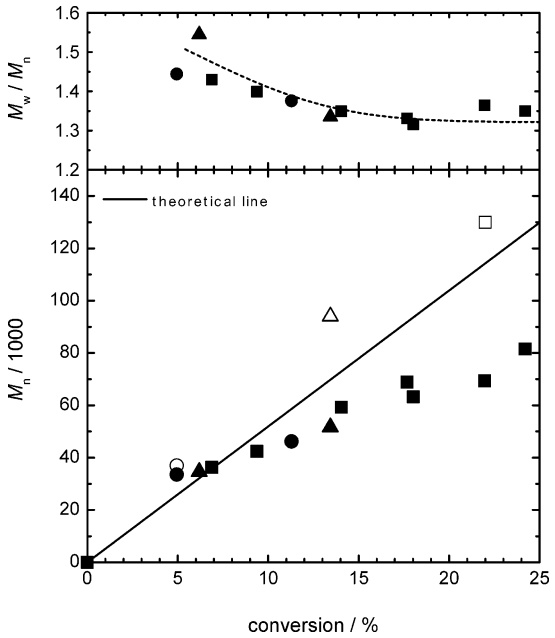
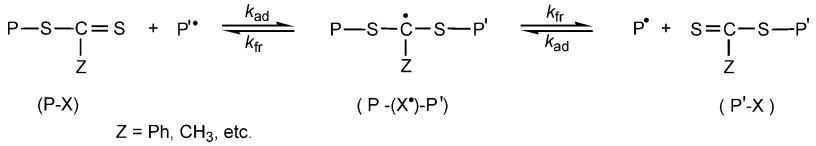


Figure 2. Plots of M_n and M_w/M_n of free polymer vs monomer conversion for the plasma-treated FEP film/HEMA/cumyl dithiobenzoate/V70/methanol system (40 °C): $[HEMA]_0$ = 4 M; $[\text{cumyl dithiobenzoate}]_0$ = 1 mM; $[V70]_0$ = 0.1 mM in methanol (50 vol %). The plasma-treated time for the FEP film was (■ and □) 60 s, (▲ and △) 80 s, and (● and ○) 120 s. The data indicated by filled and open symbols were obtained by PEG-calibrated GPC and GPC-MALLS, respectively.

localized near the free surface of the graft layer, the RAFT process can effectively occur among graft chains. A higher frequency of the RAFT reaction can result in a lower polydispersity for graft chains than that for free chains. On the other hand, such a sequential RAFT reaction can be viewed as a reaction−diffusion process of the otherwise strictly localized propagating radicals, and this process would increase bimolecular termination between graft radicals, thus giving a higher polydispersity. This was in fact observed in a styrene system,[45] where the exchange (RAFT) rate constant k_{ex} was extremely large (hence an extremely fast reaction−diffusion process). However, k_{ex} is much smaller for MMA (about 1/30 of that for styrene[46]), and thus this surface termination should be much less important in the present HEMA system as well as in a MMA system. (The polydispersity, hence the chain transfer constant $C_{ex} = k_{ex}/k_p$, for HEMA (Figure 2 for free polymer) resembles that for MMA.[46])

Estimation of Graft Density. After polymerization, the film was rinsed in a Soxhlet extractor with methanol for 6 h to remove physisorbed polymers and impurities and dried under vacuum at room temperature. The AFM imaging of the film showed a smooth surface morphology with a root-mean-square surface roughness of about 6 nm in 1 × 1 μm^2 at any position of the film (similar to that for pristine FEP), suggesting the formation of a homogeneous graft layer and hence homogeneity in graft density, even though the film of a crystalline

Scheme 2. Reversible Addition−Fragmentation Chain Transfer



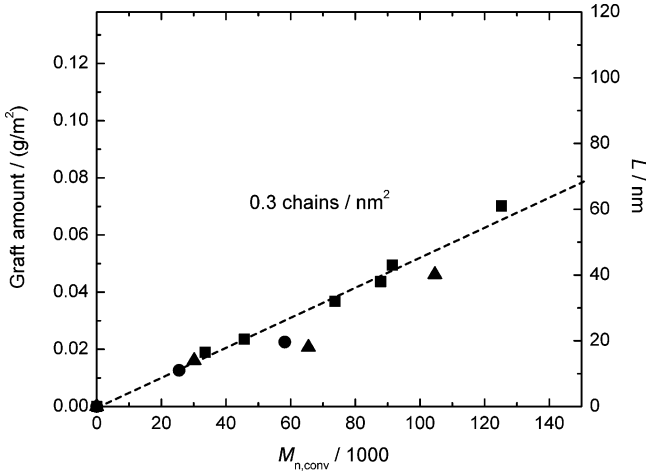


Figure 3. Plot of graft amount and L vs $M_{n,theor}$. For symbols and experimental conditions, see the caption for Figure 2.

polymer, FEP, may have crystalline and amorphous regions on the surface. The amount of grafted PHEMA was determined by the ATR-IR intensity of the absorption band (at 1725 cm^{-1}), characteristic of the carbonyl group of PHEMA. Further Soxhlet extraction did not change the observed amount of PHEMA. In addition, no PHEMA graft chains were formed on the plasma-untreated film as well as on the film with all the peroxides thermally decomposed before the graft polymerization. These results mean that the graft chains grew only from the peroxides chemically anchored at their sites and that physisorbed PHEMA could completely be removed even from the plasma-treated hydrophilic surface.

The M_n of the graft polymer was approximated by the theoretical values ($M_{n,theor}$), as mentioned above. Figure 3 shows the plot of the amount of graft polymers vs $M_{n,theor}$. We calculated the thickness L of the graft layer on the basis of the two-layer model consisting of pure PHEMA and pure FEP layers without a boundary layer between them (Scheme 1b). This hypothetical layer thickness L is indicated on the right-hand vertical axis. The grafted amount or L was proportional to $M_{n,theor}$, suggesting uniform growth of graft chains with a constant density. From the slope of the linear line, the graft density σ was estimated to be about 0.3 chains/nm^2. This proportionality demonstrates that the added *N*,*N*-dimethylaniline accelerated the decomposition of the peroxides on the FEP film so that the initiation was sufficiently faster than the chain growth. The graft density was the same as that obtained on an inorganic (silicon) surface by the RAFT polymerization.[47] This is presumably because the boundary layer, if there is any, is sufficiently thin, as will be discussed below. The L values obtained in this study reached ~25% of the full length of graft chains, which is somewhat smaller than the value (~40%) for high-density PMMA brushes[9,11] but still higher than those (<10%) for the semi-dilute brushes previously studied. The obtained PHEMA brushes may be viewed as being in the high-density brush regime.

Surface Properties and Rearrangement. The contact angle θ on the film surface was measured in water with an air bubble. Prior to the measurement, the film was immersed in water at room temperature for 24 h. The angle θ is sensitive to chemical composition of the outermost surface of the specimen (within a depth of a few angstroms). Figure 4a shows the plot of θ vs L,

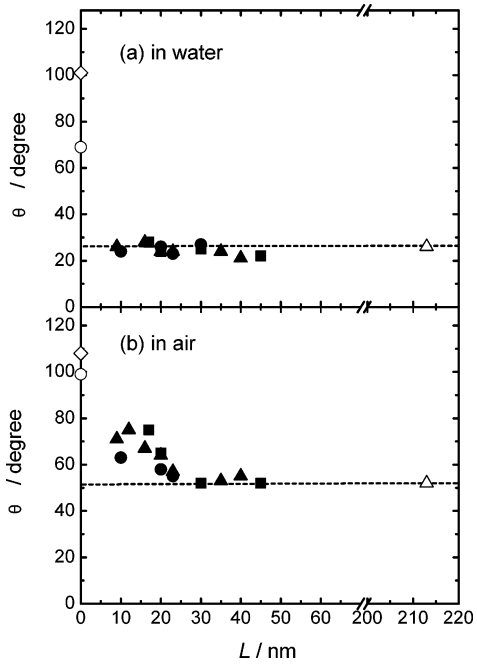


Figure 4. Plot of θ vs L (a) in water with air bubbles and (b) in air with water droplets: (◇) pristine FEP film, (○) 120 s plasma-treated FEP film, (△) PHEMA-spin-casted FEP film, and PHEMA-grafted FEP film with plasma-treatment time of (■) 60 s, (▲) 80 s, and (●) 120 s. The broken lines show the contact angles of the pure PHEMA surface.

in which θ decreased from 100° (pristine FEP) to 70° (plasma-treated FEP) by the plasma treatment because of the introduction of hydrophilic groups. All the PHEMA-grafted samples gave a θ of 26°, which was equal to the value for the spin-cast PHEMA film (pure PHEMA surface). This means that the uppermost surface was totally covered with PHEMA for all the films, which had L larger than about 10 nm.

To discuss the surface rearrangement, θ was also measured in air with a water droplet (Figure 4b). Prior to the measurement, the film was dried under vacuum at room temperature for 24 h. The value of θ was 110° for pristine FEP and 100° for plasma-treated FEP. Figure 4b indicated that the θ of PHEMA-grafted samples was dependent on L. Samples with $L > 20$ nm showed almost the same θ value as the spin-cast PHEMA film (pure PHEMA surface), while thinner samples showed a more hydrophobic property. For samples with $L < 20$ nm, the uppermost surface was covered with a pure PHEMA layer in water (Figure 4a), while it was not in air (Figure 4b). This can be ascribed to the rearrangement of FEP and PHEMA chains at the surface; in air (hydrophobic environment), hydrophilic PHEMA chains tend to escape from the surface, and hydrophobic FEP chains tend to come out to the surface.[48] Such surface rearrangement was completely suppressed for samples with $L = 20$ nm or larger. This suggests that a molecular-scale orientation of FEP and PHEMA chains occurs in the boundary layer. For samples with $L \geq 20$ nm, the boundary layer would be covered with a longer PHEMA high-density brush, and the surface rearrangement would hardly occur. Another type of rearrangement concerns the orientation of the hydroxyl group of the HEMA unit,[49] as observed for the pure PHEMA surface as a difference in θ ($\theta = 56°$ in air vs 26° in water).

The surface composition in a hydrophobic environment (in a vacuum) was complementarily examined by

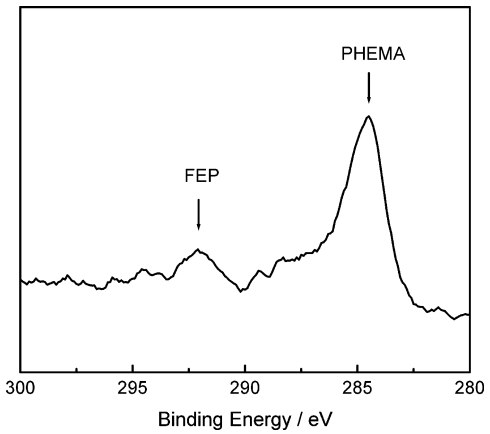


Figure 5. C_{1s} XPS spectrum of PHEMA-grafted FEP film. The plasma-treatment time was 120 s and $L = 10$ nm.

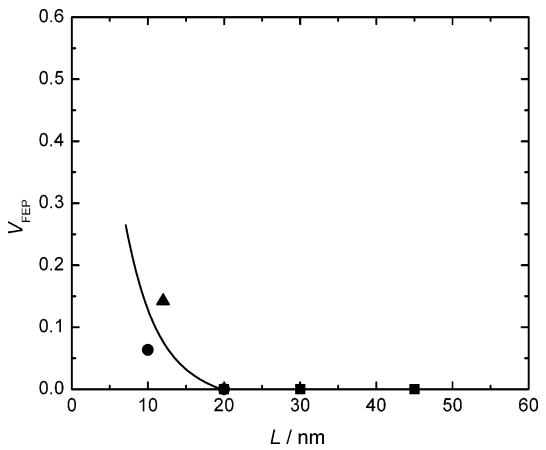


Figure 6. Plot of V_{FEP} vs L. The plasma-treatment time was (■) 60 s, (▲) 80 s, and (●) 120 s.

ESCA. ESCA spectra were measured at the takeoff angle of 15° (not 90°) to examine the uppermost surface. The analytical depth (95% signal) was ~2 nm (a value reported for polystyrene and PMMA[50]). Figure 5 shows an example of the C_{1s} core-level spectra. The C_{1s} signals for PHEMA appeared at 285−290 eV, while those for the perfluoropolymer FEP appeared at a higher-energy field of 290−295 eV because of the larger electron negativity of the fluorine atom. From the intensities of the signals, we estimated the volume fractions of FEP (V_{FEP}) and PHEMA ($1 - V_{FEP}$) using the bulk densities of FEP (2.2 g/cm^3) and PHEMA (1.15 g/cm^3). Figure 6 shows that V_{FEP} decreased with increasing L to reach zero at $L = 20$ nm. This result is consistent with that obtained by the contact angle measurement in air. Notably, even the samples with $L = 10$ nm had only a small amount of FEP (10%) in the surface layer (within about 2 nm). Thus, we conclude that the thickness of the boundary layer between FEP and pure PHEMA layers is smaller than 20 nm. Taking into consideration the fact that both the contact angle and ESCA measurements carried out in the air or vacuum sensitively detected the uppermost layer of the surface in which the hydrophobic FEP chains would be much more concentrated than in a hydrophilic environment, the boundary layer may be practically considered to be even thinner than 10 nm, as suggested by Figure 4a. An increase of L will simply increase the thickness of the pure PHEMA layer, decreasing the relative contribution of the boundary layer. In this context, we may conclude that samples with L sufficiently larger than 20 nm have a well-defined, high-density brush structure with a negligibly thin boundary layer, such as illustrated in Scheme 1b.

In the above-mentioned experiment, we carefully prevented the film surface from swelling during graft polymerization. As a reference, we also attempted graft polymerization at a high temperature, 80 °C, to intentionally swell the film surface. We obtained the grafted FEP film with $L = 90$ nm, where $M_{n,theor}$ was 79000. The graft density was 0.6 chains/nm^2, which is higher than those obtained at 40 °C. As illustrated in Scheme 1a, graft chains can grow up, in the swollen condition, not only from the outermost surface but also from a somewhat deep inner part of the film, giving a poorly defined brush structure with an apparently higher value of graft density. The θ value was 26° in water ($\theta = 26°$ for pure PHEMA) and 75° in air ($\theta = 56°$ for pure PHEMA), meaning that surface rearrangement of FEP and PHEMA chains occurred even at $L = 90$ nm. This contrasts to the results obtained at 40 °C and stresses the importance of careful design of experimental conditions for preparing well-defined, high-density polymer brushes on polymer substrates.

Conclusions

High-density PHEMA brushes were fabricated on the surface of a FEP film by using the O_2-plasma treatment to introduce initiating moieties and carrying out a RAFT-mediated living radical graft polymerization. The O_2-plasma treatment afforded peroxides on the film surface with a density as high as about 10 peroxides/nm^2, as determined by a radical trapping method. A fast decomposition of the peroxides could be attained by the addition of *N,N*-dimethylaniline. To prevent the chain growth from deep inside of the FEP film, the polymerization was conducted at a mild temperature (40 °C) in methanol, a nonsolvent for FEP, which minimized the swelling of the FEP film surface. Such careful design of experimental conditions enabled us to prepare well-defined, high-density PHEMA brushes on the FEP surface. The graft density actually achieved was about 0.3 chains/nm^2, a value close to that achieved on an inorganic solid surface. The contact angle and ESCA measurements showed that, even in hydrophobic media, the PHEMA-grafted films with $L = 10$ nm were covered mostly (>90%) by PHEMA, and those with $L \geq 20$ nm formed a pure PHEMA layer on the film surface in both hydrophilic and hydrophobic media. This was because PHEMA graft chains were densely anchored to a considerably thin (≤10 nm) boundary layer.

Independent experiments have shown that high-density PHEMA brushes formed on *inorganic* substrates exhibit excellent biocompatibility.[12] By taking the best advantage that the plasma treatment followed by RAFT polymerization is applicable to various polymeric substrates with various shapes, we are planning to find their applications to novel biointerfaces.

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