Polymer–Diluent Interaction in Cross-Linked Gels of Poly(2-hydroxyethyl methacrylate)

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ABSTRACT: Thermoelasticity, photoelasticity, and small-angle light-scattering data over a temperature range from 24 to 70° are reported for several cross-linked poly(2-hydroxyethyl methacrylate) hydrogels, prepared in the presence of varying amounts of water. The equilibrium retractive force of such gels first increases up to 55° and then decreases at higher temperatures. Further thermodynamic data and analysis reveal that over most of the temperature range the entropy *increases* upon stretching, in contradistinction to the loss in entropy normally observed in rubber elastic materials. The partial molar heat of dilution, $\overline{\Delta H}_{1,\mathrm{dil}}$, calculable from the same data, is found to be negative below 55°, which is indicative of a water-structure-enhancing hydrophobic interaction. Above 55° the normal dispersion forces lead to a positive $\overline{\Delta H}_{1,\mathrm{dil}}$. The equilibrium stress–strain curves indicate a twofold *increase* in apparent molecular weight between cross-links up to 55°. This is ascribed to the gradual elimination of hydrophobically induced physical cross-links. Over the whole temperature range, the stress and the stress-induced birefringence relax at *different* rates to their final equilibrium value. Also, the equilibrium stress-optical coefficient, $\Delta n_e/\sigma_e$, decreases *strongly* with increasing temperature. The latter two phenomena are absent if the gels are swollen in good diluents as, *eg.*, ethylene glycol. The abnormal behavior in water is explained in terms of a temperature-sensitive, stress-induced rearrangement of regions of different cross-linking densities. The intensity of the scattered light (V_v) increases particularly strongly with increasing temperature if hydrogels are investigated which are prepared close to the critical dilution of 45%. The same has been noted previously by Dušek and Sedlaček and can be explained in terms of temperature-induced microsyneresis in inhomogeneously cross-linked hydrogels.

Networks of poly(2-hydroxyethyl methacrylate) (PHEMA) are formed by copolymerization of 2-hydroxyethyl methacrylate and ethylene glycol dimethacrylate usually in the presence of water. The amphiphilic nature of the polymer chains making up the three-dimensional network leads to a fairly low degree of swelling in water (about 45%), which is essentially independent of the network formation conditions. Previous work from this laboratory[2,3] and elsewhere[4] has provided evidence for the existence of a certain amount of diluent-induced supramolecular ordering in these hydrogels. In addition, the presence of increasing amounts of diluent during polymerization is known to enhance the formation of inhomogeneously cross-linked networks and eventually to lead to a microphase separation (microsyneresis) and thus to the formation of a heterogeneous gel.[5] As long as the water content during polymerization is below 45%, hydrogels which are visually clear at room temperature are formed. These gels are therefore amenable to investigation by various optical techniques in addition to measurements of the mechanical properties. PHEMA gels are thus well suited for a study of structure–property relations, which may also serve as a guide for similar relations in other polymer systems, as, for example, multiphase block copolymers or segmented polyurethanes. Practical interest in PHEMA hydrogels has grown in recent years because of their expanded usage in various biomedical applications.[6-10] In the present article we exploer the role of polymer–diluent interaction as a function of temperature by means of thermoelasticity, photoelasticity, and light scattering.

Upon replacement of the water in PHEMA gels by increasing amounts of ethylene glycol a rather sudden increase in swelling is observed at 20 mol % CH_2OH groups.[2a] At the same concentration, the light scattering between crossed polaroids—which is independent of the refractive index—shows a sudden decrease in intensity until in pure ethylene glycol the scattering is very low indeed.[2a] In pure ethylene glycol the gels are highly swollen, and their elasticity follows the classical gaussian elasticity equation.[2b] The swelling is governed by the cross-linking conditions in the usual fashion, in contrast to the constant swelling in water. Furthermore, it has been found that the swelling in 50/50 binary mixtures of water–acetone, water–dioxane, and water–tetrahydrofuran is several times larger than in any of these diluents separately.[11]

The above observations have led to the conclusion that a certain amount of diluent-induced supramolecular ordering exists in water, acetone, tetrahydrofuran, and dioxane, which is caused by the amphiphilic nature of the PHEMA chains. The ordering is removed ("melted out") by ethylene glycol and by the binary mixtures, because these diluents are capable of more completely solvating the polymer chains.

The temperature dependence of the swelling in water—as originally observed by Refojo and Yasuda[12]—bears out the hypothesis that hydrophobic forces are operative. Some typical results[11] in Figure 1 show that the size of a gel first decreases with temperature and then increases once $T > 55°$. This behavior indicates that below $T = 55°$ the enthalpy of dilution, ΔH_{dil}, is negative: in absorbing heat from the surroundings, the system moves to a state of higher enthalpy, which apparently is the more deswollen state; consequently, $\Delta H_{\mathrm{dil}} < 0$. Since, in spite of the lowering of the enthalpy upon dilution of the polymer with water, the swelling of the gel is limited, the entropy of dilution must be unfavorable, *i.e.*, $\Delta S_{\mathrm{dil}} < 0$. This decrease in entropy might be ascribable

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(1) Based upon a thesis submitted by T. C. W. in partial fulfillment of the requirements for the Ph.D. in chemistry at Syracuse University.

(2) (a) J. H. Gouda, K. Povodator, T. C. Warren, and W. Prins, *J. Polym. Sci., Part B*, **8**, 225 (1970). (b) M. Ilavsky and W. Prins, *Macromolecules*, **3**, 415 (1970).

(3) M. Ilavsky and W. Prins, *ibid.*, **3**, 425 (1970).

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(7) M. Tollar, M. Stol, and K. Kliment, *ibid.*, **3**, 305 (1965).

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(11) T. C. Warren, Ph.D. Thesis, Syracuse University, Syracuse, N. Y., 1971.

(12) M. F. Refojo and H. Yasuda, *J. Appl. Polym. Sci.*, **9**, 2425 (1965).

to the water structure, which is known to become more pronounced upon solvating hydrophobic groups, in this case the backbone of the polymer.[13] At the same time the increase in water structure leads to a lower enthalpy (more hydrogen bonding), in line with the negative ΔH_{dil}.

In view of the earlier evidence for supramolecular ordering, which melts out at 20 mol % CH_2OH groups in ethylene glycol–water mixtures, it seems very likely that the action of the water on the polymer is a cooperative one, *i.e.*, such that hydrophobic backbone portions of several chains are squeezed together so as to minimize the extent of hydrophobically induced structuring of the water. Thus, the existence of so-called hydrophobic bonds in PHEMA gels can be inferred, perhaps leading to ribbonlike micelles, in which alternating hydrophobic backbone regions and hydrophilic side chain regions occur.[2a]

Above 55° the gels increase in size, as they also do in good diluents. This is explainable by noting that above this temperature the structure of water has essentially disappeared so that the special hydrophobic forces no longer exist.[14] In this range $\Delta H_{\mathrm{dil}} > 0$ because the water–water dispersion forces are stronger than the water–polymer forces.

Thermoelastic measurements were undertaken because they can be analyzed thermodynamically to yield further information as regards the above general picture. The retractive force, f, of an elastically stretched gel strip of length L in swelling equilibrium with surrounding diluent contains an energy and an entropy component

$$f = (\partial F/\partial L)_{\mathrm{VTN}} = (\partial E/\partial L)_{\mathrm{VTN}} - T(\partial S/\partial L)_{\mathrm{VTN}} = (\partial E/\partial L)_{\mathrm{VTN}} + T(\partial f/\partial T)_{\mathrm{LVN}} \quad (1)$$

In eq 1 all further symbols have their customary meaning and N is the number of diluent molecules in the gel. The temperature coefficient of the force appears in eq 1 through a Maxwell relation taken from the differential of the Helmholtz free energy, F. The quantity $(\partial f/\partial T)_{\mathrm{LVN}}$ is experimentally difficult to obtain, but it is approximately equal to the more accessible quantity $(\partial f/\partial T)_{\mathrm{PT\Lambda}}$, where $\Lambda = L/L_0$, with L_0 being the unstretched length at the temperature T. An improvement upon this approximation is available,[15] but it is not needed here because of the limited experimental accuracy attainable with the swollen strips. For isotropically swollen gels one has furthermore[16]

$$(\partial f/\partial T)_{\mathrm{PN\Lambda}} = (\partial f/\partial T)_{\mathrm{PLe}} - (\partial f/\partial V)_{\mathrm{PLT}}(\partial V/\partial T)_{\mathrm{PLe}} \quad (2)$$

where e denotes that equilibrium is maintained with the surrounding diluent. Since all three quantities on the right-hand side of eq 2 are experimentally accessible (see below), this analysis yields the quantity $(\partial f/\partial T)_{\mathrm{LVN}}$ and thus the desired separation in energy and entropy contributions to the retractive force (eq 1).

The partial molar heat of dilution of the diluent, $\overline{\Delta H}_{1,\mathrm{dil}}$, follows from a similar analysis[16]

$$\overline{\Delta H}_{1,\mathrm{dil}} = -T(\partial f/\partial N)_{\mathrm{PLT}}(\partial N/\partial T)_{\mathrm{PLe}}(\partial N/\partial L)_{\mathrm{PTe}}^{-1} \quad (3)$$

Equation 3 is particularly useful because it allows us to determine whether the diluent component and its variable structure are indeed involved in the anomalous temperature dependence of the swelling.

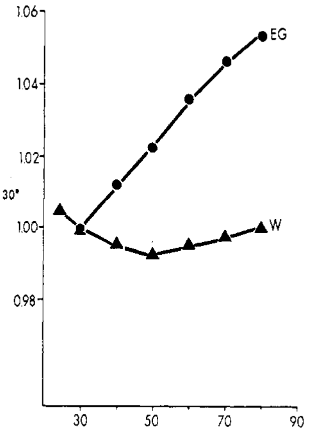

Figure 1. The swelling of a visually clear PHEMA gel (2.4×10^{-5} mol of cross-linker per cubic centimeter of monomer, no water present during polymerization) in water (W) and ethylene glycol (EG) as a function of temperature; plotted as length relative to the length at 30°.

PHEMA hydrogels can be reversibly stretched up to about 50%, but samples with lower cross-linking density and more dilution during the network formation exhibit stress relaxation of progressively longer duration.[3] From the time dependence of the stress, which can be written as $\sigma(\Lambda, t) = \sigma_e(\Lambda)\sigma_2(t)$, and the time dependence of the resulting birefringence, which can be written as $\Delta n(\Lambda, t) = \Delta n_e(\Lambda)\Delta n_2(t)$, mechanical and optical relaxation spectra can be constructed according to procedures outlined before[3]

$$\sigma_2(t) = 1 + \int_{-\infty}^{+\infty} h^{(\mathrm{m})} \exp(-t/\tau)\mathrm{d}\log\tau = 1 + (t/t_0^{(\mathrm{m})})^{-m} \quad (4)$$

$$\Delta n_2(t) = 1 + \int_{-\infty}^{+\infty} h^{(\mathrm{o})} \exp(-t/\tau)\mathrm{d}\log\tau = 1 + (t/t_0^{(\mathrm{o})})^{-m} \quad (5)$$

In these equations $h^{(\mathrm{m})}$ and $h^{(\mathrm{o})}$ represent the reduced logarithmic mechanical and optical relaxation spectra. The time dependencies are describable in terms of the parameters $t_0^{(\mathrm{m})}$ ($t_0^{(\mathrm{o})}$) and m, so that the spectra follow from the inverse Laplace transform

$$h(\log\tau) = 2.303(t_0)^m\tau^{-m}/\Gamma(m) \cong 2.303mt_0^m\tau^{-m} \quad (6)$$

The last relation follows because m is found to be about 0.15, so that the Γ function can be approximated by m^{-1}. The spectra are of interest because the mechanical and optical time dependencies—and thus the spectra—are not identical. At room temperature the spectra have been found to be proportional to each other.[3] The difference has been ascribed[3] to structural rearrangements during relaxation, absent in ideal networks. Ideal networks only show Rouse-type configurational relaxation and thus have $h^{(\mathrm{o})} = h^{(\mathrm{m})}$.[17] In the present study spectra were determined in water as a function of temperature.

The equilibrium stress, $\sigma_e(\Lambda)$, and the equilibrium birefringence, $\Delta n_e(\Lambda)$, obtained—if necessary—after suitable extrapolation of the relaxation data,[3] are best described by Mooney–Rivlin equations

$$\begin{aligned} \sigma_e(\Lambda) &= (C_1{}^* + C_2{}^*\Lambda^{-1})(\Lambda^2 - \Lambda^{-1}) \\ \Delta n_e(\Lambda) &= (A_1{}^* + A_2{}^*\Lambda^{-1})(\Lambda^2 - \Lambda^{-1}) \end{aligned} \quad (7)$$

(13) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, No. **24**, 133 (1957).

(14) G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962).

(15) P. J. Flory, C. A. J. Hoeve, and A. Ciferri, *J. Polym. Sci.*, **34**, 337 (1959).

(16) H. Abe and W. Prins, *ibid.*, *Part C*, No. **2**, 527 (1963).

(17) B. E. Read, *Polymer*, **3**, 143 (1962).

which means that there are deviations from the classical equilibrium behavior of gaussian networks

$$\begin{aligned} \sigma_e(\Lambda) &= G_d^* q^{-1/3}(\Lambda^2 - \Lambda^{-1}) = G^*(\Lambda^2 - \Lambda^{-1}) \\ \Delta n_e(\Lambda) &= A_d^* q^{-1/3}(\Lambda^2 - \Lambda^{-1}) = A^*(\Lambda^2 - \Lambda^{1}) \end{aligned} \tag{8}$$

Equations 8 are valid provided the volume degree of swelling, q, does not change with elongation. In our case there is about a 0.3% increase in swelling as a result of an imposed elongation of 10%. This is of minor consequence in the stress–strain curves (although it *is* of importance in the $\overline{\Delta H}_{1,\mathrm{dil}}$ determination). In eq 8 we have

$$\begin{aligned} G_d^* &= q_0^{-2/3}\nu^* RT \\ A_d^* &= (G_d^*/RT)(2\pi/45)(\bar{n}^2 + 2)^2\bar{n}^{-1}\Delta\alpha_S \end{aligned} \tag{9}$$

where ν^* is the number of moles of elastically effective network chains per cubic centimeter of dry network, $\bar{n}$ is the (average) refractive index of the gel, and $\Delta\alpha_S$ is the optical anisotropy per polymer chain segment. The parameter q_0 is defined by

$$q_0^{-2/3} = \frac{\langle r^2\rangle_d}{\langle r^2\rangle_0} = \frac{\langle r^2\rangle_d}{\langle r^2\rangle_c}\frac{\langle r^2\rangle_c}{\langle r^2\rangle_0} = q_c^{-2/3}\frac{\langle r^2\rangle_c}{\langle r^2\rangle_0} \tag{10}$$

where $\langle r^2\rangle$ values denote the average chain dimensions in the dry state (d), unperturbed state (0), and after network formation (c), respectively.[18] One often puts $\langle r^2\rangle_c = \langle r^2\rangle_0$, although there is new evidence[19] suggesting that $\langle r^2\rangle_c \cong (^1/_2) \times \langle r^2\rangle_0$.

In the present work we are solely concerned with the temperature dependence of σ_e and Δn_e. In ideal networks, ν^* is a constant and the temperature dependence of G_d^*/RT is exclusively related to $q_0^{-2/3}$ or $\langle r_0^2\rangle$. Since our networks do not obey eq 8, we will more generally consider the temperature dependence of an apparent molecular weight between cross-links (whether pyhsical or chemical) defined by

$$M_{\mathrm{app}} = (RT\rho_d q^{-1/3})/(C_1^* + C_2^*) \tag{11}$$

where ρ_d is the density of the dry network. In an ideal network M_{app} would equal $RT\rho_d/G_d^*$; if, moreover, q_0 were unity, M_{app} would be the true molecular weight between cross-links (eq 9).

Similarly, in an ideal network the product of the stress-optical coefficient C_e $(=\Delta n_e/\sigma_e)$ and the temperature would be equal to

$$C_e T = (2\pi/45R)(\bar{n}^2 + 2)^2\bar{n}^{-1}\Delta\alpha_S \tag{12}$$

Since $\bar{n}$ changes only by a negligible amount over the temperature range under investigation, the temperature dependence of C_eT would reflect only changes in segmental anisotropy. In nonideal networks, $\Delta\alpha_S$ represents an apparent anisotropy, which may reflect the existence of supramolecular organization or inhomogeneities and may include form anisotropy.[3]

Direct information about the temperature dependence of the network structure is obtained from the light scattering of the unstrained hydrogels. Denoting by V_v the Rayleigh ratio under a scattering angle θ, as observed in a horizontal plane encompassing the incident and scattered wave vectors, with incident and scattered polarization vertical to this plane, and by H_v the Rayleigh ratio with horizontally polarized scattering, one has[20]

$$V_v - (4/3)H_v = \left(\frac{64\pi^5}{\lambda_0^4}\right)\langle n^2\rangle \int_v \gamma(r)\,\frac{\sin hr}{hr}\,r^2\mathrm{d}r \tag{13}$$

In eq 13 the integration extends over the scattering volume; $h = (4\pi \sin \theta/2)/\lambda$, with λ the wavelength in the gel and λ_0 the same quantity in vacuum; $\langle\eta^2\rangle$ is the mean-square polarizability fluctuation and $\gamma(r)$ is the corresponding correlation function. In the present study $H_v \ll V_v$ and the observed angular dependence of V_v (or $H_h = V_v \cos^2 \theta$) is a monotonically decreasing function. Since the data do not allow a Fourier transformation with sufficient accuracy, the desired information is extracted by approximating $\gamma(r)$ as a sum of two gaussians[20]

$$\gamma(r) = X\exp(-r^2/a^2) + (1 - X)\exp(-r^2/b^2) \tag{14}$$

Substitution of eq 14 into eq 11 and performing the integration yields

$$\begin{aligned} V_v \cong V_v - (4/3)H_v = (16\pi^5/\lambda_0^4)\langle\eta^2\rangle \times \\ [X\pi^{1/2}\exp(-h^2a^2/4) + (1 - X)\mathrm{b}^3\pi^{1/2}\exp(-h^2b^2/4)] \end{aligned} \tag{15}$$

If the parameters a and b are sufficiently different, a graphical representation of log V_v *vs.* h^2 will allow the determination of a, b, X and $\langle\eta^2\rangle$.

Experimental Section

Thermoelasticity. The sample chosen for this phase of the work was polymerized without any water present. The amount of crosslinker was 2.4 × 10^{-5} mol per cubic centimeter of monomer (sample 9 in ref 3). At this level of cross-linking, the equilibrium retractive force is reached in at most 2 hr. Strips of 40 × 10 × 1 mm^3 were clamped between a micrometer capable of measuring 0.01 mm and an inductive transducer, capable of registering 1-g force changes through a carrier wave amplifier–recorder arrangement. The quantities $(\partial f/\partial T)_{\mathrm{PL}e}$ were calculated from a family of force–length curves taken at various temperatures after 12-hr equilibrations, plotted as fL^2 *vs.* L^3. For a network obeying gaussian theory, eq 8 shows that such a representation should be linear, yielding L_0^3 as the intercept. The particular sample chosen was sufficiently close to ideal behavior at small strains $(C_2^*/C_1^* = 0.19)$ to indeed yield linear plots. The initial volume at room temperature and the observed changes in L_0 with T were utilized to calculate the volume at constant length, V_L, as a function of temperature. To this end it was assumed that $(1/V) \times (\partial V/\partial T)_L = (2/L_0)(\partial L_0/\partial T)_{f=0}$. Since it was separately established that $(1/L_0)(\partial L_0/\partial T)_{f=0} = (1/L)(\partial L/\partial T)_f$, this approximation cannot be very wrong. Previous experience with isotropic poly(vinyl alcohol) filaments, where actual cross-sectional changes at constant L were measured,[16] bear this out. The term $(\partial f/\partial V)_{\mathrm{PLT}}$ in eq 2 was measured as the ratio of $(\partial f/\partial C)_{\mathrm{PLT}}$ and $(\partial V/\partial C)_{\mathrm{PLT}}$, where C is the concentration around the gel of a poly(ethylene glycol) of sufficient molecular weight (15,000–20,000) to prevent penetration into the gel phase. The changes in force as a result of the deswelling of the strip under these circumstances were measured after 12-hr equilibration; a horizontally traveling microscopy with a dial gauge was used to measure width changes. It was found that the relative width changes (W) at constant length and the relative length changes at constant force were the same within 5%. Thus $(1/V)(\partial V/\partial C)_{\mathrm{PLT}}$ could be safely obtained from either $(2/W) \times (\partial W/\partial C)_{\mathrm{PLT}}$ or $(2/L)(\partial L/\partial C)_{\mathrm{P}f\mathrm{T}}$.

For the determination of $\overline{\Delta H}_{1,\mathrm{dil}}$, the three differentials in eq 3 had to be obtained. The first one, $(\partial f/\partial N)_{\mathrm{PLT}}$, equals $(\partial f/\partial V)_{\mathrm{PLT}} \times (\partial V/\partial N)_{\mathrm{PLT}}$; of the two terms in this product, the first one was already obtained earlier and the second one is equal to the partial molar volume of the water under the constraint of constant length, which we assumed to be the same as that without the constraint. The change in water content with temperature, $(\partial N/\partial T)_{\mathrm{PL}e}$, follows from the previously obtained change in volume with temperature, if we subtract the thermal expansion of the gel at constant water content. The thermal expansion is written as $(1/V)(\partial V/\partial T)_{\mathrm{NPL}} =$

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[18] K. Dušek and W. Prins, *Fortschr. Hochpolym-Forsch.*, 6, 1 (1969).

[19] D. Froelich, D. Crawford, T. Rozek, and W. Prins, *Macromolecules*, 5, 100 (1972).

[20] See, *e.g.*, W. Prins in "Polymer Networks, Structural and Mechanical Properties," A. J. Chompff and S. Newman, Ed., Plenum Press, New York, N. Y., 1971.

TABLE I

ENERGY AND ENTROPY CONTRIBUTIONS TO THE RETRACTIVE FORCE CALCULATED FROM THE THERMOELASTICITY DATA (EQ 2)

T, °C	V_L, cm^3	L_0, cm	f, g	$(\partial V/\partial T)_{PLe} \times 10^4$	$(\partial f/\partial c)_{PLT}$	$(\partial V/\partial c)_{PLT}^{-1}$	$(\partial f/\partial T)_{PLe}$	$T(\partial S/\partial L)_{VTN}$	$(\partial E/\partial L)_{VTN}$
				$\Lambda = 1.05$					
30	0.352	4.36	30	−6.2			+0.32	−21	9
40	0.349	4.35	32	−3.0			+0.19	+12	44
50	0.346	4.33	34	0	1.25	−381	+0.01	+10	47
60	0.350	4.35	32	+5.4			−0.18	+10	42
70	0.357	4.38	30	+6.6			−0.28	+10	40
80	0.363	4.41	26	+7.6			−0.41	−21	5
				$\Lambda = 1.11$					
30	0.352	4.36	58	−6.2			+0.29	−30	28
40	0.350	4.35	60	−3.0			+0.21	+19	79
50	0.345	4.33	62	0	1.25	−381	+0.06	+26	88
60	0.351	4.35	61	+5.4			−0.12	+40	101
70	0.358	4.38	60	+6.6			−0.24	+24	84
80	0.362	4.41	56	+7.6			−0.33	+7	63

$(1/V)(\partial V/\partial T)_{NP} = q^{-1}\gamma_N + (1 - q^{-1})\gamma_W$, where γ_N and γ_W are the expansion coefficients of the dry network in the rubbery state ($\gamma_N = 4.6\ 10^{-4}$, see ref 2b) and of water,[21] respectively. The final differential needed was the change in swelling with the strain, $\epsilon (= (L - L_0)/L_0)$, which was measured by following the width of a strip; a value of $(1/V)(\partial V/\partial \epsilon)_{PTe} \cong 3 \times 10^{-2}$ was obtained.[22]

Photoelasticity. A sample of low cross-linking density (6.5×10^{-6} mol of cross-linker per cubic centimeter of monomer), polymerized in the presence of 20% water (sample 4 in ref 3) was chosen, because it was known to exhibit different time dependencies of force and birefringence at room temperature. The strip was mounted between clamps in a rectangular glass cell containing water kept at a given temperature between 24 and 68° by a copper water jacket through which thermostated water was circulated. The sample temperature was measured with a local thermocouple after several hours of equilibration before elongation. The force was measured by means of an inductive transducer attached to the top clamp and mounted on a micrometer screw used to impose a given elongation. The length of the strip was measured to an accuracy of 0.007 cm by following two black lines—placed on the edge of the sample—with a cathetometer. Simultaneously, the optical retardation was measured to 0.3° in a de Sénarmont arrangement as before.[2b,23] The change in L_0 with temperature was obtained as before and used to calculate the stretched cross section and thickness at each temperature assuming constant volume. From the combined data the true stress and birefringence were calculated. Relaxation was normally followed for about 2 hr at five elongations and five temperatures, with several runs extending to 12 hr. Two gel pieces were used, because a recovery period of ten times the test period is needed after each relaxation experiment. The equilibrium stress and birefringence were obtained by an extrapolation procedure analogous to the one described earlier[2b] and fitted to Mooney–Rivlin equations by an iterative least-squares procedure, keeping L_0 constant and equal to its value determined experimentally at the various temperatures.

Light Scattering. Samples were prepared by polymerization in a rectangular light-scattering cell of 2-mm optical path. The cross-linker concentration was 7.8×10^{-5} mol per cubic centimeter of monomer, and the dilution during polymerization 42 wt %. Because of the contraction during polymerization, the latter assured that the gel would fit in the light-scattering cell, since such a gel exhibits only a slight increase in swelling after equilibration in water. Moreover, samples prepared in this way are most interesting for a study of the temperature dependence of the scattering, because conditions for inhomogeneous cross-linking are most pronounced close to the phase separation limit of 45% water. The light-scattering cell was placed in a copper block with appropriate holes for the light beams. Constant-temperature water was circulated through the block for at least 2 hr before light-scattering data were taken. Data were collected at scattering angles between 2 and 30° at temperatures from 33 to 65° using the instrument[24] and Rayleigh ratio conversion described earlier.[11,25]

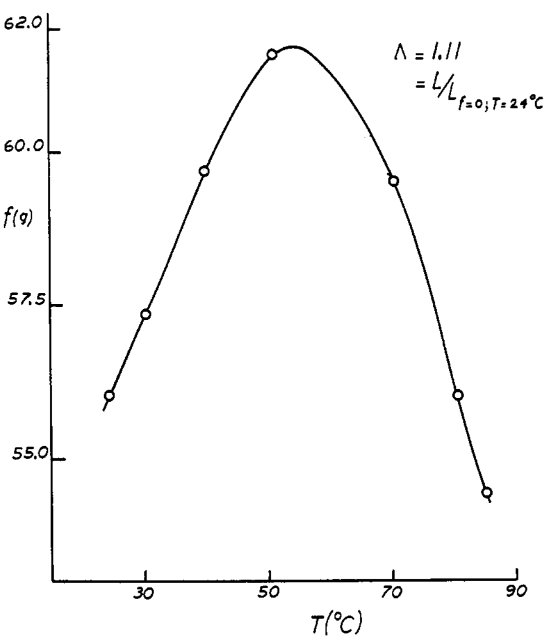

Figure 2. Equilibrium force *vs.* temperature at constant length for a gel strip in water under 11% elongation at room temperature; data points constructed from a family of equilibrium stress–strain curves at various temperatures (see Experimental Section). Same type of gel as in Figure 1.

Results and Discussion

Thermoelasticity. In Table I all quantities needed for the evaluation of the energy and entropy component of the retractive force in the elastically stretched PHEMA gel are given. Figures 2 and 3 give the force–temperature and volume–temperature results, obtained as described above. Because

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[21] "International Critical Tables," McGraw-Hill, New York, N. Y., 1963.

[22] M. Ilavsky, personal communication.

[23] M. C. A. Donkersloot, J. H. Gouda, J. J. van Aartsen, and W. Prins, *Recl. Trav. Chim. Pays-Bas*, **86**, 321 (1967).

[24] A. E. M. Keyzers, J. J. van Aartsen, and W. Prins, *J. Appl. Phys.*, **36**, 2874 (1965).

[25] J. H. Gouda, Ph.D. Thesis, Technological University, Delft, Netherlands, 1969.

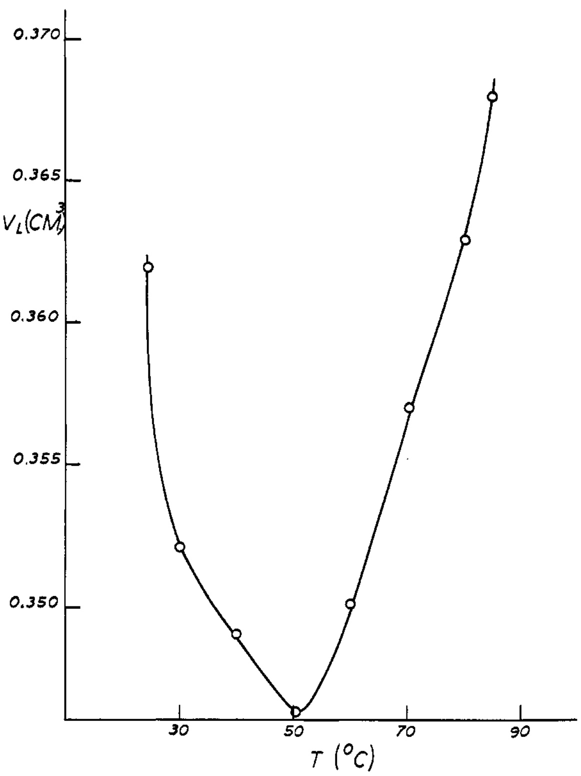

Figure 3. The equilibrium swollen volume at constant length as a function of temperature; data points constructed from length changes (see Experimental Section). Same type of gel as in Figure 1.

of the cumulative errors in the various slope determinations, only semiquantitative meaning can be attached to the values for $T(\partial S/\partial L)_{VTN}$ and $(\partial E/\partial L)_{VTN}$. Nevertheless, it is clear from Table I that the thermoeleasticity behavior is fundamentally different from that exhibited by a normal rubber-elastic network. Instead of the normal decrease in entropy on stretching due to the loss of conformational entropy of the polymer chains, accompanied by a small energy change due to a shift in population of the various rotational isomeric states around the backbone carbon–carbon bonds, we find at most temperatures an entropy *increase* accompanied by a *large* energy increase. It has to be remembered that we are measuring the overall changes of the binary polymer–water system, so that it is difficult to assess the contribution of each component separately. With nonpolar rubbers in nonpolar diluents, the polymer–diluent interaction is unimportant, but with our amphiphilic polymer in water that is not the case. The increase in entropy and energy might be a reflection of the reduction in intra- and intermolecular ordering as a result of the imposed elastic strain. At low temperature the—apparently more normal—entropy decrease may actually be a reflection of increased water structure, resulting from the partial removal of hydrophobically induced micellization, which overrides the entropy increase of the polymer component mentioned earlier.

A more definitive implication of the role of water structure is obtained from the partial molar heat of dilution of the water (eq 3). Table II shows that up to 55° $\overline{\Delta H}_{1,\mathrm{dil}}$ is negative, and that it is positive at the higher temperatures. The lowering of the enthalpy of the water upon entering the gel strip below 55° can only be due to more extensive water–water hydrogen bonding, caused by the encounter with the hydrophobic backbone of the polymer. At higher temperatures the water behaves as a fluid with normal dispersion forces and exhibits a positive $\overline{\Delta H}_{1,\mathrm{dil}}$. Although conceivably the polymer component of ΔH_{dil} also decreases below 55° because of diluent-induced micellization, the role of water in lowering the enthalpy below 55° (Figure 1) is firmly established as a result of this thermoelastic analysis.

TABLE II

PARTIAL MOLAR HEAT OF DILUTION, $\overline{\Delta H}_{1,\mathrm{dil}}$, AS OBTAINED FROM THE THERMOELASTICITY DATA (EQ 3)

T, °C	$\left(\frac{\partial \ln V}{\partial T}\right)_{NPL}$ × 10^4	V, cm^3	$\left(\frac{\partial V}{\partial T}\right)_{NPL}$ × 10^4	$\left(\frac{\partial V}{\partial T}\right)_{PLe}$ × 10^4	$\left(\frac{\partial V}{\partial L}\right)_{PTe}^{-1}$, cm^{-2}	$\overline{\Delta H}_{1,\mathrm{dil}}$,[a] cal/mol
30	4.2	0.352	1.48	−6.2		−19
40	4.6	0.349	1.61	−3.0		−12
50	4.9	0.346	1.67	0	420	−3
60	5.2	0.350	1.82	+5.4		+7
70	5.5	0.357	1.96	+6.6		+13
80	5.7	0.363	2.07	+7.6		+16

[a] From (see eq 3) $\overline{\Delta H}_{1,\mathrm{dil}} = -T(\partial f/\partial V)_{PLT}(\partial V/\partial L)_{PTe}^{-1}v_1 \times [(\partial V/\partial T)_{PLe} - (\partial V/\partial T)_{NPL}]$, where $(\partial f/\partial V)_{PLT} = (\partial f/\partial C)_{PLT} \times (\partial V/\partial C)_{PLT}^{-1}$ has been tabulated in Table I; $(\partial V/\partial L)_{PLe}^{-1}$ follows from the observed value for $(\partial \ln V/\partial \epsilon)_{PTe} = 310^{-2}$ in a straightforward manner ($\epsilon = (L - L_0)/L_0$).

Photoelasticity. The time dependencies of the force and the birefringence were found to differ over the whole temperature range. Table III shows the differences in terms of the parameters introduced in eq 4 and 5. The temperature shift factor a_T was obtained graphically by shifting the relaxation data along the time axis so as to obtain the master curve at the reference temperature 33°. According to eq 6, the shift factor a_T should equal (t_0/t_{0TR}) if all relaxation times τ are shifted by the same factor as a result of a change in temperature. Table III shows that this is the case. The power m in eq 4–6 was found to be 0.15 ± 0.01 over the whole temperature range for the optical as well as the mechanical relaxation. The differences reside in $t_0^{(o)}$ and $t_0^{(m)}$. The ratio of these parameters remains the same over the whole temperature range, with perhaps an indication of a merging at the highest temperature (Figure 4). The difference in $t_0^{(o)}$ and $t_0^{(m)}$ has been previously explained[2b] as being caused by the formation of interchain correlated regions which give a contribution to the birefringence. Such a contribution is absent in randomly coiling rubbery networks, which therefore do not exhibit any differences in mechanical and optical relaxation.[17] Clearly then, the supramolecular organization in stretched PHEMA networks does not disappear in the temperature range covered. Since hydrophobically induced micellization is absent above 55°, the supramolecular rearrangement during relaxation must be of a different nature. Previous work has shown that the birefringence is at least partly form birefringence.[2a,3] This type of birefringence only occurs if anisometric regions are present in the stretched gel matrix with an average refractive index which differs from that of the immediate surrounding. Since differences in PHEMA relaxation spectra have only been detected in samples of low cross-linking density and in samples prepared with water present during polymerization,[3] it seems likely that inhomogeneous cross-linking has led to regions of varying refractive index, which subsequently rearrange internally or with respect to each other into anisometric regions during relaxation.

Table IV presents the Mooney–Rivlin parameters which were obtained from the extrapolated equilibrium photoelasticity data. Two important conclusions can be drawn from these results as regards hydrophobically induced order and inhomogeneous cross-linking. Figure 5 shows a plot of

TABLE III
THE PARAMETERS DEFINING THE MECHANICAL AND OPTICAL RELAXATION SPECTRA

T, °C	Log $(t_0^{(m)}/t_0^{(m)}{}_{TR})^a$	Log $a_T^{(m)}$	Log $(t_0^{(o)}/t_0^{(o)}{}_{TR})$	Log $a_T^{(o)}$	$t_0^{(m)}$	$t_0^{(o)}$	$h^{(o)}/h^{(m)}$
33	0	0	0	0	112	7.9	0.67
42	−0.41	−0.45	−0.78	−0.46	34	2.6	0.68
51	−0.72	−0.75	−1.18	−0.90	15	0.36	0.57
60	−1.51	−1.50	−1.82	−2.60	2.8	0.058	0.56
68	−1.87	−2.02	−2.48	−2.10	0.85	0.06	0.67

[a] TR stands for reference temperature. Same type of gel as in Figure 4.

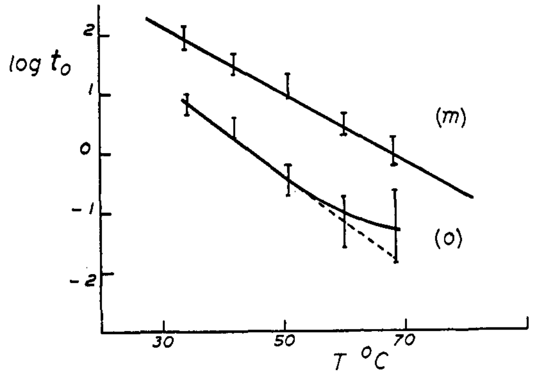

Figure 4. The t_0 parameters for mechanical (m) and optical (o) relaxation (eq 4 and 5) for gel strips prepared in the presence of 20% water and containing 6.5 × 10^{-6} mol of cross-linker per cubic centimeter of monomer.

TABLE IV
EQUILIBRIUM MECHANICAL AND OPTICAL CHARACTERISTICS OF PHEMA GELS AT VARIOUS TEMPERATURES[a]

T, °C	24	33	42	51	60	68
q	1.85	1.79	1.77	1.75	1.76	1.78
$10^{-5}G^*$	8.8	5.0	4.8	4.7	6.2	6.9
$10^{-5}(C_1^* + C_2^*)$	11	6.8	4.9	5.7	6.5	5.3
$10^{-5}A^*$	2.1	0.97	0.90	0.79	0.89	0.69
$10^{-5}(A_1^* + A_2^*)$	2.4	1.2	1.1	0.91	0.91	1.1
C_2^*/C_1^*	1.0	1.6	1.1	0.96	0.22	2.0
A_2^*/A_1^*	1.1	1.1	1.2	0.59	0.08	44
$10^{11}\Delta n_e \sigma_e^{-1}$	2.4	2.0	1.8	1.6	1.4	1.3

[a] 6 × 10^{-6} mol of cross-linker per cubic centimeter of monomer, 20% water during polymerization. G^*, C_1^*, C_2^*, and σ have units of dyn/cm².

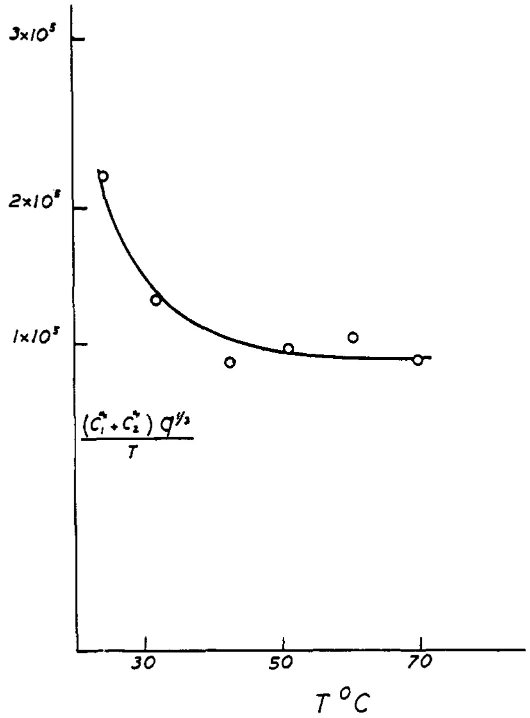

Figure 5. According to eq 11, the decrease in $(C_1^* + C_2^*)q^{1/3}/T$ up to 55° reflects an increase in the apparent molecular weight between cross-links. Same type of gel as in Figure 4.

$(C_1^* + C_2^*)q^{1/3}/T$ *vs.* T. According to eq 11, this quantity is proportional to M_{app}^{-1}. Apparently, M_{app} increases about twofold up to about 55° and then remains constant. It seems logical to connect this finding with the gradual elimination of hydrophobically induced order. This would reduce the number of junction zones acting as cross-links and therefore would lead to a larger apparent molecular weight among the remaining cross-links. Secondly, the product of the equilibrium stress-optical coefficient and the temperature can be plotted *vs.* the temperature. The resulting quantity, which is proportional to $\Delta\alpha_S$ in an ideal network (eq 12), should be only slightly dependent on T. In ethylene glycol, for example, $\Delta\alpha_S$ changes only 6% over a 40° temperature range.[26] The results in Figure 6 show, however, that in water this quantity decreases drastically with increasing temperature, without an arrest at 55°. The major part of C_e can therefore not be attributed to hydrophobically induced micellization. Instead, the previously mentioned rearrangement of regions of varying degrees of cross-linking, which should be temperature dependent, seems to be a likely explanation. The temperature dependence may be a reflection of some microsyneresis which creates some microdroplets of water. It should be remembered that at high cross-linking densities and low dilution during network formation—both factors reducing inhomogeneous cross-linking and microsyneresis—the value of C_eT becomes lowest of all.[3] The horizontal line in Figure 6 represents this value.

Light Scattering. If the dilution during network formation comes close to the 45% limit of compatibility, the network will be very inhomogeneously cross-linked and the deswelling caused by increasing the temperature up to 55° (Figure 1) will then affect the hydrophobic interaction to locally different extents. Microdroplets of water are consequently formed, which are trapped in the gel matrix. The differences in local refractive index thus become more pronounced and the light scattering increases. During the course of this study, Dušek and Sedlaček[27] published turbidity measurements illustrating this effect. They also reported a decrease in turbidity above 55°, where the swelling again increases. Our samples prepared at 42 wt % dilution exhibited an increase in turbidity up to 65° (Table V), conceivably because insufficient time was allowed for the microsyneresis to disappear again. Samples

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(26) K.-L. Wun, Syracuse University, unpublished results.

(27) K. Dušek and B. Sedlaček, *Collect. Czech. Chem. Commun.*, 36, 1569 (1971).

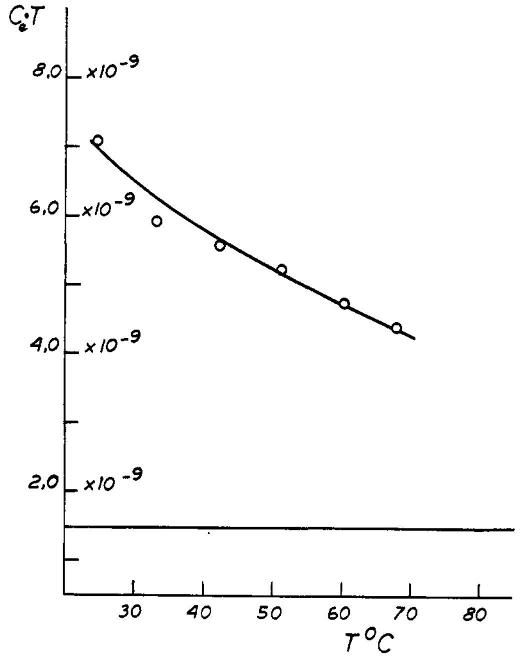

Figure 6. The drastic decrease of the temperature-corrected stress-optical coefficient indicates temperature-induced microsyneresis in the inhomogeneously cross-linked gel. Same type of gel as in Figure 4.

prepared at lower dilution but the same amount of cross-linking exhibit less turbidity,[25] in line with the expectation that such gels have a lower degree of inhomogeneous cross-linking.

Our measurements of the angular distribution of the scattered light allow an assessment in terms of the mean-square polarizability fluctuation $\langle\eta^2\rangle$ and the range of the correlation function (eq 15). An example of the scattering data is given in Figure 7. The slope of the line at larger angles allows the determination of the parameter a in eq 15, and by extrapolation to zero angle the quantity $X\langle\eta^2\rangle$ is obtained. After subtraction of the large-angle data, the remaining small-angle points define a straight line which yields b and $(1 - X)\langle\eta^2\rangle$ analogously. Because a, b, and X are now known, the total extrapolated intensity yields $\langle\eta^2\rangle$

$$[V_v]_{\theta=0} = (16\pi^5/\lambda_0^4)\langle\eta^2\rangle(Xa^3\pi^{1/2} + (1 - X)b^3\pi^{1/2}] \quad (16)$$

The accuracy obtained by this procedure for the parameters is about 20% and should not be given a too precise physical meaning since they derive essentially from a curve fitting procedure. The range of the correlation function $\gamma(r)$ as measured by a and b nevertheless gives some idea of the range of supramolecular organization in PHEMA gels. The scattering of similar gels in ethylene glycol is many times lower,[2b] proving that we are not simply looking at the scattering of dust particles or interfaces.

Conclusions

In summary, the role of the polymer–diluent interaction in PHEMA gels as a function of temperature emerges in the following manner.

(1) The molecular events occurring upon elastic deformation differ fundamentally from those occurring in a rubbery network of randomly coiling, homogeneously cross-linked chains. The observed entropy increase—rather than decrease—over most of the temperature range (Table I) might reflect a stress-induced reduction in intra- and intermolecular ordering. The negative $\overline{\Delta H}_{1,\mathrm{dil}}$ below 55° (Table II) can be ascribed to the formation of additional water structure (with more hydrogen bonding) caused by the encounter with the hydrophobic backbone of PHEMA. Above 55° $\overline{\Delta H}_{1,\mathrm{dil}}$ is positive because the normal dispersion forces take over. The previously observed[12] minimum swelling of PHEMA gels as a function of temperature (see also Figure 1) is in line with this explanation. In addition, earlier light scattering data[2a] support the existence of hydrophobically induced micelles at room temperature.

TABLE V
SMALL-ANGLE LIGHT-SCATTERING ANALYSIS FOR PHEMA GELS PREPARED CLOSE TO THE CRITICAL DILUTION

T, °C	τd	$\langle\eta^2\rangle^{1/2} \times 10^5$	a, cm × 10^4	b, cm × 10^4	X
30	0.18	7.8	0.77	2.5	0.74
50	0.25	12	0.69	1.8	0.71
65	0.34	14	0.67	1.7	0.70

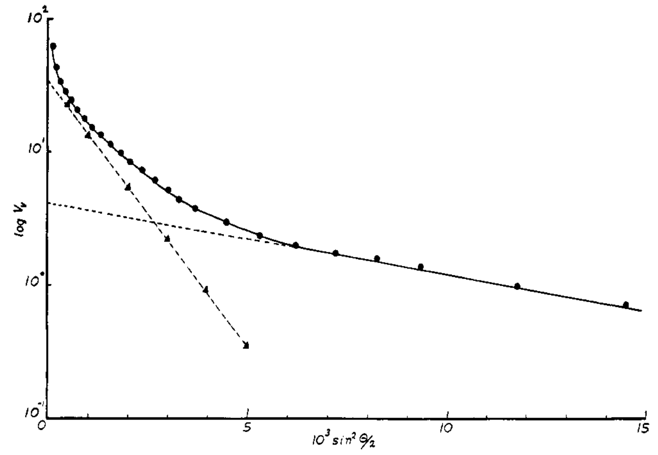

Figure 7. Small-angle light-scattering data plotted as the logarithm of the absolute V_v Rayleigh ratio *vs.* $\sin^2 \theta/2$. The dashed lines indicate the fitting of two gaussian correlation functions to the data (eq 15).

(2) The equilibrium stress–strain curves indicate an increase in apparent molecular weight between cross-links up to 55° (Figure 5). This is taken as an indication of the gradual elimination of hydrophobically induced order, which reduces the number of junction zones acting as cross-links.

(3) The difference in stress and birefringence relaxation over the whole temperature range (Table III, Figure 4) can be explained by the formation of (additional) interchain correlation during relaxation. Since the difference does not disappear above 55° and shows up most strongly in networks prepared under conditions which favor inhomogeneous cross-linking, a stress-induced rearranging of regions of varying degrees of cross-linking is proposed.

(4) The equilibrium stress-optical coefficient C_e decreases about twofold over the whole temperature range (Figure 6). In conjunction with the relaxation data, it is thought that this decrease is due to the reduction in the birefringence (form as well as intrinsic) of regions of different cross-linking density (and different refractive index), probably caused by temperature-induced microsyneresis.

(5) The drastic increase in light scattering with increasing temperature (Table V) exhibited by the samples prepared at a stage of dilution close to the critical value of 45% is also ascribed to temperature-induced microsyneresis, which results from the deswelling of an inhomogeneously cross-linked network.