Effects of Various Salts on the Mechanical Properties of Homogeneous Poly(2-hydroxyethyl methacrylate) Hydrogels

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ABSTRACT: Dynamic mechanical measurements were carried out by a longitudinal vibration method on homogeneous poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogels with added sodium chloride, sodium sulfate, and sodium iodide. Complex tensile moduli were measured at frequencies between 0.006 and 0.6 Hz and at various temperatures between 0 and 40°C. The effects of the addition of salts to PHEMA hydrogels on the shape of moduli and compliances and on the monomeric friction coefficient ζ were studied. It was found that the addition of sodium chloride and sodium sulfate to PHEMA hydrogels causes an increase in ζ and, that, on the other hand, sodium iodide acts as a plasticizer in the gels. The latter behavior was explained as due to specific ion—polymer interactions. The time—concentration superposition was performed for the system with added salts and the PHEMA gels without added salts, which were studied previously. The concentration reduction which was used in the superposition of the main transition region cannot be applied to the rubber-like region. The values of the reduced compliance in the rubber-like region decrease in the order of NaI—water > water > NaCl—water, Na_2SO_4—water. This effect was interpreted in terms of the difference in the influence of the added salts to a diluent-induced structure in the PHEMA gels.

KEY WORDS   Viscoelasticity / Poly(2-hydroxyethyl methacrylate) / Hydrogel / Monomeric Friction Coefficient / Fujita Theory / Berry—Fox Theory /

Amphiphilic 2-hydroxyethyl methacrylate polymers (PHEMA) crosslinked by a small amount of ethylene glycol dimethacrylate have been applied in medicine to a still increasing degree, especially as materials for soft contact lenses.[1] The mechanical behavior of PHEMA in the swollen state prepared in the absence and/or presence of water has been investigated by a number of workers.[2] Visually clear (homogeneous) gels are obtained if the water content during polymerization is less than about 40%. Above this critical dilution, heterogeneous gels and eventually white spongy materials are formed. The heterogeneity above the critical dilution is caused by the poor compatibility of the polymer with water. Recently, employing the turbidity ratio method, Dušek and Sedláček[3] showed that PHEMA chains aggregate in visually clear gels.

Previously, the authors[4] investigated the effect of water, which acts as a plasticizer or as an inert diluent during network formation, on the mechanical behavior of the networks. From a practical point of view, the mechanical behavior of PHEMA hydrogels with added salts is also interesting. A hydrogel contact lense should be boiled in water or in saline solution for the purpose of cleaning and sterilization. The swelling behavior of PHEMA hydrogels was extensively studied by Refojo.[5] The swelling degree of PHEMA hydrogels depends markedly on the species of salts.

In this paper, it is our aim to investigate the effect of various added salts on the mechanical behavior and to compare the data for simple PHEMA hydrogels studied previously[4] with the present data.

EXPERIMENTAL

Samples

Homogeneous poly(2-hydroxyethyl methacrylate) hydrogel, sample W-40 from our previous study,[4] was used. It was prepared by copolymerization of 2-hydroxyethyl methacrylate and a small amount of ethylene glycol dimethacrylate in the presence of 40% by volume of water. Pieces of water-equilibrated gel (W-40) were allowed to remain at room temperature in aqueous solutions (0.1, 0.3, 0.6, and 1 mol/l) of sodium chloride, sodium sulfate, and sodium iodide. After 3-months equilibrium swelling was assumed to be reached. We determined the water content in the standard manner, by blotting the superficial aqueous solution and weighing the specimens both in their swollen state and after drying to constant weight.

The weight fractions of water (w_1) are shown in Figure 1. Gels equilibrated with sodium chloride solutions (series A) and sodium sulfate solutions (series B) were used for dynamic measurements. Starting from gels equilibrated with 1 mol/l solution of sodium iodide, less swollen samples (series C) were also prepared in the following way: first deswollen by drying to the desired extent at room temperature, and then soaked in liquid paraffin (which is immiscible with the polymer) at 25°C for 1 day in order to insure homogeneous swelling throughout the sample. The w_1's are 0.160, 0.180, and 0.254. Some characteristics of the samples used are given in Table I. w_s are the weight fractions of salt in the gels, in which the salt concentration was assumed to be that outside the
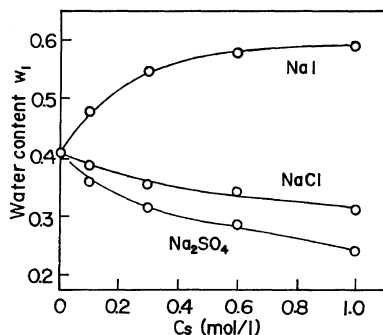

Figure 1. Effect of NaCl, Na$_2$SO$_4$, and NaI on the swelling of PHEMA.

Table I. Some characteristics of the sample used

Sample	w_1	w_s	w_s'	$v_{1,s}$
W-40[a]	0.409			
A-1	0.388	0.002		0.453
A-2	0.356	0.006		0.422
A-3	0.345	0.012		0.414
A-4	0.312	0.018	0.015	0.382
B-1	0.361	0.005		0.426
B-2	0.315	0.013		0.381
B-3	0.288	0.025		0.356
B-4	0.242	0.035		0.308
C-1	0.254	0.167	0.171	0.399
C-2	0.185	0.182		0.322
C-3	0.160	0.188		0.293

[a] W-40 from a previous study[4]: a copolymer of PHEMA with 0.5×10^{-4} mol/cm^3 of ethylene glycol dimethacrylate prepared in the presence of 40% of water.

gels. The weight fractions of salt in the gels w_s' were determined for samples A-4 and C-1 from the elemental analysis. Results are also shown in Table I. w_s' is not equal to w_s, because adsorption or desorption of salt with the polymer may occur. From the results of the elemental analysis we use w_s instead of w_s', taking account of the errors of about 20% with respect to the salt concentration of the gels. The volume fractions of salt solution $v_{1,s}$ were calculated using the equation $v_{1,s} = 1/[1 + d_2 w_2/d_{1,s}(w_1 + w_s)]$; d_2 is the density of the polymer (1.3 g/cm^3) and $d_{1,s}$ that of salt solution.

Measurements of Complex Tensile Modulus

Measurements are carried out by use of a modified Fukuda and Date's apparatus[6] in liquid paraffin in the frequency range 0.006 to 0.6 Hz and the temperature range 0 to 40°C. The specimens were about 5 cm in length, 0.5 cm in width, and 0.1 cm in thickness. The measuring technique is described elsewhere.[4]

RESULTS AND DISCUSSION

Transition Region

The data for the sample B-4 are illustrated. Values of E' and E'' for this system are shown in Figures 2 and 3. Data for each system were superimposed to find log a_T values. The reduc-
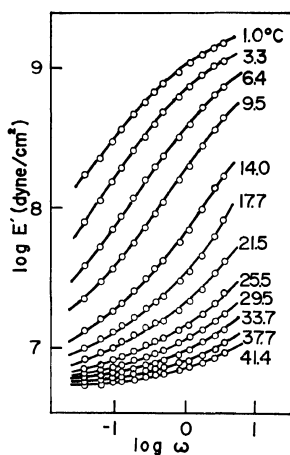
Figure 2. Log E' of B-4 plotted against $\log \omega$ at 12 temperatures as indicated.
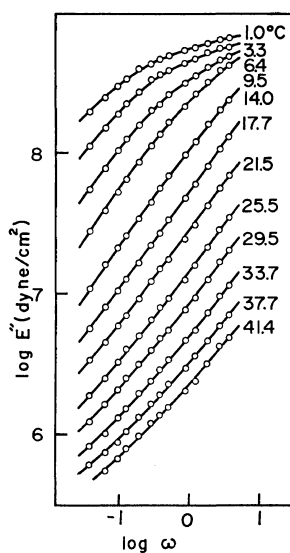

Figure 3. Log E'' of B-4 plotted against $\log \omega$ at 12 temperatures as indicated.

tion equations are: $E_p{'}=E'(Td/T_0d_0)$, $E_p{''}=E''(Td/T_0d_0)$ where d and d_0 are the densities at the absolute temperature T of the measurements and the standard temperature T_0. Composite curves of $E_p{'}$ and $E_p{''}$ for series A, B, and C are plotted logarithmically against the reduced circular frequency ωa_T in Figures 4 and 5. In these figures composite curves of the water-equilibrated sample W–40, taken from ref 4, are also shown.
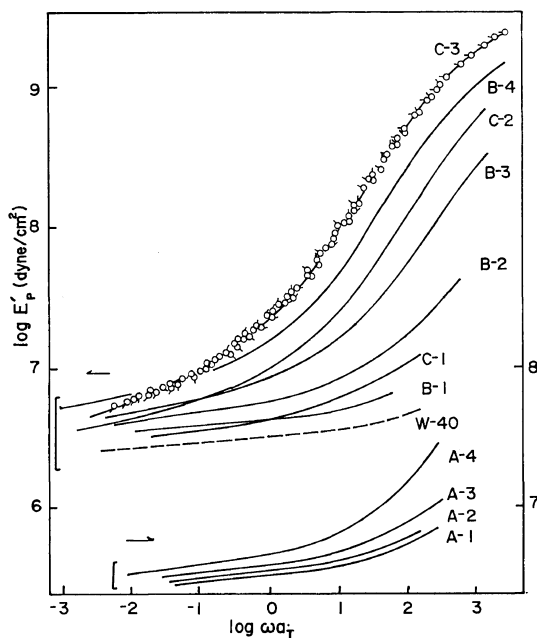

Figure 4. Log $E_p{'}$ vs. $\log \omega a_T$ for PHEMA hydrogels with added NaCl, Na$_2$SO$_4$, and NaI, at various temperatures reduced to 25°C. Water and salt concentrations are listed in Table I. Measurements for C-3 were performed at the temperatures, 1.4, 7.9, 13.2, 18.0, 24.5, 29.6, 34.4, and 39.6°C; pip pointing left denotes the lowest temperature and successive 45° clockwise rotations denote successively higher temperatures. Similar sequences were used for the other systems. The curve of W–40 was taken from ref 4.

From the values of $\log a_T$, the constants c_1 and c_2 of the WLF equation[7] were evaluated by the well-known procedure, for the reference temperature 25°C. Results are shown in Table II.

The curves extending over 7 decades have the usual shape in the transition from rubber to glass-like consistency. Decreasing concentration of PHEMA shifts $\log E_p{'}$ and $\log E_p{''}$ curves toward lower frequencies with relatively little change in shape at high-frequency. Viscoelastic properties in the transition region are supposed to be governed by short-range configurational motions of the polymer chain between coupling points on a molecule.[7] The position of the transition zone reflects the magnitude of the monomeric friction coefficient ζ. The storage and loss modulus curves at various concentra-
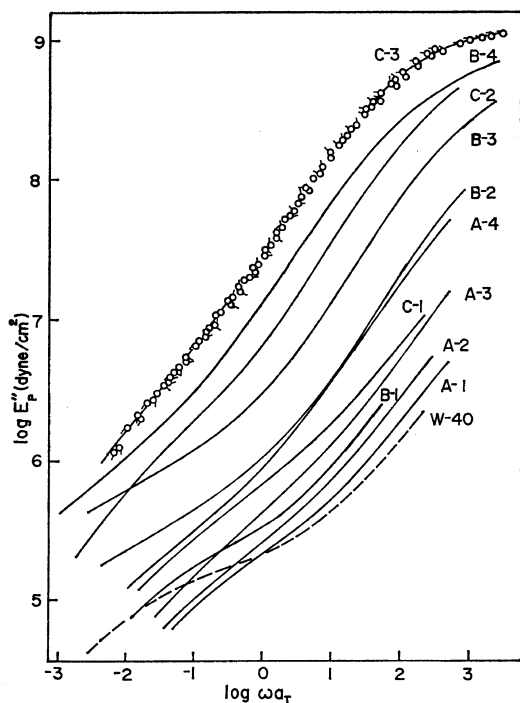
Figure 5. Log E_p'' vs. log ωa_T for PHEMA hydrogels with added NaCl, Na₂SO₄, and NaI. The data correspond to those in Figure 4.

Table II. Log a_c and the constants of the WLF equation of various systems at 25°C

Sample	log a_c	c_1^0	c_2^0, deg
W–40	0		
A–1	0.44		
A–2	0.61		
A–3	0.83	6.2	120
A–4	1.43	9.3	130
B–1	0.55		
B–2	1.60	8.6	115
B–3	2.53	8.9	110
B–4	3.51	9.1	96
C–1	1.06		
C–2	3.04	12.3	135
C–3	3.98	11.4	110

tions should be reduced to a single curve in the transition region, if $(d_2/c)E'(\omega)$ or $(d_2/c)E''(\omega)$ is plotted against $\omega a_c'$. Here d_2 is the density of pure polymer, c is the polymer concentration in grams per cm³, and a_c' is the shift factor on the frequency scale, which can be regarded

as the ratio of ζ in solution to ζ in undiluted polymer. The reduced variables may be rewritten in terms of a reference concentration c_0 other than the undiluted polymer in the form, $E_c'(\omega)=(c_0/c)E_{c_0}'(\omega a_c)$ and $E_c''(\omega)=(c_0/c)E_{c_0}''(\omega a_c)$ where a_c is defined as the ratio $a_c'(c)/a_c'(c_0)$. In a present study, 0.618 g/cm³ of the water-equilibrated sample W–40, which was studied previously,[4] was chosen as the reference c_0. The values of a_c are given in Table II.

Free Volume Parameters. In a previous paper,[4] values of ζ for W–40 swollen with water (the volume fraction of water v_1=0.475, 0.434, 0.418, 0.378, and 0.326) were calculated with the aid of[7]

$$\log \zeta = 2 \log H + \log \tau + \log (6/kT)$$
$$+ 2 \log (2\pi M_0/acN_0) \qquad (1)$$

from the part of the spectrum H where the logarithmic dependence has the theoretically predicted slope $-1/2$. In eq 1, k denotes the Boltzmann constant, N_0 is Avogadro's number, and a^2 is the mean-square molecular length per monomer unit. Here a was taken as 7×10^{-8} cm.[8]

The friction coefficient $\log \zeta_{1,s}$ for the systems with added salt, defined as $\log \zeta_{1,s} = \log a_c + \log \zeta_{W-40}$, is given in Table III. Here $\log a_c$ is the shift factor obtained by the method of the time—concentration superposition (Table II), and $\log \zeta_{W-40}$ for the water-equilibrated sample W–40 is -3.84 dyn sec/cm.

Table III. Free volume parameters and the ζ values for PHEMA hydrogels with added salts at 25°C

Sample	log $\zeta_{1,s}$	log ζ_w	log ζ_0	$f(v_{1,s})$ (a)	(b)	(c)
W–40	-3.84[a]			0.101[a]	0.058[a]	
A–1	-3.40	-3.60	-3.60	0.092	0.055	
A–2	-3.23	-3.26	-3.25	0.089	0.054	
A–3	-3.06	-3.17	-3.13	0.086	0.053	0.070
A–4	-2.41	-2.74	-2.68	0.076	0.049	0.047
B–1	-3.29	-3.31	-3.29	0.090	0.055	
B–2	-2.24	-2.73	-2.71	0.074	0.048	0.049
B–3	-1.31	-2.36	-2.31	0.063	0.044	0.048
B–4	-0.33	-1.46	-1.35	0.056	0.040	0.048
C–1	-2.78	-2.99	-2.47	0.082	0.047	
C–2	-0.80	-1.74	-0.64	0.059	0.042	0.035
C–3	0.14	-1.11	0.38	0.053	0.038	0.038

[a] Values taken from ref 4.

Previously,[4] from the dependence of ζ on the volume fraction of water v_1, the free volume parameters were calculated by use of two types of the free volume equation. One is the Fujita—Kishimoto equation in the form[9,10]

$$-\frac{(v_1-v_1{}^0)}{\log a_c} = 2.303\frac{f(v_1{}^0)^2}{\beta} + 2.303f(v_1{}^0)(v_1-v_1{}^0)$$ (2)

Here, a_c is the ratio between the friction coefficients ζ at the concentrations v_1 and $v_1{}^0$, and β characterizes the concentration dependence of the fractional free volume. The other is the Berry—Fox equation[11] recast by the authors into the form[4]

$$-\frac{(v_1-v_1{}^0)}{\log a_c} = \frac{2.303f(v_1{}^0)^2}{\alpha_f(v_1{}^0)T_g(v_1{}^0)^2k'} + 2.303f(v_1{}^0)$$
$$\times\left[\frac{f(v_1{}^0)}{\alpha_f(v_1{}^0)T_g(v_1{}^0)} + 1\right](v_1-v_1{}^0)$$ (3)

Here, α_f is the thermal expansion coefficient of the fractional free volume, $T_g(v_1{}^0)$ is the glass transition temperature at concentration $v_1{}^0$, and k' is a constant, defined as

$$k' = \frac{1}{v_1}\left[\frac{1}{T_g(v_1)} - \frac{1}{T_g(0)}\right]$$ (4)

The $-(v_1-v_1{}^0)/\log a_c$ vs. $(v_1-v_1{}^0)$ plot was made to test their applicability to experimental data for PHEMA hydrogels. The values of $f(v_1{}^0=0.326)$ and β estimated from eq 2 are 0.069 and 0.217 at 25°C, respectively. The values of $T_g(v_1{}^0=0.326)$ and k' obtained from a dilatometric measurement are 248°K and 4.0×10^{-3} deg^{-1}, respectively. Using these values, the $f(v_1{}^0=0.326)$ and $\alpha_f(v_1{}^0=0.326)$ values estimated from eq 3 are 0.046 and 3.8×10^{-4} deg^{-1}, respectively. According to the Fujita—Kishimoto theory and the modified Berry—Fox theory, the dependence of f on v_1 is expressed by the equations

$$f(v_1) = f(v_1{}^0) + \beta(v_1-v_1{}^0)$$ (5)

$$f(v_1) = f(v_1{}^0) + \frac{\alpha_f(v_1{}^0)T_g(v_1{}^0)^2k'(v_1-v_1{}^0)}{1+k'T_g(v_1{}^0)(v_1-v_1{}^0)}$$ (6)

The water concentration $v_1{}^g$ corresponding to $T_g=25°C$ is 0.157.[4] Choosing 0.157 as a reference concentration, we can rewrite eq 2 in the following equation:

$$\log\zeta = \log\zeta_g - \frac{1}{2.303f_g}\left[\frac{\beta(v_1-v_1{}^g)}{f_g+\beta(v_1-v_1{}^g)}\right]$$ (7)

where the fractional free volume f_g at $T_g(v_1{}^g)$ is 0.032 by use of eq 5, the monomeric friction coefficient $\log\zeta_g$ at $T_g(v_1{}^g)$ is 5.43 dyn sec/cm, and β is 0.217. $\log\zeta$ changes linearly with $\beta(v_1-v_1{}^g)/[f_g+\beta(v_1-v_1{}^g)]$. Assuming that the values of f_g and $\log\zeta_g$ for the systems with added salts are equal to those for the system without added salts, $f(v_{1,s})[=f_g+\beta(v_{1,s}-v_{1,s}^g)]$ values can be determined by use of the plot of $\log\zeta$ versus the term of eq 7 in the bracket; the value of the abscissa corresponding to $\log\zeta=\log\zeta_{1,s}$ (Table III) is equal to $1-[f_g/f(v_{1,s})]$. $f(v_{1,s})$ values are given in column (a) of Table III.

Similarly, eq 3 is rewritten in the following equation

$$\log\zeta = \log\zeta_g - \frac{1}{2.303f_g}$$
$$\times\left[\frac{\dfrac{\alpha_f(v_1{}^g)T_g(v_1{}^g)^2k'(v_1-v_1{}^g)}{1+k'T_g(v_1{}^g)(v_1-v_1{}^g)}}{f_g+\dfrac{\alpha_f(v_1{}^g)T_g(v_1{}^g)^2k'(v_1-v_1{}^g)}{1+k'T_g(v_1{}^g)(v_1-v_1{}^g)}}\right]$$ (8)

where f_g is 0.027 by use of eq 6, $\alpha_fT_g(v_1{}^g)^2k'$ is 0.135, and $k'T_g(v_1{}^g)$ is 1.19. The value of the abscissa corresponding to $\log\zeta=\log\zeta_{1,s}$ is also equal to $1-[f_g/f(v_{1,s})]$ in the plot of $\log\zeta$ versus the term of eq 8 in the bracket. Results are shown in column (b) of Table III. $f(v_{1,s})$ values estimated from the equation, $f(v_{1,s})=1/2.303c_1{}^0$, are given in column (c) of Table III. Previously[4] it was found that the $f(v_1{}^0=0.326)$ value derived from the analysis of the dependence of $\log a_T$ on T is 0.043, and this value is in close agreement with the $f(v_1{}^0=0.326)$ value estimated from the modified Berry—Fox equation. From Table III, it follows that the agreement between the $f(v_{1,s})$ values calculated from c_1 parameters and those from eq 8 is satisfactory. This again supports the previous statement[4] that the dependence of ζ on v_1 for the homogeneous hydrogels (W–40) is described by the concept of the free volume on the basis of the modified Berry—Fox equation.

Effects of the Addition of Salts on the Monomeric Friction Coefficient. In order to compare the effect of the addition of salts on ζ, we estimated the friction coefficient $\log\zeta_w$ at the
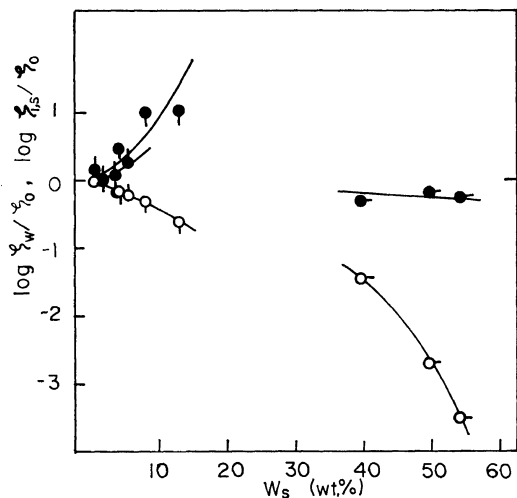
Figure 6. Log $\zeta_{1,s}/\zeta_0$ and log ζ_w/ζ_0 plotted against W_s. Pips pointing up, down, and right denote series A, B, and C, respectively. Filled circles denote log $\zeta_{1,s}/\zeta_0$, and open ones log ζ_w/ζ_0.

concentration v_1 equal to the volume fraction of aqueous salt solution $v_{1,s}$, and the friction coefficient log ζ_0 at the concentration v_1 corresponding to w_s (Table I)=0 from eq 8. log $\zeta_{1,s}/\zeta_0$ and log ζ_w/ζ_0 are plotted as functions of the weight percent of salts $w_s[=100w_s/(w_1+w_s)]$ in Figure 6. From Figure 6, it follows that log $\zeta_{1,s}/\zeta_0$ for the gels with added sodium chloride and sodium sulfate has a positive value and increases with increasing W_s, and that, for the gels with added sodium iodide, log $\zeta_{1,s}/\zeta_0$, on the contrary, has a slightly negative value. The addition of sodium chloride and sodium sulfate causes the increase in ζ, and sodium iodide causes the reduction of ζ in the gel. As was remarked in the experimental section, the exact value of salt concentration 'in the gel' cannot be estimated. However, the above-mentioned results are not much affected by the uncertainty with respect to w_s. For example, log ζ_0 values calculated from eq 8 by use of the analytical concentration for A-4 and C-1 are −2.67 and −2.49 respectively. These values are very similar to log ζ_0 in Table III. This peculiar plasticizing effect observed for sodium iodide, though it is much less than that of water (cf. log $\zeta_{1,s}$ and log ζ_w), will be discussed later.

In a previous paper,[12] we reported that the

effect of plasticizers on ζ depends on their own rheological properties, i.e., their viscosity or T_g. The viscosity of aqueous solutions of sodium chloride and sodium sulfate increases with increasing salt concentration. Accordingly, the addition of sodium chloride and sulfate causes a decrease in the plasticizing effect of water, in other words, a reduction of free volume of water. It seems that this effect is responsible for the increase in ζ for the gels with added sodium chloride and sodium sulfate. Sodium iodide also has the effect of increasing the water viscosity, which is comparable to sodium sulfate in the concentration range tested.[13] This suggests that it is necessary to take account of the influence of sodium iodide not only on water but also on PHEMA. In analogy with the work of Lundberg, et al.,[14] on the interaction of inorganic salts with poly(ethylene oxide), it seems quite conceivable that the iodide anion is the species directly associating with the polymer. In this connection, Refojo[5] reported in a study of swelling behavior that the mechanism by which ion—polymer interaction occurs is not clear, but that in the case of the iodide ion it is very likely to be ion—dipole interactions. Thus we believe that the plasticizing effect observed for the gels with added sodium iodide reflects the specific interaction of the iodide ion with PHEMA.

Rubbery Region

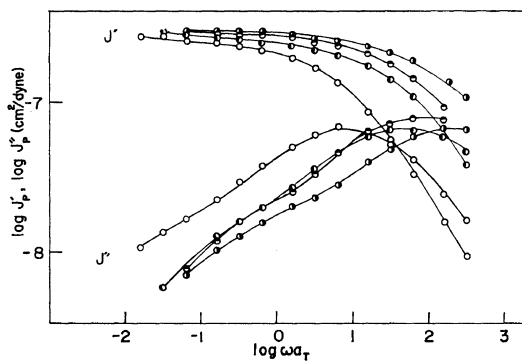*Time—Concentration Superposition.* For a better comparison of the low-frequency area, we con-

Figure 7. Log J_p' and log J_p'' versus log ωa_T for PHEMA with added NaCl: (◑), A-1; (◓), A-2; (◐), A-3; (○), A-4.
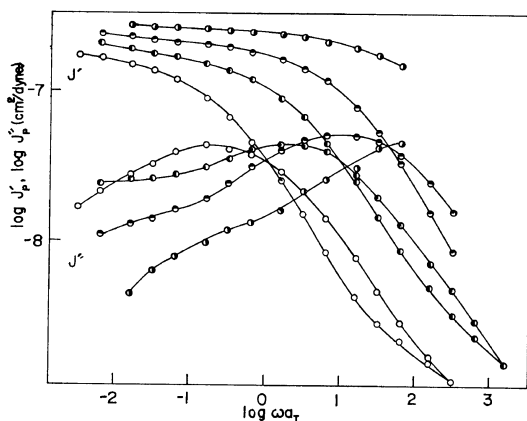
Figure 8. Log J_p' and log J_p'' versus log ωa_T for PHEMA with added Na$_2$SO$_4$: (◑), B–1; (◒), B–2; (◓), B–3; (○), B–4.
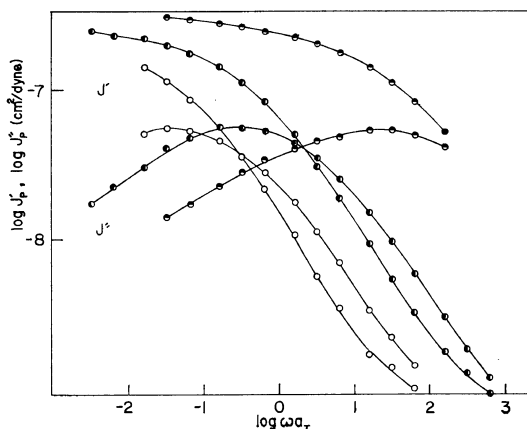

Figure 9. Log J_p' and log J_p'' versus log ωa_T for PHEMA with added NaI: (◓), C–1; (◑), C–2; (○), C–3.

verted the log E_p' and log E_p'' values from Figures 4 and 5 to J' and J'' using log $E_p' = -\log J_p' - \log(1 + \tan^2 \delta)$. Log J_p' and log J_p'' for series A, B, and C are plotted against log ωa_T in Figures 7—9.

In order to compare the effect of the addition of salts on the shapes of J' and J'', $J_c' = J_{c_0}'(c/c_0)$ and $J_c'' = J_{c_0}''(c/c_0)$ for samples A–4, B–2, and C–1 can be superposed by utilizing log a_c previously obtained with W–40 swollen to v_1 of 0.382 as a reference state; results are shown in Figure 10. The polymer volume fractions of A–4, B–2, and C–1 are very similar to that of W–40. Composite curves of B–4, C–2, and

W–40 swollen to v_1 of 0.326 are also plotted against log ωa_c in Figure 11. In Figures 10 and 11 the time—concentration superposition was successful in the transition region, as seen in Figures 4 and 5. But in the rubber-like region J_c' takes higher values with the addition of sodium iodide, and lower values with the addition of sodium chloride and sodium sulfate, than in the simple PHEMA gels. Therefore, the concentration reduction which is used in the superposition of the main transition region cannot be applied to the rubbery region of the systems with added salts. It was found previously[4] that for simple PHEMA hydrogels the
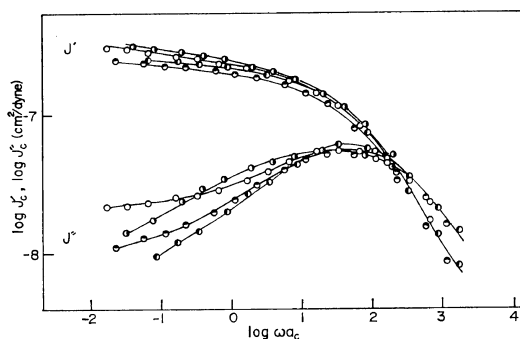

Figure 10. Composite curve for A–4, B–2, C–1, and W–40 swollen to v_1 of 0.382 plotted against log ωa_c: (◑), A–4; (◒), B–2; (◓), C–1; (○), W–40. Compliances and the circular frequency were reduced to those of W–40 swollen to v_1 of 0.382 (ref 4).
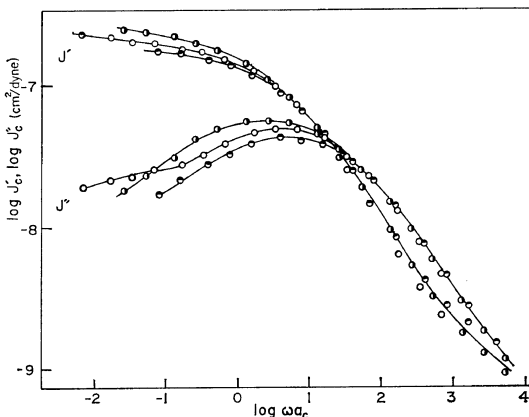

Figure 11. Composite curve for B–4, C–2, and W–40 swollen to v_1 of 0.326 plotted against log ωa_c: (◒), B–4; (◓), C–2; (○), W–40. Compliances and the circlar frequency were reduced to those of W–40 swollen to v_1 of 0.326 (ref 4).

time—concentration superposition is successful in both the transition and rubbery regions.

For the dependence of compliance on the degree of swelling v_2, we also have, from the kinetic theory of the rubber elasticity,[15] the relationship[16] $J'^0_{v_2} = J'_{v_2}(v_2/v_2^0)^{1/3}$. However this correction factor is negligible compared to the present experimental uncertainty, because the systems in Figures 10 and 11 are very similar to each other with respect to the polymer concentration v_2. These results suggest that a deviation from the superposition caused by the addition of salts corresponds to a change in some structure of the PHEMA hydrogels.

An additional reduction deduced by analogy with the so-called f-shift[7] was made to test its applicability to the data in Figures 10 and 11: $\log J_c'f'$ or $\log J_c''f'$ is plotted against $\log \omega a_c/f'^2$. Here the degree of polymerization P_c changes by a factor $1/f'$. It was found that this reduction is successful in the rubbery region, except for a slight deviation in the region of the maximum in J'' for A-4. With PHEMA hydrogels without added salts as a reference state, $\log f'$ values of C-2, C-1, B-4, B-2, and A-4 are -0.09_6, -0.05_0, 0.05_6, 0.02_4, and 0.04_8, respectively. Accordingly, a deviation from the reduction used in the superposition of the main transition region caused by the addition of salts is supposed to be attributable to a change in P_c.

Dušek and Sedláček[3] reported from optical measurements that PHEMA gels generally regarded as homogeneous contain heterogeneities of several microns in diameter. These heterogeneities are most probably formed during polymerization; in the swollen state they manifest themselves by local differences in the concentration of the polymer. A similar phenomenon was observed by Prins, et al., in measuring the light scattering[17] and stress-induced birefringence[18,19] of gels. They suggested that these heterogeneities should not be considered as rigid rods in an amorphous matrix, and that diluent-induced aggregation phenomena could be expected, possibly leading to some local mesomorphic order of either nematic or smectic type for PHEMA gels. Presumably the existence of this diluent-induced structure causes the reduction of the compliances of gels, leading to an increase in the number of coupling points. However, the behavior of the friction coefficient in the transition region may not be much affected by the existence of such structure, because the viscoelastic properties in the transition region are supposed to be attributable to the motions of a short segment of the polymer, which are oblivious of the number of coupling points.[7]

It was observed by Sedláček, et al.,[20] that samples prepared in the presence of diluent were perfectly transparent after polymerization, but turned optically heterogeneous if the solvent was replaced by a poorer one. Chlorides and sulfates decrease the solubility of PHEMA in water (salting-out), and iodides excercise salting-in on PHEMA, as shown in Figure 1. These tendencies are in favor of the position of these ions in the lyotropic series. We can regard aqueous solutions of sodium chloride and sodium sulfate as poorer solvents than water, and those of sodium iodide as better ones. Accordingly the decrease of the reduced compliance J_c' for the systems with added sodium chloride and sodium sulfate is attributed to an increase in diluent-induced structure with the addition of these salts. For the systems with added sodium iodide, a reinforcement effect caused by a diluent-induced structure decreases with the addition of sodium iodide. Thus, the effect of the addition of salts on the reduced compliance is well interpreted in terms of the difference in the influence of the added salts on a diluent-induced structure in PHEMA hydrogels.

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