

Effect of Sorbed Water on Dielectric and Mechanical Properties of Polyion Complex

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Synopsis

Effect of sorbed water on dielectric and mechanical properties is studied for three kinds of polyion complex (PIC) membranes formed from equal moles of polyanion [poly(sodium 4-vinylbenzenesulfonate)] and three polycations of different structural isomerisms [poly(4-vinylphenethyltriethylammonium bromide), poly(3-vinylphenethyltriethylammonium bromide), and random copolymer of these monomers]. Sorption isotherms and swelling characteristics indicate that PIC of para-polycation includes more water microphases than PIC of meta-polycation. Complex dielectric constants of three PICs with varied water contents are measured at frequencies from 10 Hz to 100 kHz and the relaxation is analyzed in terms of the heterogeneous structure. Stress–elongation relationships of PICs equilibrated with water and aqueous NaBr indicate that yield and break stresses are higher for PIC of meta-polycation than that of para-polycation and decrease with increasing NaBr concentration above 0.1M.

INTRODUCTION

Polyion complexes (PICs) are ionically bonded hydrogels of polyanions and polycations and have drawn attention as new materials for medical use.^{1–5} Formation reactions of PICs have been studied by many workers.^{6–10} Permeabilities and mechanical properties of PIC membranes were reported by several authors.^{1–5} Dielectric constant and loss factor of PIC membrane were measured by Michels and his co-workers^{1,11} with varying concentration of added salt (NaBr) at a fixed relative humidity.

Very recently, Kataoka et al.¹² showed that the blood compatibility of PIC prepared from poly(sodium 4-vinylbenzenesulfonate) and poly(vinylphenethyltriethylammonium bromide) depends greatly on the structural isomerism of the latter. The primary purpose of the present work is to investigate the properties of the PIC hydrogels and to elucidate the probable physical cause for the difference in blood compatibility of the hydrogels.

For the purpose of basic understanding of the fine structure of PIC and the behavior of sorbed water in PIC, we studied in detail the complex dielectric constant of PIC in a wide frequency range at varied water contents. Dielectric properties of hydrophilic polymers are in general quite sensitive to the state of sorbed water,¹³ and therefore a detailed dielectric spectrometry is expected to provide us with useful information on the structure of the material.

We describe also stress–elongation relationships of PIC membranes swollen in water and aqueous NaBr because PIC membranes are applied to practical use in contact with aqueous solution.

EXPERIMENTAL

Polyanion [poly(sodium 4-vinylbenzenesulfonate) (PVBS)] and polycation [poly(vinylphenethyltriethylammonium bromide) (PVPEA)] were prepared in the laboratory of Professor T. Tsuruta, the University of Tokyo, and kindly supplied to us.¹⁴ Three kinds of polycations of different structural isomerisms were used: (a) side-chain attached at the para position [para-polycation, Fig. 1(b)], (b) side-chain attached at the meta position [meta-polycation, Fig. 1(c)], and (c) random copolymer of (a) and (b) (*m,p*-polycation, comonomer ratio being *m:p* = 69:31). Molecular weights were given as 4.7×10^5 for PVBS and about 2×10^6 for PVPEA.

Polyanion and polycation were dissolved in equal mole in a ternary solvent comprising water, NaBr, and acetone (approximately 6:2:2 in weight) in a concentration of 10 wt %. The gel of PIC was formed on a substrate of poly(ethylene terephthalate) by evaporation of acetone. The gel was subsequently washed with water several times at 50°C and was left in water at room temperature into a membrane with thickness of 200–500 μm . The PIC membranes prepared in this manner are denoted *p*-PIC, *m*-PIC, and *m,p*-PIC, respectively, after the polycation used. The residual NaBr in the membrane was analyzed as 0.035 mole per molar pair of monomeric units of polycation and polyanion for *p*-PIC and 0.08 for *m,p*- and *m*-PICs.

According to Kataoka et al.,¹² the phase diagram of PIC in the ternary solvent shows that *p*-PIC exhibits a narrower soluble region than *m*-PIC, indicating that the former possesses a better electrostatic binding between polyanion and polycation. The smaller amount of residual NaBr in *p*-PIC supports this conclusion.

Measurements of dielectric constant and water content were made with stepwise increase of relative humidity (RH) for a sample in an air thermostat. The PIC sample was left for one day in the air thermostat (30°C) in which RH was regulated by circulating air through a saturated salt solution. The RH was measured with an electrical hygrometer (Ace Scientific Laboratory, model AH-1P). The water content defined by weight ratio of sorbed water to wet sample was determined by weighing the sample before and after drying. The zero regain was obtained by drying the sample at 50°C in 10^{-3} torr for 10 hr. The complex dielectric constant $\epsilon' - i\epsilon''$ of the sample in the thermostat was measured with a dielectric bridge (General Radio, GR 1621) at frequencies from 10 Hz to 100 kHz. The electrodes on the sample were made by silver paste; their diameters were 1 cm.

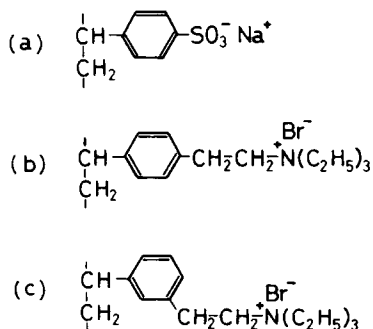


Fig. 1. Chemical formulas of monomeric units of (a) polyanion, (b) para-polycation, and (c) meta-polycation.

Swelling of the sample in water and aqueous NaBr was measured by weighing the sample which had been equilibrated in the medium for several days. In the case of the swollen sample in aqueous NaBr, the NaBr crystals that were formed on the surface of sample during drying were removed and weighed.

The stress–elongation curve of the sample equilibrated in water and aqueous NaBr was measured by uniaxially drawing at a constant rate of 1 cm/min. The length of the sample was 1 cm. The apparatus for this mechanical test was the same as described elsewhere.¹⁵ The sample showed nonuniform neck draw at low concentrations of NaBr and the stress was evaluated by dividing the force by the original cross-sectional area.

RESULTS AND DISCUSSION

Sorption Isotherms and Swelling Characteristics

The sorption isotherms of three PICs are shown in Figure 2 where the curves are successively shifted upwards to avoid overlapping. According to the Brunauer–Emmett–Teller (BET) theory on multilayer sorption,¹⁶ the water content m is related to the relative humidity x by the following relation:

$$m = m_0 C x / \{ (1 - x) [1 + (C - 1)x] \} \quad (1)$$

The curves in Figure 2 up to $x = 50\%$ obey eq. (1) as shown in Figure 3. The BET constants m_0 and C obtained from the intercept on the ordinate and the slope of straight lines in Figure 3 are listed on Table I.

The monolayer sorption m_0 which is approximately 7.5% for the three PICs is equivalent to two water molecules per pair of monomeric units of polyanion

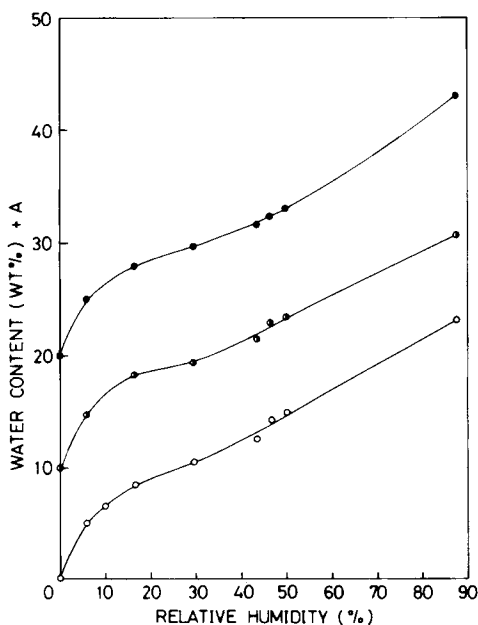


Fig. 2. Sorption isotherms of PICs at 30°C. Curves are shifted successively upwards by A to avoid overlapping: (○) $A = 0$, p -PIC; (●) $A = 10$, m,p -PIC; (●) $A = 20$, m -PIC.

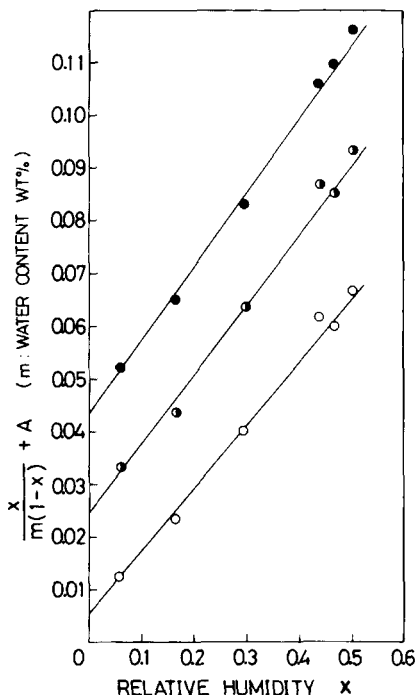


Fig. 3. BET plots of the curves in Figure 2. Plots are shifted upwards successively by A to avoid overlapping: (O) $A = 0$, p -PIC; (●) $A = 0.02$, m,p -PIC; (●) $A = 0.04$, p -PIC.

and polycation. This value of m_0 seems reasonable if we assume that the ionized site of the polyanion alone is hydrated at low RH. The N^+ ion of the polycation is surrounded by hydrophobic ethyl groups and may have no monolayer sorption.

A lower value of C for p -PIC than for m -PIC in Table I indicates an easier multilayer sorption. In fact, the water content at $x = 90\%$ is the highest for p -PIC. This property of p -PIC is more pronounced in the swelling experiments.

Figure 4 shows the water content of PICs which have been equilibrated in pure water and in aqueous NaBr. The water content of p -PIC swollen in pure water is twice that of m -PIC, as expected from the sorption isotherms.

Figure 4 shows also the swelling of PICs in aqueous NaBr. The water content is almost independent of NaBr concentration for p -PIC, but for m,p -PIC and m -PIC, the water content increases with increasing salt concentration, almost to reach the hydration of p -PIC in NaBr solutions.

The ratio of NaBr crystals formed by drying on the surface of the swollen

TABLE I
BET Constants of Three Polyion Complexes at 30°C

Sample	m_0 (wt %)	C
p -PIC	7.5	25
m,p -PIC	7.3	27
m -PIC	7.0	36

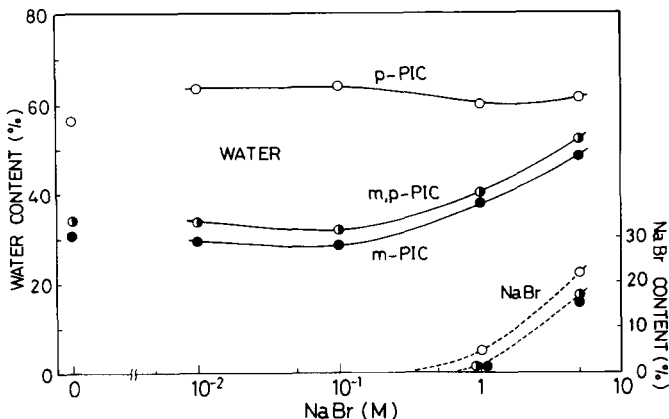


Fig. 4. Contents of water (solid curve) and extracted NaBr (broken curve) of PIC equilibrated in pure water and aqueous NaBr at 30°C plotted against NaBr concentration.

sample to sorbed water is 36% in weight at 5M NaBr for all PICs, being somewhat lower than the concentration of NaBr in the equilibrating solution, 52% at 5M.

Dielectric Relaxation

Figures 5 through 10 illustrate real and imaginary parts of complex dielectric constant for three PICs at various water contents.

Three processes are found for all the samples α , β , and γ in order of increasing frequency, as indicated in Figures 5 and 6. Each process shifts to a high-frequency side with increasing water content. The α process, which is manifested by the upswing of both ϵ' and ϵ'' at the low-frequency side, may be attributed to effects of dc conductivity and electrode polarization, as is usual for electrically conductive polymers with ionic conduction.¹⁷ The γ process with a low loss peak at the highest-frequency side may be attributed to some motion of polymer segments cooperated with water.

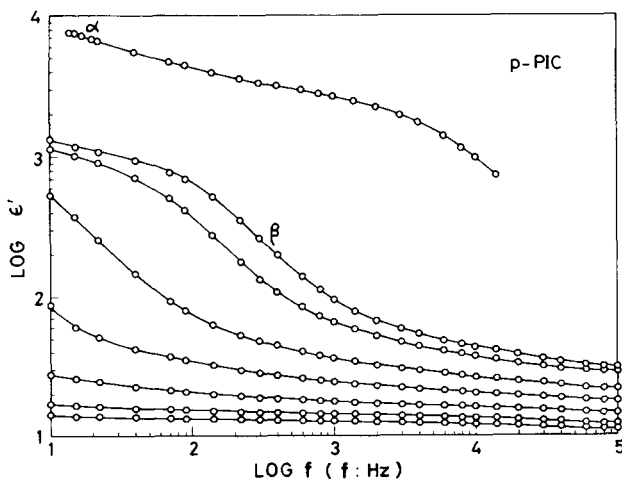


Fig. 5. Real part of dielectric constant of *p*-PIC at 30°C for water contents: 23.2, 15.0, 14.4, 12.4, 10.5, 8.5, 6.4, and 5.1 wt % from top.

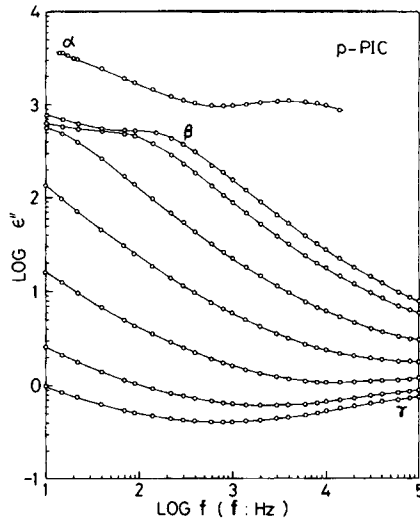


Fig. 6. Imaginary part of dielectric constant of *p*-PIC at 30°C. Water contents are the same as Fig. 5.

In the following, we will focus our attention to the β process which is most dominant in the present frequency range. By the Cole-Cole plot of ϵ'' vs. ϵ' , we separated the β process from other processes and obtained the dielectric increment $\Delta\epsilon$ (difference between low- and high-frequency limits of ϵ') and the loss peak frequency f_m as plotted in Figures 11 and 12, respectively.

Figure 11 indicates that the β process appears at water content higher than the monolayer sorption m_0 and $\Delta\epsilon$ increases with increasing water content up to the order of magnitude of 10^3 . Such a high value of $\Delta\epsilon$ cannot be explained by the dipolar orientation and should be ascribed to an interfacial polarization of a heterogeneous system¹¹ (Maxwell-Wagner relaxation¹⁸). It is generally believed that a hydrogel consisting of polymers with hydrophobic backbone and

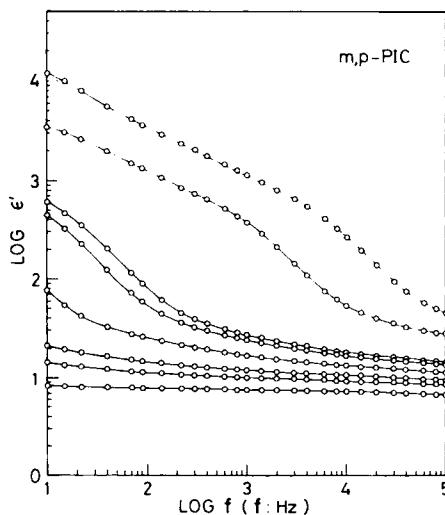


Fig. 7. Real part of dielectric constant of *m,p*-PIC at 30°C for water contents: 20.7, 17.9, 13.7, 13.3, 11.5, 9.5, 8.4, and 4.9 wt % from top.

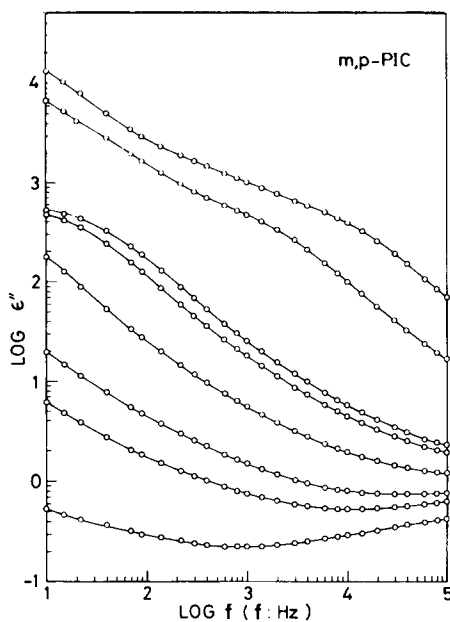


Fig. 8. Imaginary part of dielectric constant of *m,p*-PIC at 30°C. Water contents are the same as Fig. 7.

hydrophilic side groups contains water heterogeneously. It is thermodynamically stable that water molecules at a high water content form microphases or clusters in the region rich in hydrophilic groups. We assume, therefore, that in PIC part of the sorbed water forms microphases that are surrounded by positively and negatively ionized side groups.

We may reasonably assume that the microphase grows more easily in *p*-PIC, in which bindings of anionic and cationic side groups have been originally more regularly formed. Water is introduced into such a region, breaking the bindings. This model is consistent with the fact that the water content of *p*-PIC is higher than that of *m*-PIC at a high RH or at the equilibrium with water. The model

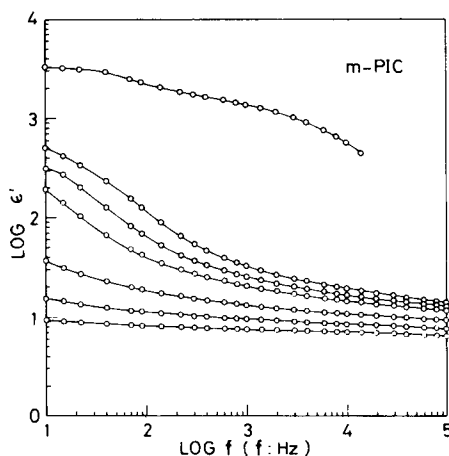


Fig. 9. Real part of dielectric constant of *m*-PIC at 30°C for water contents: 23.0, 13.1, 12.4, 11.7, 9.8, 8.0, and 5.2 wt % from top.

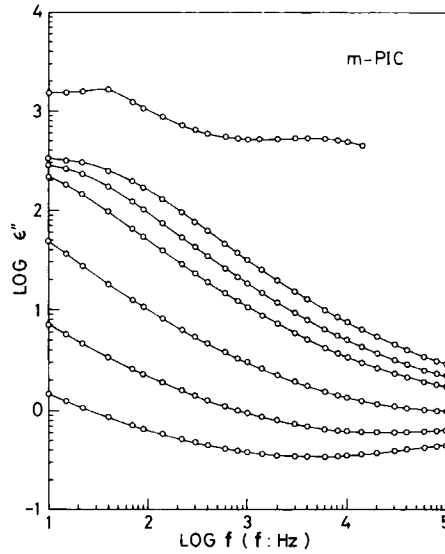


Fig. 10. Imaginary part of dielectric constant of *m*-PIC at 30°C. Water contents are the same as Fig. 9.

interprets the fact in Figure 11 that $\Delta\epsilon$ grows linearly with water content for *p*-PIC, but levels off for *m*-PIC.

According to the Maxwell-Wagner theory¹⁸ on the heterogeneous system, dielectric increment $\Delta\epsilon$, the high-frequency limiting dielectric constant ϵ_∞ , and the relaxational frequency f_m are given, respectively, by

$$\Delta\epsilon = \frac{9(\epsilon_1\sigma_2 - \epsilon_2\sigma_1)^2}{(\epsilon_2 + 2\epsilon_1)(\sigma_2 + 2\sigma_1)^2} \phi \quad (2)$$

$$\epsilon_\infty = \epsilon_1[1 - 3\phi(\epsilon_1 - \epsilon_2)/(\epsilon_2 + 2\epsilon_1)] \quad (3)$$

$$f_m = 2(\sigma_2 + 2\sigma_1)/(\epsilon_2 + 2\epsilon_1) \quad (4)$$

where ϵ and σ are the dielectric constant and the DC conductivity, respectively,

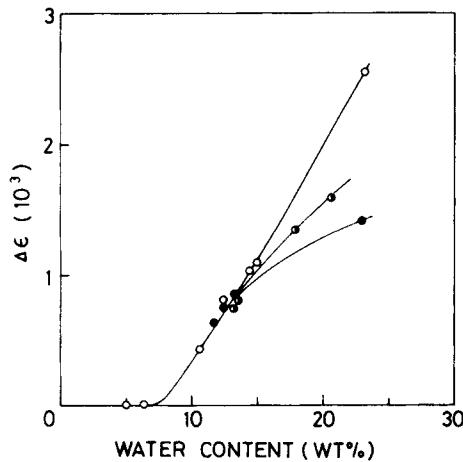


Fig. 11. Dielectric increment of β process plotted against water content for three PICs: (O) *p*-PIC; (◐) *m,p*-PIC; and (●) *m*-PIC.

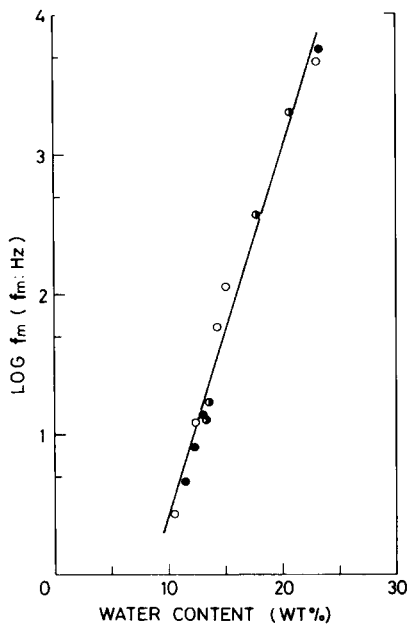


Fig. 12. Dielectric relaxation frequency of β process plotted against water content for three PICs. Points are identified as in Fig. 11.

subscripts 1 and 2 stand for matrix and microphase (assumed as sphere), respectively, and ϕ is the volume fraction of the microphase. In eqs. (2)–(4), we assumed $\phi \ll 1$ for simplicity.

The dielectric constant of microphase ϵ_2 may be close to or less than the dielectric constant of free water, 80, and assumed to be much lower than that of matrix ϵ_1 , which is roughly estimated by

$$\epsilon_1 = [4\pi N(el)^2/(3kT)][3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)] \tag{5}$$

where N is the number density of ionized sites, e is the elementary charge, l is the distance of jump of the site, k is the Boltzmann constant, T is the absolute temperature, and ϵ_0 is the low-frequency limit of dielectric constant. N and l in eq. (5) are functions of water content in the matrix. If we tentatively assume that all ionized sites contribute to ϵ_1 ($N = 3 \times 10^{21} \text{ cm}^{-3}$) and $l = 10 \text{ \AA}$, we get from eq. (5), $\epsilon_1 = 1.0 \times 10^3$. On the other hand, we may assume $\sigma_2 \gg \sigma_1$ because free Br^- and Na^+ ions can move more readily in water than in one matrix.

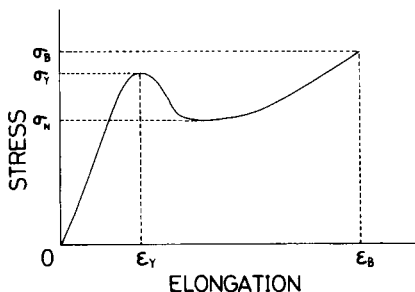


Fig. 13. Schematic diagram of stress–elongation curve of swollen PIC membrane at low NaBr concentrations.

TABLE II
 Mechanical Parameters of Three Polyion Complex Membranes Equilibrated in Water and Aqueous NaBr (30°C)

Sample	NaBr M	E 10^8 dyn/cm^2	σ_Y 10^7 dyn/cm^2	σ_N 10^7 dyn/cm^2	σ_B 10^7 dyn/cm^2	ϵ_Y %	ϵ_B %
<i>p</i> -PIC	0	3.4	4.3	3.6	4.4	17	200
	0.1	2.9	4.2	3.4	3.8	19	180
	1	1.1	0.85	0.80	1.2	11	290
	5	0.18	—	—	0.88	—	270
	0	3.3	5.2	4.5	4.9	22	145
<i>m_p</i> -PIC	0.01	4.1	3.9	2.9	3.7	14	210
	0.1	3.2	4.1	3.7	4.6	20	390
	1	1.9	1.9	1.6	2.4	15	370
	5	0.4	—	—	0.98	—	380
	0	4.5	7.2	5.6	6.6	23	150
<i>m</i> -PIC	0.01	5.2	7.9	6.3	6.9	20	140
	0.1	4.2	7.7	5.1	6.9	24	240
	1	1.8	2.4	2.0	3.3	25	310
	5	0.15	—	—	0.73	—	320

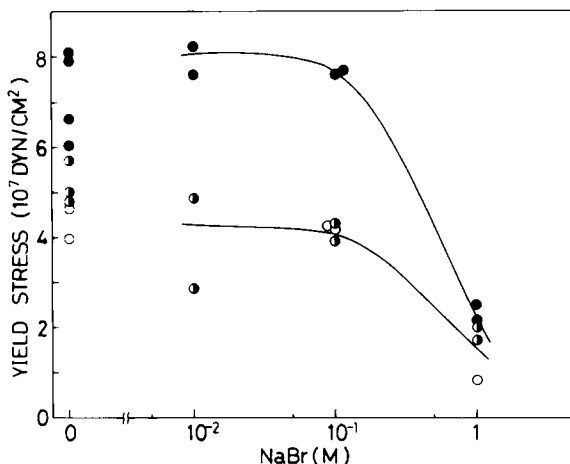


Fig. 14. Yield stress of swollen PICs at 30°C plotted against NaBr concentration in equilibrating solution. Points are identified as in Fig. 11. Top curve is for *m*-PIC and bottom for *m,p*- and *p*-PICs.

Under these assumptions, eqs. (2)–(4) are reduced to simple forms

$$\Delta\epsilon = 9\epsilon_1\phi/2 \tag{6}$$

$$\epsilon_\infty = \epsilon_1(1-3\phi/2) \tag{7}$$

$$f_m = \sigma_2/\epsilon_1 \tag{8}$$

The relation between $\Delta\epsilon$ and *m* in Figure 11 is explained by eq. (6) where both ϵ_1 and ϕ are functions of *m*. Assuming for simplicity that all sorbed water might form microphases, the microphase should have dielectric constant $\epsilon_1 = 2 \times 10^3$, which agrees roughly with ϵ_1 estimated from eq. (5). The observed value of ϵ_∞ lower than that predicted from eq. (7) suggests that the observed β relation includes both the Maxwell–Wagner relaxation and the relaxation of ϵ_1 itself.

The relaxation frequency f_m of *p*-PIC at *m* = 15% is 100 Hz (Fig. 12) which yields $\sigma_2 = 2 \times 10^5 \text{ sec}^{-1}$ from eq. (8) along with $\epsilon_1 = 2 \times 10^3$. The dc conductivity of the whole membrane σ can be estimated from ϵ'' in the α region by

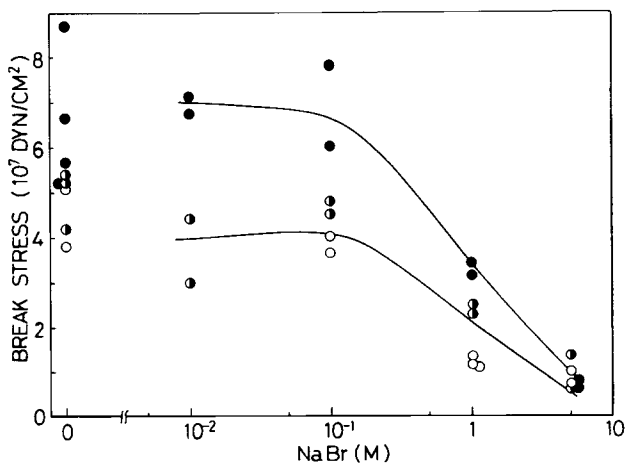


Fig. 15. Break stress of the same samples as in Fig. 14.

$$\epsilon'' = 4\pi\sigma/\omega \quad (9)$$

where ω is the angular frequency. For *p*-PIC at $m = 15\%$, $\epsilon'' = 800$ at 10 Hz, yielding $\sigma = 4 \times 10^3 \text{ sec}^{-1}$ from eq. (9). The value of σ much lower than σ_2 is in accordance with our assumption $\sigma_2 \gg \sigma_1$.

The behavior of $\Delta\epsilon$ in Figure 11 for *m,p*-PIC and *m*-PIC implies that the region capable of forming the microphase is rather limited on account of incomplete binding among ionized groups, and $\Delta\epsilon$ levels off at high water content. The residual water is sorbed homogeneously in the matrix without forming microphases.

The relaxation frequency plotted against m in Figure 12 indicates that $\log \sigma_2$ increases linearly with increasing water content. In other words, the activation energy of σ_2 decreases in proportion to Δm , water content excess over m_0 . This increase in σ_2 may be due to the increase in size of microphase.

Stress–Elongation Relationship

Since the PIC membrane is applied to practical use in contact with aqueous solution like blood, it is important to evaluate mechanical properties of the membrane in a similar environment. Salt ions in the equilibrating solution may have some effect on the ionic binding in the PIC.

We carried out the elongation test at a constant elongation rate for PIC samples that had been equilibrated in water and aqueous NaBr. The PIC showed a nonuniform neck draw at low salt concentrations and the stress–elongation curve gave a profile as illustrated in Figure 13 at salt concentrations below 1*M*. Characteristic parameters are Young's modulus E obtained from the initial slope of the curve, stress at yield σ_Y , elongation at yield ϵ_Y , stress at neck draw σ_N , stress at break σ_B , and elongation at break ϵ_B . The results are summarized in Table II and partly illustrated in Figures 14 and 15.

The high values of E , σ_Y , σ_N , and σ_B of *m*-PIC among three PICs are ascribed to the lowest water content, as shown in Figure 4. For all samples, these quantities begin to decrease at 0.1*M* NaBr with increasing salt concentration. Incidentally, 0.1*M* NaBr is roughly isoosmotic to the physiological NaCl solution. The decrease arises from the effect of NaBr which breaks the ionic binding. Elongations at yield and at break are approximately constant for all PICs through the whole range of salt concentration.

In conclusion, PIC with high water content possesses a heterogeneous structure due to microphase formation. A better blood compatibility of *p*-PIC than *m*-PIC observed by Kataoka et al.¹² may be attributed to a higher degree of heterogeneity of the former.

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