Terminally Anchored Polymer Brushes on a Semicrystalline Microporous Polyethylene Fiber

William Lee and Shintaro Furusaki

Department of Chemistry and Biotechnology, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Jun-ichi Kanno

Ebara Research Company, Ltd., 4-2-1 Honfujisawa, Fujisawa 251-8501, Japan

Kyoichi Saito*

Department of Materials Technology, Chiba University, 1-33 Yayoicho, Inage-ku, Chiba 263-8522, Japan

Takanobu Sugo

Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, 1233 Watanukimachi, Takasaki, Gunma 370-1292, Japan

Here, we report a general strategy for the synthesis of densely anchored poly(glycidyl methacrylate) (poly-GMA) brushes on a chemically and physically stable polyethylene hollow fiber using an electron-beam-induced graft polymerization technique. The conformation of poly-GMA brushes is controlled by the total irradiation dose and the degree of grafting. We have demonstrated the rational direct experimental quantification of the density and the length of poly-GMA brushes by electron spin resonance measurement which overcomes the difficulty of isolating the polymer brush from its associated material. The total irradiation dose will govern the density while the degree of grafting will exclusively control the length of poly-GMA brushes.

Introduction

Vinyl monomer molecules, which come into contact with trapped radicals produced in a semicrystalline porous backbone polymer (BP) via electron beam irradiation, are graft-polymerized selectively with one end attached to the crystallite surface of BP. The polymer chains avoid one another by extending away from the crystallite, crossing the amorphous surrounding, extending to the pore interior of BP, and forming a "brush" (Figure 1). The formation of polymer brushes[1] is of technological importance in the architectural design of polymer bulks, surfaces, and/or interfaces for obtaining the desired moieties. Although polymer brushes are playing an increasingly important role in controlling the phase behavior[2,3] of polymer bulks, surfaces, and/or interfaces and associated material properties, their quantitative experimental characterization has been a controversial issue for many years. Yet, the conformation of polymer brushes still involves inefficient and indirect trial-and-error characterization processes,[4-9] because a polymer brush is inherently difficult to isolate

from its associated material. Theoretical predictions have been made regarding the static and dynamic structures of polymer brushes, such as the density profile above the surface.[10-14] Direct relevant experimental observation, although much needed, is difficult because of the polymer brush isolation process mentioned above. The Hagen–Poiseuille equation, for instance, has been applied to interpret the change of pore radius in a microporous membrane due to the experimental introduction of polymer brushes.[3,5,7] Characterization of polymer brushes by saturated protein-binding

* To whom correspondence should be addressed. Tel/Fax: +81-43-290-3439. E-mail: marukyo@xtal.tf.chiba-u.ac.jp.

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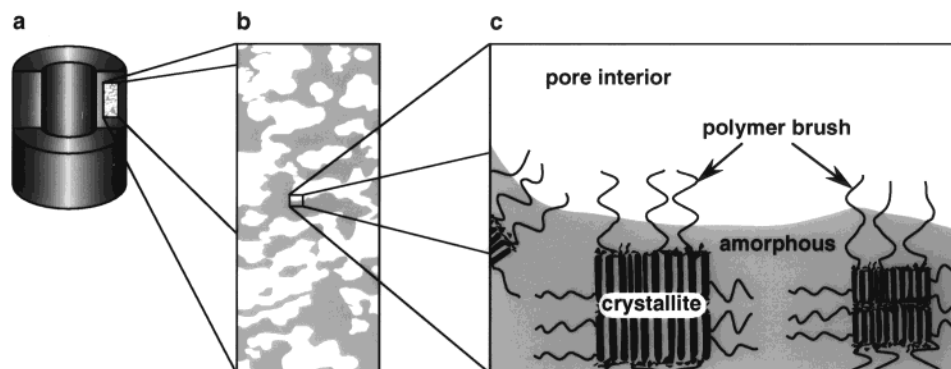
Figure 1. A structural illustration of polymer brushes formed on a semicrystalline microporous backbone polymer: (a) a microporous hollow fiber bearing terminally anchored polymer brushes; (b) cross-sectional microporous structure; the white region represents the pore interior; (c) polymer brushes extending from the crystallite surface toward the pore interior.
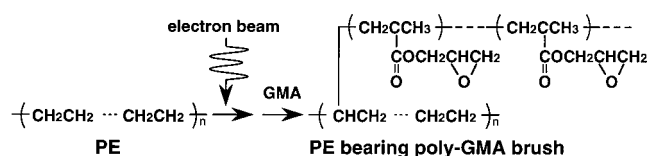

Figure 2. Reaction scheme of the synthesis of the poly-GMA brush on the polyethylene (PE) fiber.

layers on a surface[3,7,15] and acid hydrolyzation of BPs[6,16] have been performed, but the first method provides information on only a partial length of a polymer brush in the pore interior (above the amorphous surface), neglecting the entire length and the density of the polymer brush, whereas the second method is difficult to implement because it requires the degradation of BPs.

We have addressed these problems by performing two electron spin resonance measurements of the total radical concentration, one immediately after the polyethylene fibers have been irradiated with an electron beam, and the second after the graft polymerization of glycidyl methacrylate (GMA). The polyethylene fiber was selected as a model BP because of its commercial availability, high durability, and economical feasibility. GMA, a versatile vinyl monomer, was used because of its high reactivity and stability, and because its epoxy group can be converted into various functional groups via a ring-opening reaction with reactants.[17]

Experimental Section

Materials. Polyethylene hollow fiber (i.d. 1.9 mm, o.d. 3.2 mm, porosity 70%, average pore size 340 nm) supplied by Asahi Chemical Industry Co., Ltd., Japan, was used as a backbone polymer. Glycidyl methacrylate ($CH_2=CCH_3COOCH_2-CHOCH_2$) was purchased from Tokyo Kasei Co., Ltd., Japan, and used without further purification. All other reagents were of analytical grade or higher.

Graft Polymerization of GMA on Polyethylene Fibers. A reaction scheme of the synthesis of a poly-GMA brush on the polyethylene fiber is shown in Figure 2. The polyethylene fibers were set in a polyethylene package which was subsequently sealed with N_2. Electron beam irradiation was performed at ambient temperature by means of a cascade electron accelerator (Dynamitron IEA-3000-25-2, Radiation Dynamics,

Inc.) operated at a voltage of 2 MeV and a current of 1 mA. The conveyer on which the polyethylene fibers were mounted was reciprocated at a speed of 3.8 cm/s. The irradiation dose per passage of the conveyer was 10 kGy (1 Gy (gray) = 1 J/kg or 100 rad). The exposed total irradiation dose of the electron beam was set at 50, 100, 150, or 200 kGy. After irradiation the fibers were immersed in a GMA solution (10 vol/vol % in methanol) previously deaerated by nitrogen bubbles and reacted at 313 K under vacuum for a predetermined time. After the grafting of GMA, the fibers were washed with dimethylformamide and methanol, and then dried under reduced pressure. The amount of GMA graft polymerized is define as

$$\text{degree of grafting, DG} = (\text{weight gain})/(\text{weight of BP}) \times 100 \ (\%) \ \ (1)$$

Electron Spin Resonance (ESR) Measurements. For each experiment, the total initial radical concentrations, C_0 (spins/g of BP), of two 2-cm-long fibers (one sample and one control) after the electron beam irradiation in N_2 were measured separately by an ESR spectrometer (JEOL JES−RE series spectrometer), operating at 9.2 GHz at 77 K in liquid nitrogen. Before measurement, the irradiated fibers were allowed contact with air for ~2 min. This treatment was consistent with the graft polymerization procedure described in previous publications.[3,5,7,15,17−19] The samples were inserted into a Pyrex tube (5 mm i.d.) sealed at one end with a silicon stopper and placed in a cylindrical cavity. Spectra were recorded using the following instrumental parameters: sweep width, ±25 mT; modulation width, 0.1 mT; sweep time, 2.0 min; time constant, 0.1 s; and microwave power, 10^{-3} mW. The radical concentration was determined by the double-integration method using γ-irradiated alanine, strong coal, and $CuSO_4 \cdot 5H_2O$ as quantitating references. Mn^{2+} was used to position the spectra. This method is able to quantitate the radical concentration within 2% error limit. After the first measurement, one fiber was reacted with GMA in a glass ampule. The other one (control) was immersed in methanol. Both ampules were vacuumed and placed in a water bath (313 K). At a specific time, the samples were removed simultaneously, and the radical concentrations were again measured. The control experiment was performed to determine ϵ, the concentration ratio of radicals decayed in the solvent at a corresponding temperature.

Results and Discussion

Synthesis of Poly-GMA Brushes on Polyethylene Fibers. We irradiated the fibers with electron beams

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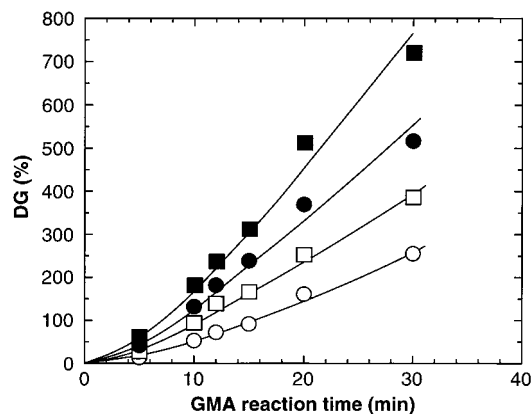
Figure 3. Amount of GMA graft-polymerized at various total irradiation doses (TIDs). Degree of grafting (DG) profiles at (○) 50 kGy, (□) 100 kGy, (●) 150 kGy, and (■) 200 kGy, as a function of GMA reaction time.

Figure 4. Identification and quantification of trapped radical species: (a, c) the derivative form of the ESR spectrum; (b, d) the integral form; (e) by reflecting the integral form spectrum from right to left vertically in the middle, the overflowing asymmetrical part S_p corresponds to the peroxy radical concentration. The symmetrical S_k part at the right end corresponds to the alkyl radical. Methods for separating each radical are detailed in ref 25.

at an exposed total irradiation dose (TID) of 50, 100, 150, and 200 kGy. The amount of GMA graft-polymerized onto the fibers can be varied and estimated from the weight gained by controlling the GMA reaction time (Figure 3). The existence of the terminally anchored poly-GMA brushes on the polyethylene fibers was confirmed spectrophotometrically by FTIR-ATR. When compared to those of polyethylene, new adsorption peaks due to the C=O stretching, epoxy, and ester groups of GMA were observed at 1733 cm^{-1} (sharp peak), 848, 908, and 993 cm^{-1}, and 1149 and 1255 cm^{-1}, respectively (data not shown).

Identification and Quantitation of Trapped Radical Species. The objective of initial electron spin resonance measurements was to quantitatively determine trapped radical species contributed to the graft polymerization of GMA. Irradiation of polyethylene with electron beams in a nitrogen atmosphere results in the formation of three kinds of radicals, alkyl, allyl, and peroxy radicals.[20-23] ESR, which can specifically probe radicals (unpaired electrons) in this empirical system, is therefore a good way to investigate reactions involving these radical species. Because the spectra assigned to these radicals overlap, identification and quantification of each radical can be made by expressing the derivative form of the ESR spectrum (Figure 4 a,c) in an integral form (Figure 4 b,d).[24,25] The identical sextet ESR spectra before (Figure 4a) and after (Figure 4c) graft polymerization of GMA indicated that the terminal radical of the poly-GMA brush perished immediately after the graft polymerization reaction was terminated. To ascribe the trapped radical species, the ESR spectra are simulated using the parameters of line shape, line width, and hyperfine splitting of a trapped radical by applying the ESR data system of ESPRIT 330 (JEOL, Ltd., Japan). Hence, the total initial radical concentra-
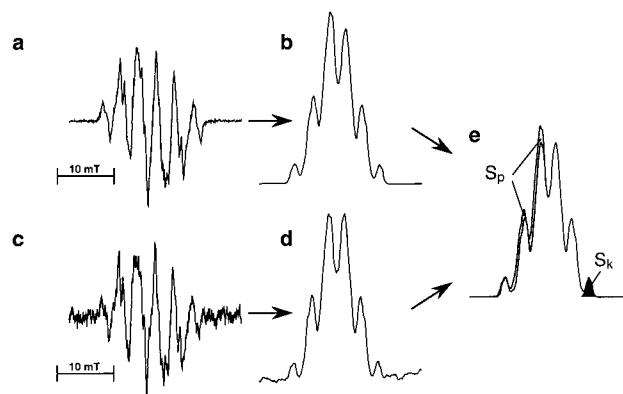
tion (spins/g of BP) from the ESR measurement after the electron beam irradiation is

$$C_0 = C_{0,\text{alkyl}} + C_{0,\text{allyl}} + C_{0,\text{peroxy}} \qquad (2)$$

After graft polymerization of GMA, the total radical concentration is

$$C_1 = C_{1,\text{alkyl}} + C_{1,\text{allyl}} + C_{1,\text{peroxy}} \qquad (3)$$

Therefore, the concentration of radicals consumed by GMA can be written as

$$C_{\text{GMA}} = (1 - \epsilon)C_0 - C_1 \qquad (4)$$

where ϵ, the concentration ratio of radicals decayed in the solvent at a corresponding temperature, can be obtained from the control experiment mentioned in the Experimental Section. For instance, using the radical separation and quantification method as illustrated and described in Figure 4e, a TID of 150 kGy produced a C_0 of 6.89 × 10^{18} spins/g of BP (alkyl, allyl, and peroxy radical concentrations of 4.96 × 10^{18}, 1.36 × 10^{18}, and 0.57 × 10^{18} spins/g of BP, respectively) and a C_1 of 3.64 × 10^{18} spins/g of BP (alkyl, allyl, and peroxy radical concentrations of 1.86 × 10^{18}, 1.25 × 10^{18}, and 0.53 × 10^{18} spins/g of BP, respectively) after graft polymerization of GMA. The percentage of the initial alkyl radical concentration (>70%) remained almost consistent irrespective of the TIDs. The alkyl radicals contributed extensively to the graft polymerization of GMA because a marked decrease (~37%) in the alkyl radical concentration was observed as compared to the concentration changes of allyl and peroxy radicals (~8% each). As a result, eq 4 can be rewritten as

$$C_{\text{GMA}} = (1 - \epsilon)C_{0,\text{alkyl}} - C_{1,\text{alkyl}} \qquad (5)$$

where ϵ is the concentration ratio of alkyl radicals decayed in methanol at 313 K. At TID 150 kGy, DG ~249%, and 15 min of GMA graft polymerization, the ϵ for the alkyl radical was 0.26.

The initial alkyl radical concentration increased from 10^{18} toward 10^{19} spins/g of BP with increasing TID from

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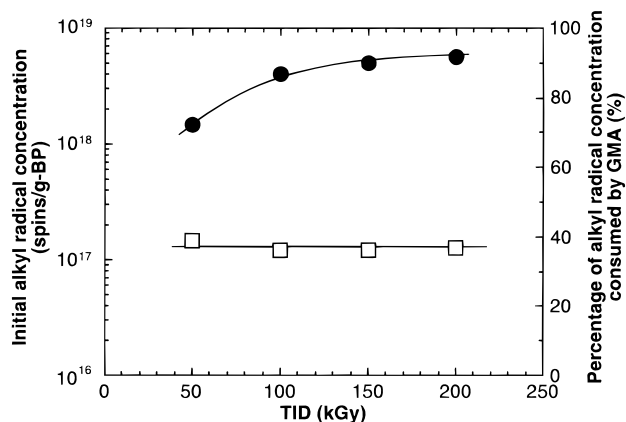(25) Uezu, K.; Saito, K.; Furusaki, S.; Sugo, T.; Ishigaki, I. *Radiat. Phys. Chem.* **1992**, *40*, 31.

Figure 5. Initial alkyl radical concentration profile at different TIDs with the percentage of alkyl radical concentration consumed by GMA. (●) shows the initial alkyl radical concentration produced at different TIDs and (□) the corresponding percentage of alkyl radical concentration consumed by GMA.

50 to 200 kGy (Figure 5). However, the percentage of alkyl radical concentration consumed by GMA (~37%) did not vary with the TID. The increment in the initial alkyl radical concentration led to the increase in the density of the anchored poly-GMA brushes due to the fact that each radical represents one reaction site for the GMA to polymerize. Hence, the spins per gram of BP consumed by GMA can also be interpreted as the number of poly-GMA brushes per gram of BP.

Density and Length of Poly-GMA Brushes. Subsequent ESR measurements were designed to determine the influence of TIDs and DGs on the density and the length of poly-GMA brushes. On the basis of the weight gained after GMA graft polymerization, the average length of each poly-GMA brush can be calculated as a number-average molecular weight:

$$M_n = (M_{GMA}/W_0 N_{Av})/C_{GMA} M_{w,GMA} \qquad (6)$$

where M_{GMA} (=(weight gained)/$M_{w,GMA}$) is the concentration of GMA graft polymerized, N_{Av} the Avogadro's constant, W_0 the starting weight of the polyethylene fiber, and $M_{w,GMA}$ the molecular weight of GMA. Here, we assumed that the recombination of neighboring poly-GMA brushes is negligible because the brushes are stretching out from the crystallite surface toward the amorphous region and entering the pore interior (Figure 1c). We demonstrated that longer poly-GMA brushes (M_n from ~670 000 to ~1 200 000) were obtained when the measured poly-GMA brush density (from eq 5) declined (due to the decreasing TID from 200 to 50 kGy) at a constant DG of ~229% (Figure 6a).

The DG exclusively governs the length of the poly-GMA brushes at a constant TID (Figure 6b). By varying the GMA reaction time, the increase in DG led to the increment of the poly-GMA brush length (M_n) at a constant TID of 200 kGy. However, the density of poly-GMA brushes remained constant (at ~2.0 × 10^18 brushes/g of BP). This indicates that, once GMA monomers start polymerizing on the crystallite surface of the polyethylene fiber, it is difficult to synthesize a new poly-GMA brush at a later time.

From a previous study, similar poly-GMA brushes (TID 200 kGy; DG 200%) with subsequent introduction of diethylamino and ethanolamino groups have shown
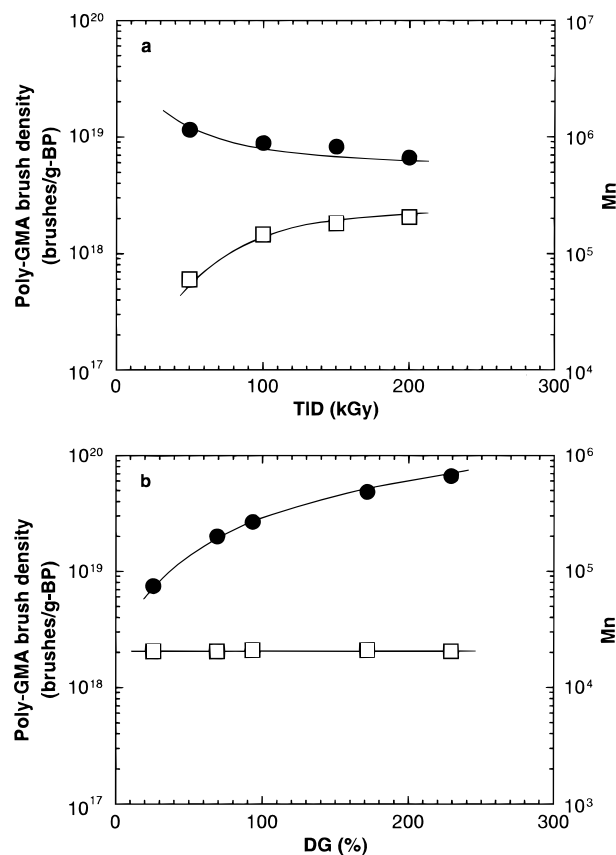

Figure 6. How the density and the length of poly-GMA brushes change with different TIDs and DGs: (a) DG was set at ~229%; (b) TID was set at 200 kGy. (□) shows the poly-GMA brush density and (●) the corresponding length M_n.

a multilayer binding behavior for bovine serum albumin (BSA; size 4 × 4 × 11 nm).[7] The poly-GMA brushes on the pore surface extended themselves[3,7,15,19] and held a maximum 11 layers of BSA in an end-on mode. Our calculation indicated that the saturated 11 layers of BSA binding was equivalent to a length of 121 nm (=11 layers × 11 nm). This calculated length is not the entire poly-GMA brush length because BSA molecules are too large to enter the amorphous region. Nevertheless, our ESR measurement allowed us to obtain reproducible quantitative data for estimating not only the entire length of a poly-GMA brush but also its density directly. For instance, a poly-GMA brush of DG ~229% (TID 200 kGy) was composed of ~4700 GMA molecules. This led to an ideal average brush length of ~730 nm (C−C bond = 0.154 nm). By using Quantasorb (Yuasa Ionics Co., Japan) according to the BET method,[7,15] the specific surface area of GMA-graft-polymerized fiber was determined as 7.5 m²/g of BP. Shown in Figure 6b, as an average of 2.0 × 10^18 poly-GMA brushes is grafted on 1 g of polyethylene, the number of brushes per surface area (m²) is calculated to be 2.7 × 10^17. Since the crystallite region of polyethylene is randomly distributed, the distance between two brushes is difficult to determine. Obviously we can tailor a high density of poly-GMA brushes with an average length ranging from submicrometers to micrometers. Likewise, such high density of poly-GMA brushes enables the hydrophilization of a hydrophobic polyethylene by converting the epoxy groups of GMA into alcoholic hydroxyl groups,[17] and such long poly-GMA brushes can alter the pore

radius.[3,5,15] We also reported previously that the density and the length of terminally anchored polymer brushes governed the ability to capture microbial cells.[18]

Our intention was to use this experiment as a model to study the conformation of polymer brushes synthesized by the electron-beam-induced graft polymerization technique. Clearly, this technique enables the rapid preparation and processing of large libraries of tailor-made smart materials with controllable density and length of polymer brushes terminally anchored onto arbitrary shapes and various kinds of semicrystalline BPs. These findings will provide new approaches for the precise architectural design of "brush-type" materials in areas such as membranes,[3,4,7,15,18,19,26] biomaterials,[27,28] hydrogels,[27] and molecular devices, and expand the synthetic and technological uses of the electron-beam-induced graft polymerization technique.[29–31] Future work will focus on expanding the ESR method in combination with this technique to characterize diverse and practical BPs bearing polymer brushes.

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