Control of pore size of polycarbonate membrane with straight pores by poly(acrylic acid) grafts

Yoshihiro Ito, Seigo Kotera, Masahiro Inaba, Kenji Kono and Yukio Imanishi*
Department of Polymer Chemistry, Kyoto University, Yoshida Honmachi, Sakyo-ku, Kyoto, 606 Japan
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The pH-dependent change of the pore size of poly(acrylic acid)-grafted, straight pored polycarbonate membrane was investigated. Peroxide groups were generated on the surface of the polycarbonate membrane by glow discharge, and the membrane was heated in the aqueous solution of acrylic acid to initiate the graft copolymerization. The density and the length of graft chains were dependent on the conditions in the glow-discharge treatment and the monomer concentration in the graft copolymerization, respectively. The water permeability to the poly(acrylic acid)-grafted membrane increased sharply in pH regions below 4, representing the expansion of pores. However, very high densities of graft chains or very long graft chains restricted the mobility of poly(acrylic acid) chains, and the pore size became pH-independent.

(Keywords: poly(acrylic acid); polycarbonate membrane; surface grafting; water permeation; pore size; conformation)

INTRODUCTION

The permeation and release control of substances has recently been investigated on the basis of the change of conformation, chain extension, hydrogen bonding and hydrophilicity of polyelectrolytes. Molecular systems using the swelling behaviour of polyelectrolyte gels[1,2], the transition of specific secondary conformations of polypeptide electrolytes[3,4], the formation of polyelectrolyte complexes[5–7], the solubility-dependent interactions with liposomes[8] and the extension/shrinkage of polyelectrolyte grafts[9,10] have been reported. These molecular systems in combination with enzymes suitable for molecular sensing could be applied for drug-delivery systems that are responsive to biological substances[11–13].

In the present investigation, the control of pore size by changing the length and the density of poly(acrylic acid) chains, which are grafted on polycarbonate membrane with straight pores of uniform size, was investigated on the basis of water permeability.

EXPERIMENTAL

Materials

Commercial straight pored polycarbonate membrane (Nuclepore) was used; the membrane diameter was 25 mm, the membrane thickness was 10 μm, the maximum pore size was 0.2 μm, the pore density was 3×10^8 cm^{-2}. Acrylic acid (extra pure, Nacalai Tesque, Co., Kyoto, Japan) was purified by vacuum distillation. 1,1-Diphenyl-2-picrylhydrazil (DPPH) and rhodamin 6G (practical grade) were purchased from Wako Pure Chem., Co. (Osaka, Japan) and used without further purification. Triply distilled water was used for permeation experiments. The buffer solution used for the permeation experiments was 5 mM tris(hydroxymethyl) aminomethane/hydrochloric acid. Toluene and *N*,*N*-dimethylformamide (DMF) were purified by distillation and vacuum distillation, respectively.

Graft copolymerization[14]

The polycarbonate membrane was placed in an ion-coater (Eiko Eng., Co., Mito, Japan) and glow-discharged under 0.2 mmHg atmosphere with 6 mA electric current for a definite time. The glow-discharged membrane was immediately transferred to aqueous solution of acrylic acid, and the mixture was heated at 60°C for 2 h under a nitrogen atmosphere. After the graft polymerization, the polycarbonate membrane was washed with deionized water using ultrasonic cleaner until the pH of the wash remained unchanged. The membrane was then subjected to the permeation experiment.

Determination of peroxides formed on the membrane[15]

The glow-discharged membrane was immersed in a toluene solution of DPPH (1.116×10^{-4} M), and the mixture was heated under the same conditions as in the graft copolymerization. After cooling the mixture, the amount of DPPH consumed was determined with 521.5 nm absorption (the molar extinction coefficient, 1.05×10^4 M cm^{-1}). The u.v. determination was corrected for the amount of DPPH non-specifically adsorbed to the glow-discharged membrane, which was taken to be the same as that of non-specific adsorption to untreated membrane.

Determination of poly(acrylic acid) graft[16]

Rhodamine 6G was dissolved in phosphate-buffered solution (pH 11, 0.1 M Na_2PO_4) and extracted with toluene. Poly(acrylic acid)-grafted membrane was

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* To whom correspondence should be addressed

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dissolved in DMF and a known amount of the toluene solution of rhodamine 6G was added to the DMF solution. After standing for 1 h, the concentration of carboxyl groups was determined by an increased absorption at 534 nm. DMF solution of a known amount of acetic acid was used for obtaining a calibration curve for the titration.

Water permeation experiment

The graft membrane was loaded on a ultrafiltration apparatus (Advantec Toyo, Co., Tokyo, Japan), and water buffered to a certain pH value was permeated under a given pressure of nitrogen. The permeability was calculated on the basis of the amount of permeation. Under each condition, three pieces of the graft membranes, which were prepared under the same conditions, were subjected to the permeation experiment. The average value of the permeability was obtained with the standard deviation of 1.6% to 3.5%.

RESULTS AND DISCUSSION

Graft polymerization

The time-dependent amount of peroxides formed on the polycarbonate membrane during the glow-discharge treatment is shown in *Figure 1*. The structure of peroxides formed by the glow-discharge treatment in air has been considered to be hydroperoxide rather than diperoxide type[17]. With an electric current of 6 mA the amount of peroxides formed increased with time, reached the maximum value after 40 s of irradiation time, and decreased. The time dependence of the peroxide concentration should indicate that a high concentration of peroxides on the membrane surface induce side reactions such as decomposition/recombination and further oxidation leading to products inactive to initiate the graft copolymerization. With an electric current of 5 mA, it took longer time than with 6 mA to reach critical surface concentration of radicals beyond which radicals are consumed by side reactions, and hence maximum value of radical concentration was not observed during the irradiation of 2 min.

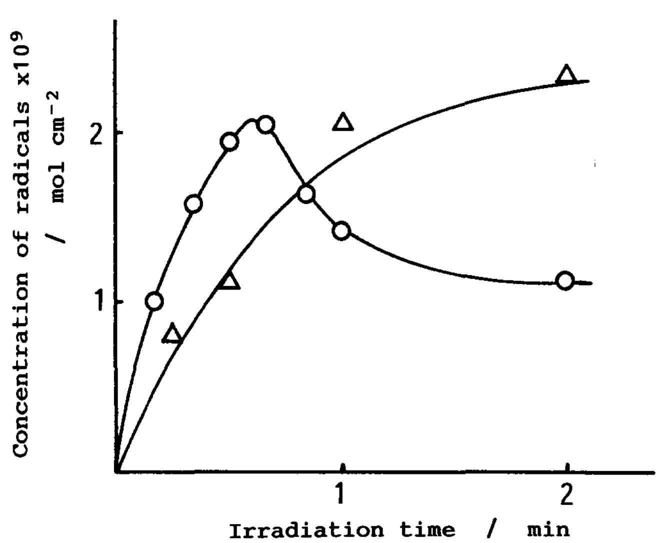

Figure 1 The time-dependent amount of radicals produced on the polycarbonate membrane surface by the glow-discharge treatment: electric current, ○, 6 mA; △, 5 mA

The reaction between the preparative conditions and the properties of the graft membrane prepared in the present investigation are shown in *Table 1*. It is found that the density of carboxyl groups, and possibly of graft chains, can be controlled either by changing the conditions of glow-discharge treatment or by changing the temperature and the monomer concentration of graft copolymerization.

Variation of pore diameter

The water permeation through ungrafted polycarbonate membrane at different pH regions is shown in *Figure 2*. The polycarbonate membrane was glow-discharged and treated with the aqueous solution without acrylic acid under the same conditions as in the graft copolymerization. The permeability was independent of pH values between 1 and 8 and much larger than that through the graft membranes which will be shown below.

The water permeation through a series of graft membranes with different densities of poly(acrylic acid) grafts is shown in *Figure 3*. On going from A-2 to C-2 with increasing densities of graft chains for nearly constant chain lengths, a higher pressure was necessary to have comparable amount of water permeated. For all graft membranes, a sharp change of water permeation occurred at pH of approximately 4. It has been reported that the pK_a value of poly(acrylic acid) is 4.28 (ref. 18). Therefore, the sharp change of water permeation could be explained in terms of the change of pore size as a result of pH-induced conformational change of poly(acrylic acid) graft. At higher pH regions poly(acrylic acid) chains are dissociated and take an extended conformation due to repulsion to reduce the pore size. It should be noted that the pH dependence of water permeation was most remarkable with the graft membrane B-2. This means that the pore size of a membrane is insensitive to the conformational state of the graft chains for the scarcity of the graft chains in A-2 and for the restricted mobility of the graft chains in C-2.

The water permeation through a series of graft membranes with poly(acrylic acid) grafts of different chain lengths is shown in *Figure 4*. It is shown that the

Table 1 Graft polymerization of acrylic acid onto polycarbonate membrane

Graft membrane	Irradiation current (mA)	Irradiation time (s)	Density of peroxides × 10^9 (mol cm^{-2})	Concentration of acrylic acid (wt%)	Polymerization temperature (°C)	Density of carboxyl groups × 10^7 (mol cm^{-2})
A-2	6	10	1.0	10	60	3.2
B-2	6	20	1.6	10	60	5.6
C-2	6	40	2.1	10	60	7.0
C-1	5	60	2.1	5	50	0.85
C-2′	5	60	2.1	10	50	5.6
C-3	5	60	2.1	30	50	13.0

increasing length of graft chains decreased the water permeation. In this series of membranes, the most remarkable pH dependence was observed with a membrane C-1 which has the shortest chains of poly(acrylic acid) grafts among the three membranes. This trend should have been caused by the insensitiveness of the water permeability to the conformational change of graft chains due to dense packing of the pores with increasing chain length in the case of grafting in high densities.

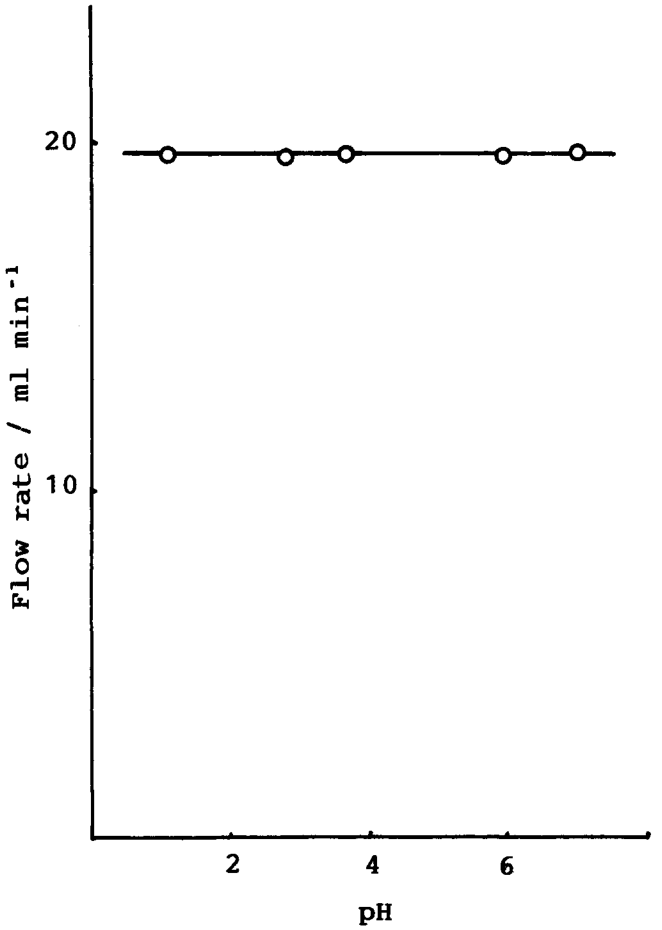

Figure 2 The pH-dependent water permeation through the ungrafted polycarbonate membrane

When a Newtonian fluid such as water flows through a thin tube, the flow rate is related with the diameter of the tube and the pressure by the Hagen–Poiseuille equation. The water permeability of the graft membranes relative to that of ungrafted membrane gave the pore size of the graft membrane by the equation. The calculated lengths of graft chains are shown in *Table 2* and are compared with the theoretical lengths of graft chains which were determined on the basis of the probable degree of polymerization and all-*trans* extended conformation of graft chains. The degree of polymerization of graft chains was obtained on the basis of the density of carboxyl groups on the acrylic-acid-grafted membrane surface (*Table 1*), assuming that the radicals produced by the glow-discharge treatment were all used for the initiation of graft copolymerization. This assumption should not be absurd, because the radicals were determined by the reaction with DPPH under the same conditions as for the graft copolymerization. The degree of polymerization of graft chains obtained on the basis of this assumption is considered to be proportional to real values and is shown in *Table 2* as probable degree of polymerization. It is found that the probable degree of polymerization of graft chains is controlled by changing the temperature and the monomer concentration of graft copolymerization, but independent of the conditions of glow-discharge treatment. In the cases of low density of graft chains (A-2 and B-2), the calculated chain lengths on the basis of the water permeabilities at pH 6.0 are smaller than the theoretical lengths, because water can permeate through chain intervals. In the case where the peroxide density of the glow-discharged membrane was 2.1×10^{-9} mol cm^{-2} (a high density of

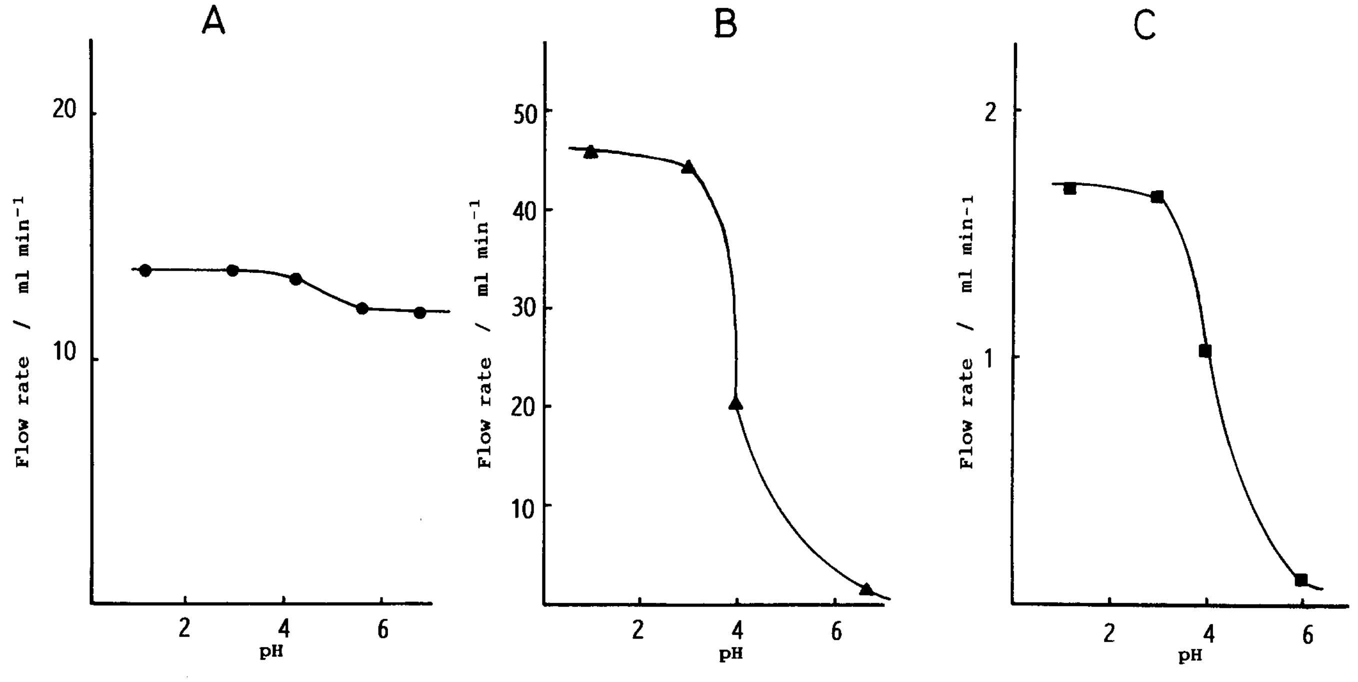

Figure 3 The pH-dependent water permeation through the poly(acrylic acid)-grafted polycarbonate membranes with different densities of graft chains: (A) membrane A-2, pressure 0.2 kg cm^{-2}; (B) membrane B-2, pressure 1.8 kg cm^{-2}; (C) membrane C-2, pressure 1.8 kg cm^{-2}

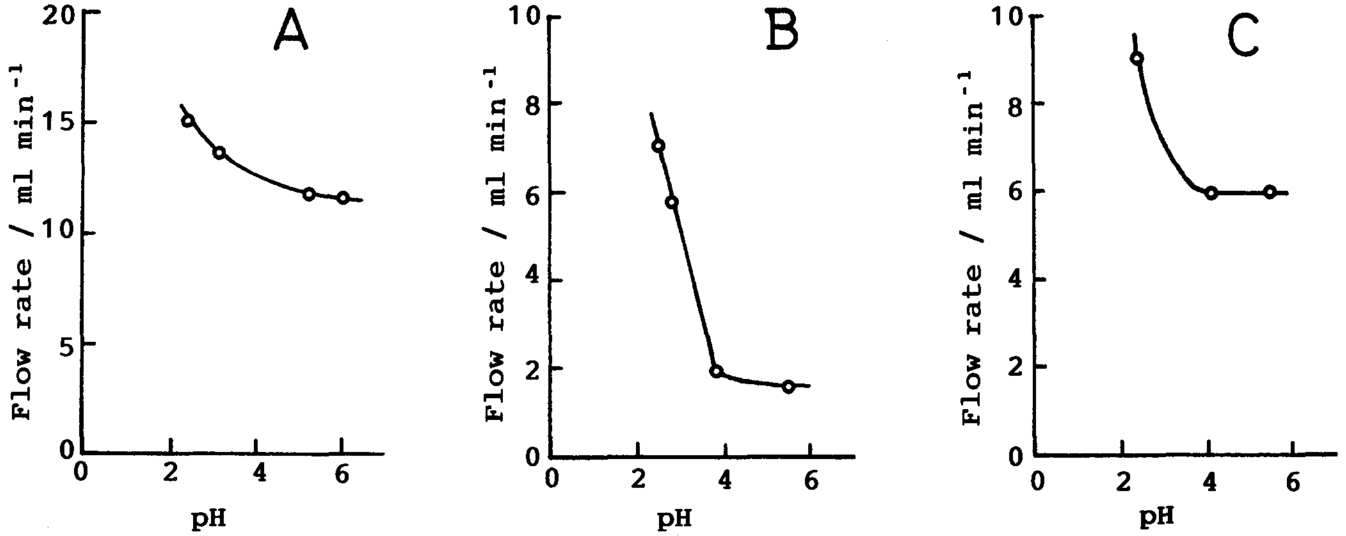

Figure 4 The pH-dependent water permeation through the poly(acrylic acid)-grafted polycarbonate membrane with graft chains of different lengths: (A) membrane C-1, pressure 0.2 kg cm^{-2}; (B) membrane C-2′, pressure 1.8 kg cm^{-2}; (C) membrane C-3, pressure 2.0 kg cm^{-2}

Table 2 Properties of poly(acrylic acid) chains grafted onto polycarbonate membrane surface

Graft membrane	Probable degree of polymerization of graft chains	Theoretical length of graft chains in an extended state (Å)	Calculated length of graft chains (Å) pH 6.0	Calculated length of graft chains (Å) pH 2.5	Chain length at pH 2.5 / Chain length at pH 6.0
A-2	320	800	101	74	0.73
B-2	360	888	632	280	0.44
C-2	340	850	846	678	0.80
C-1	40	100	110	40	0.36
C-2′	270	668	686	544	0.79
C-3	630	1583	870	850	0.98

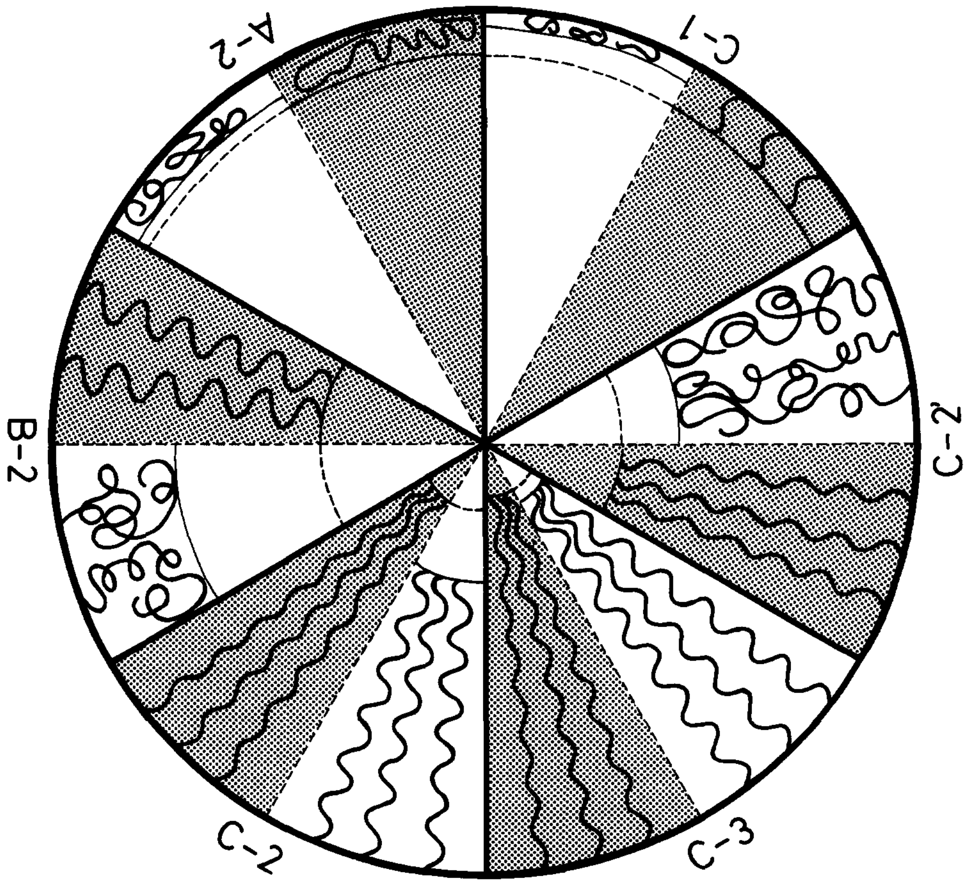

Figure 5 A schematic representation of the pH-dependent water permeation through the poly(acrylic acid)-grafted polycarbonate membrane with different densities and lengths

graft chains), the calculated chain lengths on the basis of the water permeabilities at pH 6.0 were nearly the same as the theoretical chain lengths for the all-*trans* extended conformation. With the graft membranes C-2, C-1 and C-2′, water does not permeate through the intervals of graft chains in a high density, but permeates through the median pore. Therefore, it is concluded that the graft chains in a high density take a nearly fully extended conformation at pH 6.0. However, with a graft membrane C-3, the theoretical chain length (c. 160 nm) is larger than the pore radius (100 nm). In this case it is considered that the chain propagation inside the pores was obstacled by steric interactions of growing chains and the graft polymerizations outside the pores were relatively important.

In the right-hand column of *Table 2*, the degree of chain contraction by lowering pH from 6.0 to 2.5 is shown. It is seen that the pH-induced chain contraction is most remarkable with a membrane having an intermediate density of graft chains (B-2) and a membrane having a high density of short graft chains (C-2). The whole results are explained schematically in *Figure 5*. From *Figure 5* it is understandable that a membrane having very short graft chains (C-1) shows a large degree of pH-induced contraction but a small change of water permeability.

Finally, different pH-dependent behaviours of polyelectrolytes in aqueous solution and in a grafted state should be discussed. It has been reported that poly(acrylic acid) in aqueous solution changes gently the conformation according to pH, while poly(methacrylic acid) shows a sharp change of the chain extension with pH change[19]. However, in the present investigation it was suggested that poly(acrylic acid) grafted to polycarbonate membrane changes rather drastically the chain extension as determined by the water permeability with the variation of pH. In the membranes having low densities of graft chains (A-2 and B-2) and in the membranes having short graft chains (C-1), interactions should occur between poly(acrylic acid) and the surface of polycarbonate membrane as well as between poly(acrylic acid) chains. The interaction of poly(acrylic acid) chains with the surface of polycarbonate membrane should accompany the formation of hydrogen bonds.

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