Fluorescence Study on the Conformational Change of an Amino Group-Containing Polymer Chain Grafted onto a Polyethylene Microfiltration Membrane

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ABSTRACT: The fluorescence probe technique was used to investigate the characteristics of an amino group-containing polymer chain grafted onto a polyethylene microfiltration (MF) membrane. The amino group-containing polymer chain labeled with a dansyl group that served as a fluorescence probe was grafted onto a polyethylene MF membrane by radiation-induced graft polymerization. The conformational changes of the grafted polymer chain (graft chain) in various solvents were monitored by considering that the steady-state fluorescence emission spectrum of the dansyl group was affected by the polarity of the solvent, the polyethylene, and the graft chain itself. The shift of the emission peak wavelength of graft chains with different lengths demonstrated that the graft chain containing amino groups stretched in water and methanol and shrank in dimethylformamide, acetone, and benzene. These results corresponded to changes in solvent permeability through the membrane pore to which the amino group-containing polymer chains were grafted.

Introduction

Radiation-induced graft polymerization (RIGP) has received considerable attention as an effective technique for modifying existing polymers. We have studied grafted polymer chains with functional moieties such as a chelate-forming group,[1] an ion-exchange group,[2] or an affinity ligand[3] onto the pore surface of polyethylene microfiltration (MF) membranes using RIGP. The resultant membranes specifically collected metal ions or proteins during permeation of their solutions through the membrane pores. Both solution permeability[4−11] and molecule adsorptivity[12,13] of the modified membranes strongly depend on the properties of the grafted polymer chain (graft chain), such as its length, density, and conformation. Therefore, characterization of the graft chain is necessary for designing a membrane suitable for high-rate and high-capacity collection of ions and proteins.

Yamagishi et al.[14] isolated grafted poly(methyl methacrylate) (MMA) chains from a cellulose triacetate MF membrane by acid hydrolysis. They determined the molecular weight distribution of the MMA graft chain by gel permeation chromatography and demonstrated that the length of the MMA graft chain was about 10^3 monomer units, whose stretching length was comparable to the pore radius of the MF membrane.

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A polyethylene MF membrane has been exclusively used as a base polymer for grafting because of its good mechanical strength and chemical stability. Since the isolation of the graft chains from polyethylene is difficult, an alternative method is required to clarify the characteristics of graft chains. In our previous report, we measured water/acetone permeability through a polyethylene MF membrane, to which diethylamino group-containing polymer chains had been grafted, and demonstrated that the density of the diethylamino group had a decisive effect on the stretching/shrinking of the graft chains.[15]

The fluorescence probe technique is a powerful and sensitive tool for studying the equilibrium and dynamics of polymers.[16] For example, this technique was applied to the investigation of discontinuous volume transition of an ionic poly(acrylamide) gel in acetone/water mixed solvents.[17] To our knowledge, however, no characterization of grafted polymer chains by the fluorescence probe technique has been reported. We focus on the dansyl group as a fluorescence probe because its photophysical property provides information on the local polarity and mobility of the microenvironment.[18−21] The objective of this study is threefold: (1) immobilization of dansyl group in amino group-containing polymer chains of various lengths that are grafted onto a polyethylene MF membrane; (2) evaluation of the

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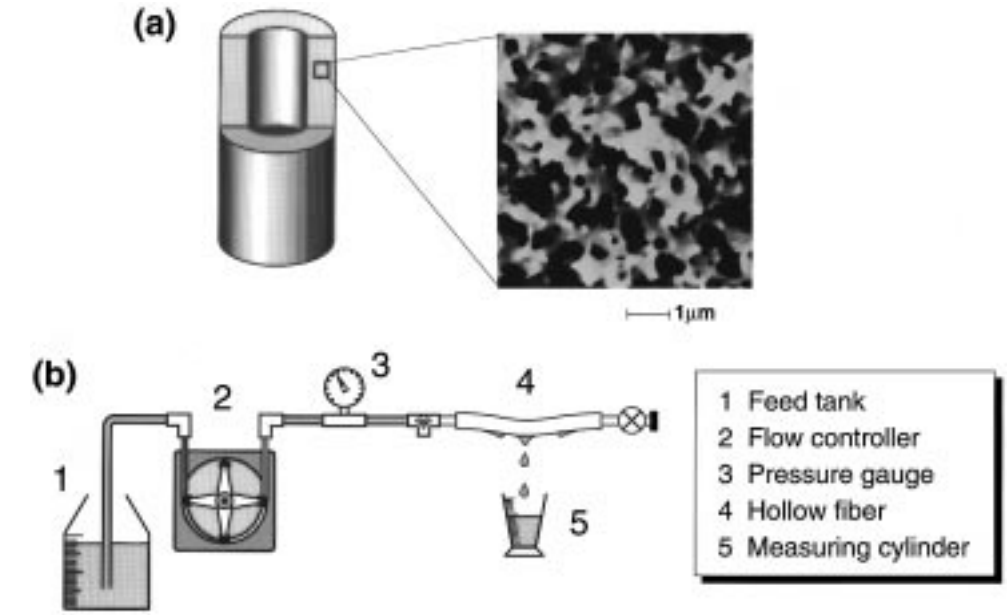

Figure 1. (a) Appearance of the hollow-fiber-type membrane and the picture of pore structure observed by SEM. (b) Experimental apparatus for solvent permeability through the hollow-fiber membrane.

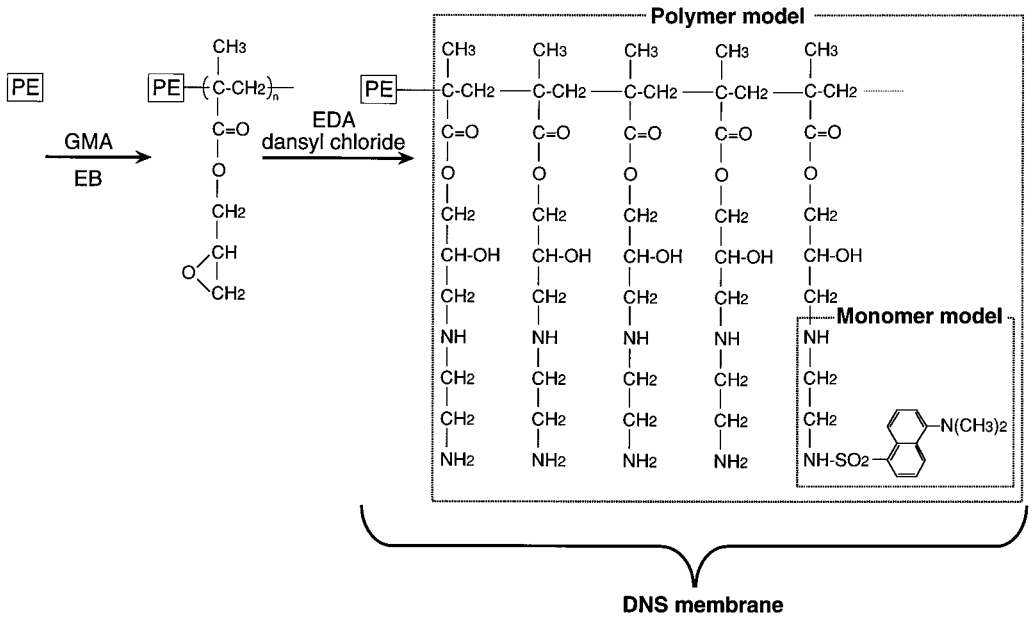

Figure 2. Reaction scheme for grafting dansyl group-containing polymer chains to polyethylene: PE, polyethylene; EB, electron beam; GMA, glycidyl methacrylate; EDA, ethylenediamine.

solvent effect on the conformation of the graft chains based on steady-state fluorescence spectra; and (3) comparison of information on polymer conformation based on microscopic evaluation with that based on macroscopic evaluation, i.e., solvent permeability through the membrane.

Experimental Section

Materials. A commercially available hollow-fiber-type microfiltration membrane (Asahi Chemical Industry Co.) was used as a base polymer for grafting. This hollow fiber was made of polyethylene with 0.34-μm pore diameter and 71% porosity. In the industrial process, an ethylene suspension with silica was polymerized and the polyethylene thus obtained was used for preparing hollow fibers. The porous structure of the hollow fibers was obtained by extraction of the silica from the polyethylene.[22] The inner and outer diameters of the hollow fiber were 1.95 and 3.01 mm, respectively. The appearance of the hollow fiber and the picture of pore structure observed by scanning electron microscopy (SEM) are shown in Figure 1a. In the SEM picture, the light and dark parts indicate polyethylene and pore, respectively.

Technical-grade glycidyl methacrylate (GMA) was purchased from Tokyo Kasei Co. and purified by evaporation. Ethylenediamine (EDA) and dansyl chloride purchased from Wako Pure Chemical Industry were mixed at a molar ratio of 200:1 in order to prepare the reactant mixture for the epoxide ring-opening reaction. Five solvents of fluorescence analytical grade, water, dimethylformamide (DMF), methanol, acetone, and benzene, were used to evaluate the solvent effect on the conformation of the polymer chain.

Preparation of Monomer and Polymer Models Containing Fluorescence Probes. We prepared two compounds containing fluorescence probes and called them the "monomer model" and the "polymer model" (Figure 2). The monomer model was used to determine directly the polarity effect of solvent on a bare dansyl group; the polymer model was used

to determine the polarity effect of solvent and polymer chains (without polyethylene) on a dansyl (DNS) group in the amino group-containing ungrafted polymer chain. The monomer model containing one dansyl group was synthesized by reacting ethylamine with dansyl chloride at 30 °C for 1 h. Poly-GMA was synthesized by free-radical polymerization at 60 °C under a nitrogen atmosphere for 3 h with 2,2′-azobisisobutyronitrile as initiator and purified by reprecipitation from methanol. The epoxide of poly-GMA dissolved in DMF was reacted with an EDA/dansyl chloride mixture to introduce fluorescence probes.[23] The produced polymer gel was used as a DNS group-containing polymer model.

Preparation of a Graft Chain Containing Fluorescence Probes. Figure 2 shows the preparation scheme for the graft chain containing fluorescence probes, which consists of three steps: (1) irradiation of the polyethylene hollow fiber by an electron beam at a total dose of 200 kGy at ambient temperature in a nitrogen atmosphere for free-radical production; (2) immersion of the irradiated hollow fiber in a 10% GMA/methanol solution for graft polymerization; and (3) reaction of the epoxide on the graft chain with EDA/dansyl chloride mixture to introduce the amino group and dansyl probe. Here, we introduced a very low concentration of dansyl probe into the graft chain in order to avoid the energy transfer between dansyl probes on fluorescence measurement.

The degree of GMA grafting, which varied with grafting time at 40 °C, is defined as follows:

$$\text{degree of GMA grafting (dg)} = 100[(W_1 - W_0)/W_0] \quad (1)$$

where W_0 and W_1 are the weights of the untreated polyethylene membrane and the GMA-grafted membrane, respectively. The resultant membrane containing DNS group as a fluorescence probe on the graft chain is referred to as a DNS(dg) membrane, where the dg of each membrane is given in parentheses.

Fluorescence Emission Measurements. The steady-state fluorescence emission spectra of the dansyl groups on the graft chain, the polymer model, and the monomer model were recorded in the range of 400−600 nm. Measurements were performed using an Hitachi F650-40 spectrofluorometer with an excitation wavelength of 340 nm in five solvents at 25 °C. Here, the hollow fiber was sliced off for the purpose of exposure of the inner section of the hollow fiber to the incident light.

Solvent Permeability through the DNS Membrane. The experimental apparatus for solvent permeability through the hollow-fiber-type DNS membrane is shown in Figure 1b. One of the inlets of the 5-cm-long hollow-fiber membrane was stoppered, and five solvents were forced to permeate through the hollow-fiber membrane from the inside to the outside under a transmembrane pressure of 0.1 MPa at 25 °C. The solvent flux was calculated by dividing the flow rate by the inside surface area of the hollow-fiber membrane. The Hagen−Poiseuille equation was applied to estimate the pore radius on the assumption that the pores in the membrane are cylindrical with a constant mean radius. According to derivation made in our previous paper,[15] the pore radius ratio of the DNS membrane to that of the untreated membrane, r/r_0, can be expressed as

$$r/r_0 = [(F/F_0)(S/S_0)(L/L_0)]^{1/4} \quad (2)$$

where F, S, and L are the flux, inside surface area, and thickness of the hollow-fiber membrane, respectively, and subscript 0 denotes untreated membrane.

Results and Discussion

Graft Polymerization. The degree of GMA grafting as a function of grafting time is shown in Figure 3. Yamagishi et al.[14] demonstrated that the molecular weight of the graft chains increased with increasing degree of grafting. Thus, GMA graft chains with different molecular weights can be obtained by varying grafting time from 4 to 20 min.

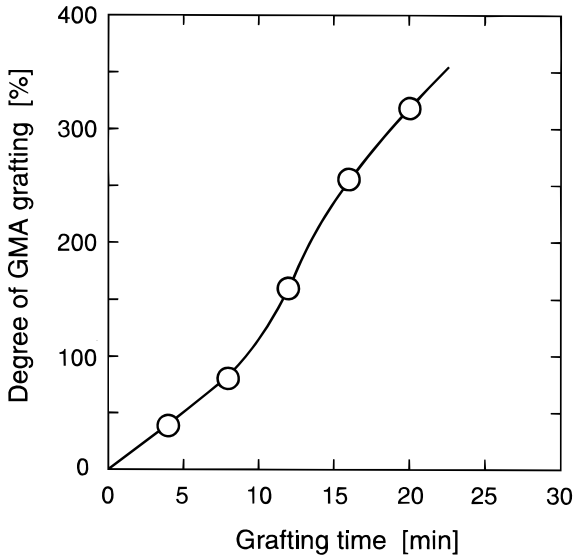

Figure 3. Time dependence of GMA grafting to polyethylene MF membrane. The 200 kGy irradiated base polymer was immersed in 10 vol % GMA/methanol solution at 40 °C.

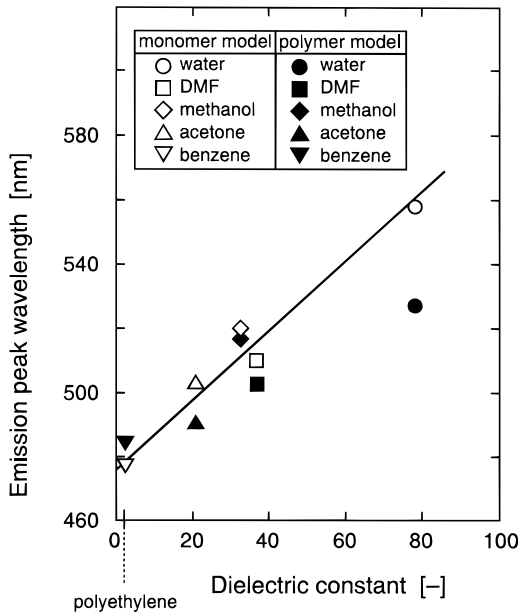

Figure 4. Emission peak wavelength of monomer model and polymer model in various solvents.

Fluorescence Study on Monomer and Polymer Models. The emission peak wavelengths of the monomer and polymer models in various solvents are shown in Figure 4. The emission peak of the monomer model tended to shift to longer wavelengths in a polar solvent. This is because the dimethylamino group in the DNS group takes a twisted intramolecular charge-transfer (TICT) state with the naphthyl group in a polar microenvironment.[20] Thus, the shift of the emission peak gives information on the local microenvironment of DNS probes.

In all solvents except the nonpolar benzene, the emission peak wavelength of the polymer model was longer than that of the monomer model. Therefore, the dielectric constant of the polymer model, which contains both amino and DNS groups, must be located between that of benzene (2.3) and acetone (20.7). Also, the

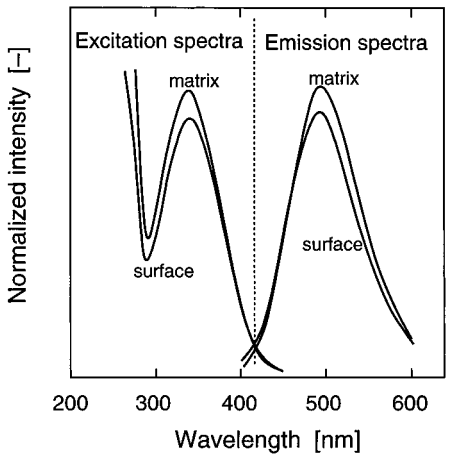

Figure 5. Excitation and emission spectra obtained from the outer surface and inner matrix of the DNS(320) membrane in the dry state. Excitation spectra were monitored at 500 nm.

difference in the emission peak wavelengths of the monomer and polymer models in methanol was smaller than in acetone, because the polymer model swells more in methanol than in acetone. This is consistent with the degree of swelling of the polymer model obtained from volume change.

Fluorescence Study on Graft Chain. The emission and excitation spectra of the DNS(320) membrane were recorded by varying the measurement positions of the membrane. Figure 5 shows typical emission and excitation spectra obtained from the outer surface and inner matrix of the DNS(320) membrane in the dry state. Both emission spectra exhibited peaks at the same wavelength (about 500 nm), which indicated that fluorescence probes (DNS groups) were uniformly distributed throughout the polyethylene inner matrix. Here, we have not experimentally examined the distribution of DNS probes along the grafted polymer chain. However, our previous experiment demonstrated that a conversion of epoxide ring-opening reaction with EDA was almost 100%. Thus, assuming that "DNS-labeled EDA" also reacts with epoxide regardless of epoxide position along the grafted polymer chain, we might obtain random distribution of DNS groups along the grafted polymer chain.

Moreover, emission and excitation spectra (monitored at 500 nm) were mirror images of each other, which indicated that the energy transfer between DNS groups was negligible due to relatively lower DNS content in the graft chain. Since a conversion of epoxide ring-opening reaction with DNS-labeled EDA is unknown, the real DNS content in the graft chain cannot be determined. However, on the assumption that "free EDA" and "DNS-labeled EDA" have the same reactivity with epoxide, the ratio of the number of DNS-labeled monomer units to all monomer units in the graft chain was estimated at about 0.5% (1:200), because we used a mixture of EDA and dansyl chloride at a molar ratio of 200:1 as a reactant for epoxide ring-opening reaction.

Emission peak wavelengths of the DNS membrane as a function of the degree of GMA grafting are shown in Figure 6. In water and methanol, the emission peak was strongly shifted to longer wavelengths when dg was lower than 100%. The amino group-containing graft chain with stretching conformation was strongly affected by solvent polarity. In contrast, the emission peak shift was smaller in DMF, acetone, and benzene,

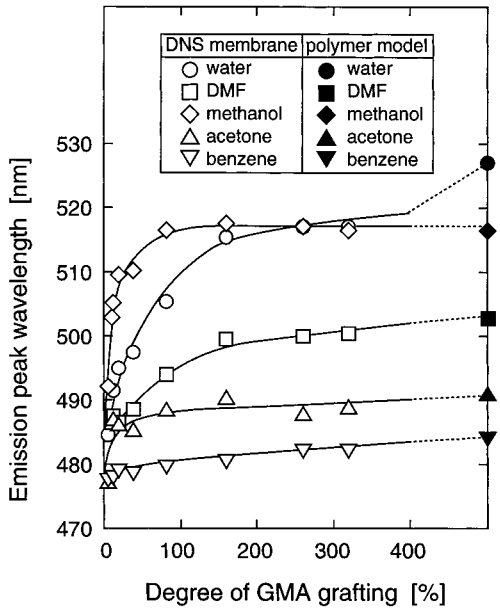

Figure 6. Emission peak wavelengths of the DNS membrane as a function of the degree of GMA grafting.

because the graft chain was expected to shrink in these solvents and the microenvironment of the DNS group was strongly affected by the polyethylene and the graft chain itself.

We cannot observe accurately an emission peak at dg = 0 corresponding to the emission peak of bare polyethylene, because a DNS group cannot be directly immobilized on the bare polyethylene. However, as can be seen from the extrapolating curves in Figure 6 to approach dg = 0, the emission peak wavelength at dg = 0 is about 480 nm in any solvents. In addition, at a high dg, the curves eventually approach each peak wavelength of the polymer model, because the microenvironmental effect of the polyethylene on the DNS group becomes negligible for very large molecular weights of the graft chains.

Solvent Permeability. The pore radius ratio derived from solvent permeability through membranes with different dg's is shown in Figure 7. A small pore size in water and methanol was attributed to the stretching conformation of the amino group-containing graft chain in these solvents. In contrast, a large pore size in DMF, acetone, and benzene implies shrinking of the graft chain in these solvents. In addition, the pore radius increased slightly with increasing dg for all solvents. This is because graft chains were formed both on the pore surface and in the polyethylene matrix; the latter caused swelling of the entire membrane, leading to a large pore size at high dg. The solvent effect on polymer conformation as determined from permeability measurement was in good qualitative agreement with that evaluated by the fluorescence probe technique.

Conclusion

The amino group-containing polymer chain labeled with a dansyl group that served as a fluorescence probe was grafted onto a polyethylene MF membrane by radiation-induced graft polymerization. By measuring the steady-state fluorescence spectra of the graft chain, the monomer model, and the polymer model, we characterized the microenvironment around the probe and the conformational change of the graft chain in

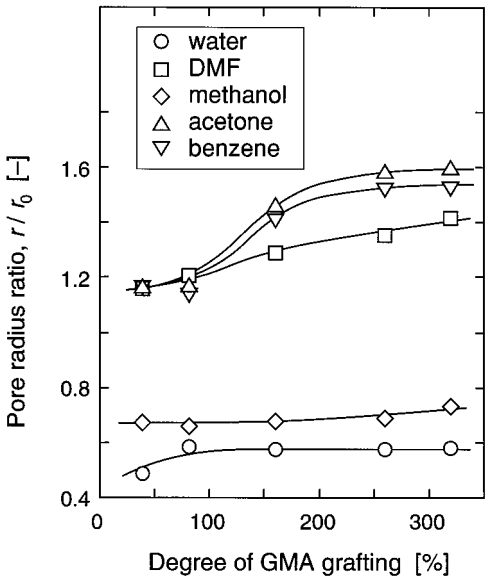

Figure 7. Pore radius ratio, r/r_0 derived from solvent permeability through the membrane as a function of degree of GMA grafting.

various solvents. The results are summarized as follows.

(i) The fluorescence spectra of the monomer model showed a linear relationship between the emission peak of a dansyl group and the polarity of the solvent, while those of the polymer model reflected the influence of polarity of the polymer chain containing amino groups, especially in poor solvents.

(ii) The conformational changes of the amino group-containing graft chain on polyethylene MF membrane in various solvents, i.e., stretching in water and methanol and shrinkage in DMF, acetone, and benzene, were monitored by microscopic characterization, i.e., DNS fluorescence emission peak shift, as well as by the macroscopic characterization, i.e., solvent permeability through the membrane.

A thorough understanding of the solvent effect on the conformation of the amino group-containing graft chain is useful for designing a functional porous membrane by which ions and proteins are efficiently collected during permeation.

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