Thermoelasticity of the poly(2-hydroxyethyl methacrylate) gel

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Anomalous thermoelastic behaviour has been reported by Warren and Prins for water swollen gels of poly(2-hydroxyethyl methacrylate) (PHEMA) subjected to simple tension. The central feature of the assertion that the molecular deformation mechanism in this polymer differs radically from that of all other known long range elastomers has been the claim that the entropic component of the tensile load is negative ($f_s < 0$; $f_e/f > 1$) for certain temperatures in the range 30°–80°C. The experiments described here utilize a new technique to demonstrate, conversely, that the elasticity of the PHEMA gel is conventionally rubber-like in displaying a decrease in entropy on stretching. While confirming the similarity between PHEMA and other polymeric elastomers in this respect we note, however, an unusually large energy contribution to the tensile load ($f_e/f = 0.78$) which distinguishes PHEMA from all other elastomers for which the energy component of force has been measured. It is suggested that the hydrophilicity of the PHEMA molecule may account for this.

INTRODUCTION

PHEMA is one of a large number of hydrogels in which an increasing interest has been shown as materials displaying high compatibility with body tissues[1]. The suitability of PHEMA and similar hydrogels for biomedical applications arises mainly as a result of the hydrophilicity of the main-chain side groups which permit the absorption of electrolytes and body fluids, thereby avoiding the severe gradients in concentration of these molecular agents which are common to hydrophobic materials implanted *in vivo*[2]. Successful applications of PHEMA have included its use as burn dressings[3], for breast augmentation[4], in reconstructive facial surgery[2], for internal administration of antibiotics[5], and for suture coatings[6]. Potential uses in opthalmology[7], dentistry[8], for haemodialysis[9], and the coating of polyurethane prosthetic heart valves are fields of continuing research.

Equilibrium isothermal deformational behaviour of PHEMA gels has been interpreted in terms of the kinetic theory of rubber elasticity, with the Mooney–Rivlin equation being widely used in the discussion of the effect of swelling upon equilibrium characteristics[9]. The conclusions of Warren and Prins[10], however, regarding the temperature dependence of the elastic behaviour of PHEMA gels are inconsistent with the classical rubber elastic model for the retractive mechanism of the polymer and have therefore put into doubt the validity of this theory as applied to these gels. The experiments reported here have been undertaken to extend our understanding of the thermoelasticity of the gels, which in turn provides evidence for the elucidation of the molecular structure of the material.

THEORY

The variable relating to the simple tensile experiment on a solvated polymer which is of interest in the interpretation of molecular structure is the change in internal energy U with length L, at constant volume and fixed composition[11]:

$$f_e \equiv (\partial U/\partial L)_{V,T,n} \tag{1}$$

where n denotes constancy of the mole numbers of all components present in the solvent. An ideal rubber is defined as one for which $f_e = 0$. Application of the first and second laws of thermodynamics gives the retractive force in a tensile experiment as:

$$f = (\partial U/\partial L)_{V,T,n} + T(\partial f/\partial T)_{V,L,n} \tag{2}$$

In that it is the relative magnitudes of the two terms on the right-hand side of equation (2), the energy (f_e) and the entropy (f_s) contributions to the force, which are of interest, it is customary to express the variable f_e/f. Hence:

$$f_e/f = 1 - (T/f)\,(\partial f/\partial T)_{V,L,n} \tag{3}$$

Practical limitations usually prevent the direct determination of the coefficient $(\partial f/\partial T)_{V,L,n}$ in equation (3). Experiments are usually undertaken at constant pressure and the condition of constant volume is then unattainable.

For dry rubbers in which the bulk thermal expansion coefficient is small[12] (~6.6×10^{-4} per K), and for closed systems in which n is automatically constant, the coefficient in equation (3) has been accurately approximated at low strains[12,13] by the force–temperature coefficient at constant pressure and extension ratio, $(\partial f/\partial T)_{P,\alpha,n}$. According to Gee's analysis[13] the error involved in the approximation is, at most, of the order of $\beta L(\partial f/\partial L)_{P,T,n}$ where $\beta = (\partial \ln V/\partial T)_{P,n}$. This error is thus of the order of $f\beta$. For a material whose behaviour conforms to the kinetic theory of rubber elasticity Flory *et al.* have derived the exact relation[14]:

$$(\partial f/\partial T)_{P,\alpha,n} - (\partial f/\partial T)_{V,L,n} = f\beta/3 \qquad (4)$$

and have emphasized that even for dry rubbers the term on the right-hand side of equation (4) may contribute an appreciable error in the calculation of f_e/f from an experiment performed at constant pressure.

For an open system the analogue of equation (4), for a solvated rubber in phase equilibrium with the solvent in which it is immersed, may be shown to be[15]:

$$(\partial f/\partial T)_{P,\alpha,eq} - (\partial f/\partial T)_{V,L,n} = f\beta_s/3 \qquad (5)$$

where the subscript *eq* denotes swelling equilibrium of the polymer phase immersed in pure solvent, and $\beta_s = (\partial \ln V_s/\partial T)_{P,eq}$, where V_s is the free swollen volume of the immersed unstressed sample.

The constraint on the derivatives in equation (5) represented by the subscript *eq* is in one sense quite arbitrary; it is chosen purely for convenience in certain applications so that experiments may be performed in simple tension with the specimen in the easily controlled environment of total immersion in a solvent. We may consider some constraint on the degree of swelling other than that of osmotic equilibrium between the polymer phase and pure solvent. Let such a general constraint be denoted by the subscript ζ. Under the solvent uptake conditions of this general constraint the theory of rubber elasticity leads to the result[16]:

$$(\partial f/\partial T)_{P,\alpha,\zeta} - (\partial f/\partial T)_{V,L,n} = f\beta_\zeta/3 \qquad (6)$$

where $\beta_\zeta = (\partial \ln V_\zeta/\partial T)_{P,\zeta}$, in which V_ζ is the volume of the specimen while under zero tensile load and the swelling constraint ζ. If we wish to determine $(\partial f/\partial T)_{V,L,n}$ accurately, using equation (6), it remains to find some constraint which can be applied to the degree of swelling of the specimen for which β_ζ is preferably small and accurately determinable.

We have adopted an experimental procedure which applies a swelling constraint, ζ, to the tensile specimen satisfying two important requirements. First, the experiments are performed in such a way that the molar uptake of each specimen is very nearly constant during the entire experiment on that specimen. This ensures that β_ζ is very small in equation (6). Secondly, the experimental procedure allows the spectrum of force–temperature–strain behaviour to be to be documented in a short time (20 h) thereby preventing inexcludable irreversibilities from dominating the readings taken.

The experimental timetable is as follows. The immersed specimen is extended at a reference temperature T_0 to a number of strains, at each of which several hours were allowed for equilibration. For each strain the equilibration is followed by a temperature cycle over the range 0°–70°C in the form of a series of quick temperature jumps (T-jumps) from temperature T_0 to temperature T and back again to temperature T_0. During the short period of time (300 sec) for which the specimen is at the new temperature T, the specimen begins to establish a new molar uptake of diluent by diffusion. The associated change of load is recorded and extrapolated back to the time of the T-jump to obtain an estimate of the load at temperature T for a specimen of fixed diluent uptake, the molar uptake being the equilibrium uptake at the reference temperature T_0 at the particular value of specimen length for which the temperature cycle is being obtained. We thus induce thermal equilibrium of the polymer network in the presence of osmotic non-equilibrium of the solvent in the network.

The constraint may therefore be represented by:

$$n_\zeta(L,T) = n_{eq}(L,T_0) \qquad (7)$$

where $n_\zeta(L,T)$ is the molar uptake under constraint ζ for general length and temperature, and $n_{eq}(L,T_0)$ is the molar uptake at length L and temperature T_0 dictated by the phase equilibrium condition of total immersion. Since we expect $n_{eq}(L,T_0)$ to be only very slightly dependent on length for the range of strains within which it is necessary to work to prevent rupture (0–7%), the constraint represented by equation (7) is almost one of constant n_ζ throughout the experiment. This being the case, β_ζ takes on values which are of similar magnitude to those of the bulk expansion coefficient for a closed system, and $(\partial f/\partial T)_{V,L,n}$ can be calculated, without fear of serious error, from equation (6).

EXPERIMENTAL

Specimens

Specimens were machined from three sheets of PHEMA, polymerized by γ-radiation in the absence of water. The procedure was as follows. Glass plates were lined with 'Melinex' [poly(ethylene terephthalate)] sheeting, spaced by rubber seals of 2mm thickness, and held firmly parallel using spring clamps. These units acted as moulds into which were poured the appropriate mixtures of monomer and crosslinking agent. The units were then radiated for 4 h at a dose rate of 0.25 M/h. The 'Melinex' lining was found to ease the removal of the brittle polymer sheets from the moulds after irradiation by preventing adhesion between the polymer and the glass. The content of ethylene glycol dimethacrylate crosslinking agent in the three sheets was 0.1, 0.5 and 1% by volume of the preradiation samples at room temperature. *Table 1* lists the specimens used for the work, all of which had the approximate dry dimensions $100 \times 10 \times 2$ mm^3.

Specimens 1a, 2a and 3a were equilibrated in water at room temperature for a period of eight weeks, after which time the rate of weight increase of each specimen was extremely small (less than 0.1% of the total weight per day). These specimens were then used for thermoelastic tensile experiments. Specimens 1b, 2b and 3b were chosen for a precise evaluation of the equilibration as a function of time and were placed in water at 37° ± 0.1°C. *Figure 1* shows the uptake of these specimens, as a function of $t^{1/2}$, in terms of the variable:

$$Q = (w_t - w_0)/w_0 \qquad (8)$$

where w_0 is the weight of the dry specimen before equilibra-

Table 1

Specimen number	Density of crosslinking agent	Water uptake at 37°C after initial equilibration of 117 days in terms of Q, where $Q \equiv (w_t - w_0)/w_0$ (b specimens only) w_t is the weight after 117 days w_0 is the manufactured dry weight	Dry weight loss of b specimens during the 117 day initial equilibration as a percentage of manufactured dry weight (%)	Water uptake at 37°C of central sections of the tensile (a) specimens in terms of Q, where $Q \equiv (w - w_0')/w_0'$ w is the weight after 5 days of equilibration at 37°C following on immediately from the tensile experiments w_0 is the weight after oven drying
1a	0.1% (v/v) (0.53 X 10^{-5}			0.832
1b	g mol/cm^3 of monomer)	0.852	5.71	
2a	0.5% (v/v) (2.67 X 10^{-5}			0.828
2b	g mol/cm^3 of monomer)	0.816	5.79	
3a	1.0% (v/v) (5.33 X 10^{-5}			0.721
3b	g mol/cm^3 of monomer)	0.770	6.25	

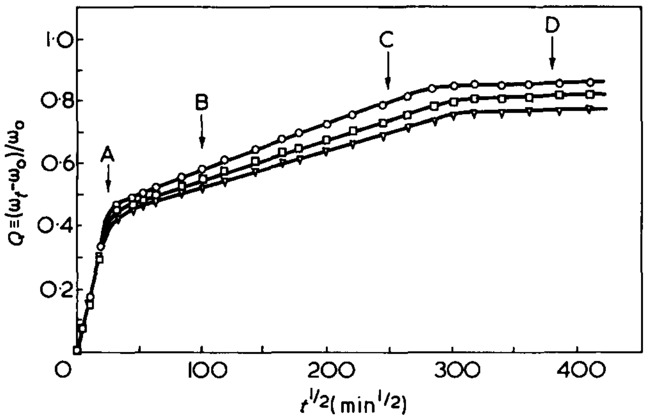

Figure 1 Water uptake in terms of Q [$\equiv (w_t - w_0)/w_0$] during first equilibration after manufacture of initially dry PHEMA specimens: ○, 1b; □, 2b; ▽, 3b. A, 10h; B, 7 days; C, 50 days; D, 100 days

tion (in this case the manufactured dry weight), and w_t is the weight at time t. Wet specimens were quickly and gently dabbed with tissue prior to weighing to remove surface water.

The initial uptake curves of *Figure 1* provide evidence for the presence of two largely independent diffusion processes, one with a time constant of about 10 h, the other with a time constant of about 50 days. If the gels are subsequently dried and then re-equilibrated, the form of uptake curve shown in *Figure 1* is not repeated, but equilibrium becomes complete within about 30 h. We have observed that the long initial equilibration of the specimens is associated with a loss of dry weight. It is therefore appropriate to postulate that the process with a time constant of about 50 days represented by the second region of uptake of *Figure 1* is one of the leaching out of monomer or isolated polymeric molecules combined with water uptake. It is an irreversible loss of sample dry mass not repeated upon subsequent equilibrations. *Table 1* records specimen details, including the dry weight loss after the initial equilibration.

Thermoelastic measurements

Attempts to assess equilibrium tensile properties of rubbery polymers are invariably made in the presence of the disturbing influence of time-dependence in the deformational behaviour. We may distinguish reversible and irreversible disturbances of this kind, the elimination of both of which may involve competing requirements in experimental procedure.

The reversible viscoelasticity can be eliminated, within experimental accuracy, by a careful choice of experimental procedure which allows sufficient time before recording data, during which the viscoelasticity has ceased to contribute significantly to the behaviour. Because the rate of approach to equilibrium is usually greatest at high temperatures it is common to schedule tensile experiments to make best use of this fact. In performing tensile experiments on water swollen PHEMA, account must be taken of two distinguishable yet partially related reversible processes of this kind. First, there is the viscoelasticity associated with the viscosity of the polymer chains themselves. Secondly, there is a time-dependence due to the diffusion into, or out of, the tensile specimen of solvent, whose equilibrium concentration in the polymer phase is partly determined by the state of stress applied to the specimen, and is highly temperature-dependent. The time constant for this latter transport mechanism in the polymer phase is expected from theory to be closely proportional to the square of specimen thickness[17,18]. For our specimens of swollen thickness just over 2 mm we observe the diffusion mechanism to have a time constant of about 5 h at 30°C. For similar specimens to those used here, Warren and Prins found that a thickness of 1 mm required, at most, 2 h for an 'equilibrium' retractive force to be reached[10]. These observations are in accord with expectations if the relaxation time for the diffusion mechanism is longer than that for the relaxation attributed to the chain viscosity of the network itself. This would seem to be further confirmed by the reversibility found in obtaining each force–temperature curve at constant length.

The irreversible time-dependent disturbances are less easily taken into account. Where there appears to be some form of polymer network degeneration occurring during the course of a tensile experiment, the diminishing of its disturbing effect usually requires that the duration of the schedule be as short as possible and that high temperatures be avoided wherever possible. These requirements are the exact opposite of those for the elimination of viscoelastic disturbances. For PHEMA, irreversible effects appear to be unusually severe. First, the process of water uptake represented by the second near-linear region of the *initial* uptake curves shown in *Figure 1* is particularly disturbing. The process takes over two months to become complete and accounts for nearly half of the change in uptake parameter (Q) occurring in the first equilibration of the manufactured specimens. We would expect experiments performed on specimens in the early regions of this uptake to give evidence of highly disturbing irreversibilities arising from the continual volume increase of the polymer phase. Secondly, we observe that even in experiments performed on specimens equilibrated for a time longer than two months a continual irreversible background decay of load is present when strain is applied.

In view of the irreversibilities found in the PHEMA samples, a short duration of thermoelastic experiment becomes vital. The procedure outlined above in Theory satisfies this requirement; the maximum period of time for recording tensile data for a complete experiment on one specimen need be no more than 20 h. The detailed specimen history we have adopted as that which gave the most reproducible results is as follows.

(i) At 30°C (T_0) the specimen was extended to a strain in the range 0–7% (rupture occurred at strains greater than this) and left to undergo relaxation for no less than 10 h. The tensile load was recorded.

(ii) The temperature of the water around the specimen was then jumped within 15 sec to another value in the range 0°–70°C using a slightly modified version of the T-jump equipment which has been developed for the measurement of activation energy for creep in polymers[19]. The specimen was kept at the new temperature for 300 sec during which time the changing load was recorded every 30 sec. (During these 300 sec the temperature was maintained to within ±0.2°C for all temperatures except those below 10°C, for which the limits were ±0.5°C.) The specimen was then returned to 30°C for not less than 900 sec.

(iii) Procedure (ii) was repeated to map out a temperature cycle over the whole range, 0°–70°C.

(iv) On completion of the temperature cycle the specimen was brought to 30°C and a new length imposed. The specimen was then allowed to relax for not less than 5 h before temperature cycling commenced. This routine (imposition of new length, relaxation, temperature cycle) was repeated several times for each specimen.

After each T-jump from the reference temperature, 30°C, the load was reproduced at T_0 to within ±2 g ($\simeq$±0.3% of the maximum load attained during the experiment). The reversibility of each force–temperature plot was extremely good.

During the long relaxation, of (iv) above, after the imposition of the new length, it was observed that the force relaxation consisted of: (a) a rapidly varying load which ceased changing within 5 h, and (b) a constant decrease in the load of the order of ½ g/h. The origin of (a) was clearly the change of equilibrium water uptake due to the imposition of the new length. The effect was therefore taken to be diffusion-controlled. The origin of (b) was not so clear, but was probably network degradation. By measuring the linear decrease in load with time due to (b) it was possible to apply additive corrections to the curve of each force–temperature cycle. For example, if the measured rate was a drop of 0.6 g/h after 7 h of relaxation, then all load readings of the following temperature cycles would be corrected by the addition of 0.6 x 7 = 4.2 g. These corrections became cumulative additions during the course of the experiment, but in no case amounted to more than 4% of the highest load attained in the course of the experiment. In none of the experiments were the applied corrections sufficiently large to alter significantly the overall conclusions of this paper.

Extrapolation of load plots following upon the T*-jumps*

The change in temperature of the water surrounding the specimen[19] was completed within 5 sec of initiating the new water flow past the specimen from a bath at the new temperature T. The load on the specimen indicated that the temperature change of the specimen itself was completed within a further 50 sec. It was found that the load readings taken every 30 sec in the period 60–300 sec after initiating the T-jumps could be accurately fitted by the empirical function:

$$f = a\ln(t + \tau) + b \qquad (9)$$

where a, b and τ are parameters calculated by the method of least squares. The sum of the squares of deviations (χ^2) was always less than $0.0135n$ g^2, where n is the number of data points taken ($n = 9$). The parameters were calculated for each T-jump by computer, the nature of the function in equation (9) requiring a numerical solution. f_ξ was taken to be the intercept of the extrapolation back to the time of the temperature jump (taken as $t = 5$ sec). The error of this intercept was such that one standard deviation never exceeded 0.17 g. *Figure 2* shows a typical load plot immediately following on from a T-jump; the function of equation (9) is included. The error bars are those calculated by computer to represent ±1 standard deviation of the data scatter.

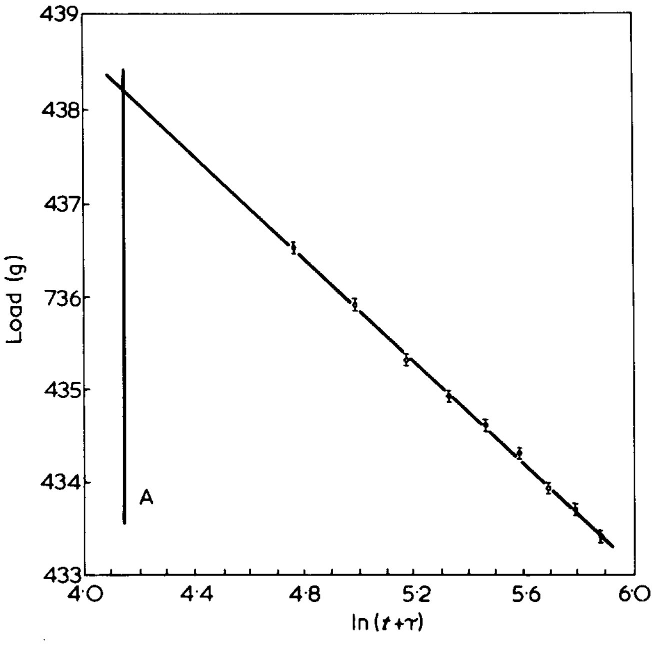

Figure 2 Load in simple tension at length 74.5 mm, for specimen 1a, following upon jump in temperature from T_0 (30°C) to T (in this case 20.6°C) as a function of ln ($t + \tau$), where $\tau = 57.84$ sec. The least-squares fit of equation (9) is plotted, for which $a = -2.758$ g, $b = 449.65$ g and $\chi^2 = 0.0187$ g^2. The extrapolation predicts a load f_ξ at the intercept $t = 5$ sec ($\ln(t + \tau) = 4.141$) of value 438.29 g. The error bars on the data points are calculated from the mean-square deviation from the fitted function and represent ±1 standard deviation from the line. The 1 standard deviation error on the intercept is 0.0685 g. This plot is illustrative of similar plots derived for each f_ξ measurement made. A, $t = 5$ sec

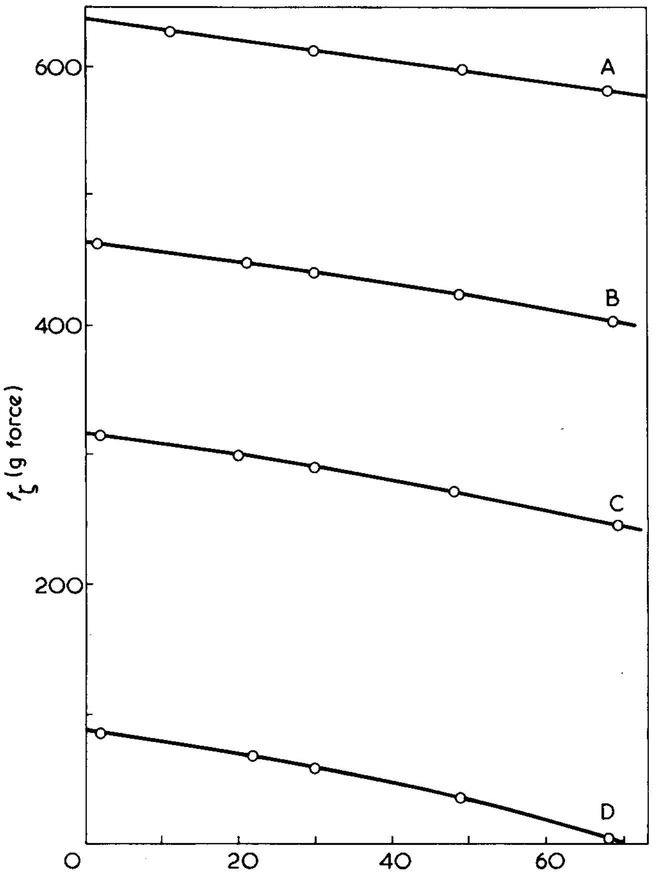

Figure 3 Load in simple tension as a function of temperature under the swelling constraint ζ (equation 7), f_ζ, for specimen 3a at the indicated constant lengths: A, L = 94.6 mm; B, L = 92.4 mm; C, L = 90.5 mm; D, L = 87.8 mm

RESULTS

Figure 3 shows a typical plot of f_ζ as a function of temperature at different specimen lengths for specimen 3a. The plots for the other tensile specimens are similar and are not presented here. Load isotherms plotted directly from the f_ζ—T data were always found to be nearly linear but slightly concave to the length axis, as is predicted by the theory of rubber elasticity. *Figure 4* shows isotherms taken from *Figure 3*. The order of imposition of lengths is given in the caption to *Figure 4*.

Assuming isotropy, the bulk thermal expansion coefficient appearing in equation (6) can be written:

$$\beta_\zeta = 3\,(\mathrm{dln}\,\gamma_\zeta/\mathrm{d}T)_{p,\zeta} \tag{10}$$

where

$$\gamma_\zeta = L^T_{\zeta,f=0}/L^{T_0}_{\zeta,f=0} \tag{11}$$

in which $L^T_{\zeta,f=0}$ is the length at temperature T of the unstressed specimen under the swelling constraint ζ. γ_ζ is derived from the load isotherms by extrapolation to zero load. In *Figure 5* are plotted values of γ_ζ obtained in this way for all three tensile specimens. The data from all three specimens coincide within experimental accuracy. Included in this plot is the near linear curve for β_ζ = 5.484 x 10^{-4}/°C. This line for γ_ζ is derived by integration of equation (10). It can be seen that throughout the temperature range the thermal expansion coefficient for each specimen under the constraint ζ is close to 5.484 x 10^{-4}/°C in value. This is indeed similar to the coefficient reported for dry rubber[12].

DISCUSSION

The force temperature plots of *Figure 3* are strikingly similar to those of dry natural rubber held at constant length in the low strain region where the phenomenon of thermoelastic inversion is pronounced[20]. For natural rubber the normally increasing tensile load with increasing temperature becomes dominated at low elongations by the positive thermal expansion of the unstressed rubber. This dominance of the thermal expansion causes the load to drop with increasing temperature for strains below about 10%. The effect was first observed in a slightly different context by Joule in

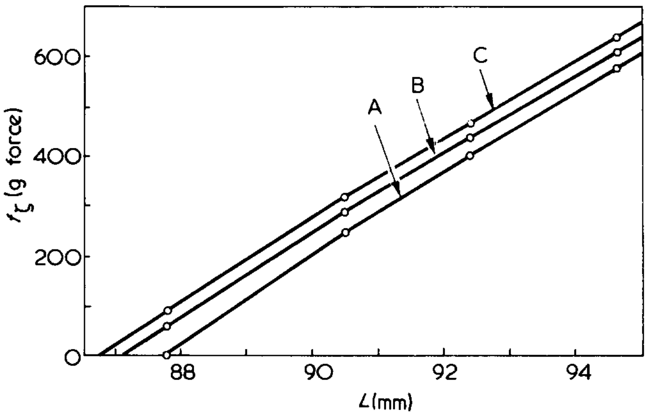

Figure 4 Load isotherms in simple tension, under the swelling constraint ζ, taken from *Figure 3*. The lengths were imposed in the order: 92.4 mm, 87.8 mm, 90.5 mm, 94.6 mm. A, T = 70°C; B, T_0 = T = 30°C; C, T = 0°C

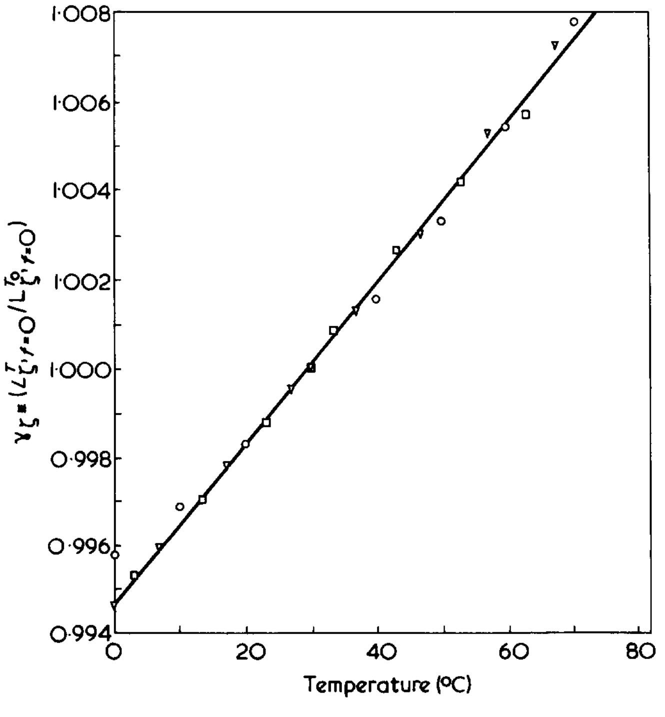

Figure 5 The normalized linear dimension γ_ζ (equation 10) as a function of temperature for specimens 1a (□), 2a (▽), and 3a (○). ———, represents a constant bulk thermal expansion coefficient of β_ζ = 5.484 X 10^{-4} °C^{-1}, under the assumption of isotropy

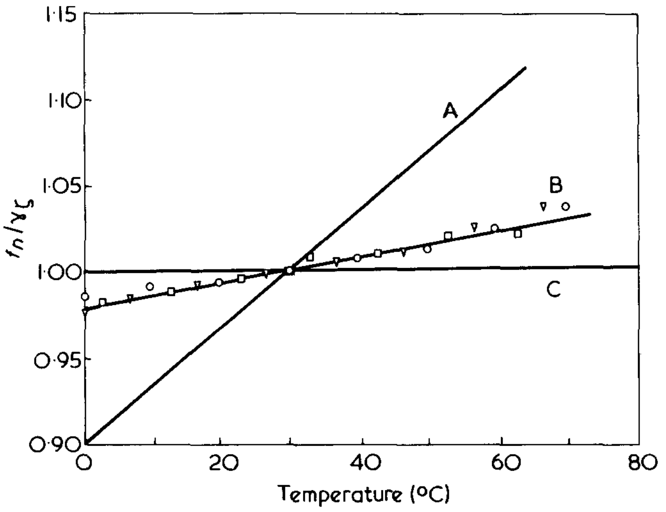

Figure 6 f_n/γ_ζ as a function of temperature for specimens 1a (□), 2a (▽), and 3a (○). The continuous lines are plotted from equation (14). It is seen that all three specimens conform to the theory in the form of equation (14) for $f_e/f \simeq 0.78$. A, $f_e/f = 0$; B, $f_e/f = 0.78$; C, $f_e/f = 1$

1859 and is well documented in the literature[12,21]. The similarity between force–temperature plots for our system and those for natural rubber, together with the similarity between the bulk expansion coefficients (both positive) for both systems, indicates that the water-swollen PHEMA gels we have examined are not radically different in their thermoelasticity from other network polymers in the region of rubbery behaviour, as has been suggested by Warren and Prins[10]. We now examine this indication in detail.

In order to normalize the results of experiments on all three tensile specimens we introduce the normalized force:

$$f_n \equiv (f_\zeta^T / f_\zeta^{T_0})_\alpha \tag{12}$$

This is the ratio of the force at temperature T to the force at the reference temperature T_0 for the same extension ratio α, where $\alpha = (L_\zeta^T / L_{\zeta,f=0}^T)$, the ratio of stretched length to undeformed length at temperature T. It is implicit in the theory of rubber elasticity as usually accepted for solvated elastomers[15] that f_n be independent of extension ratio, α. The isotherms we report show no significant α-dependence of f_n (values reported are calculated for an extension ratio of 1.06). This being the case, we may combine equations (3), (6) and (10) to obtain the relation:

$$f_e/f = -T\{\mathrm{d}\ln[f_n/(\gamma_\zeta T)]/\mathrm{d}T\} \tag{13}$$

For any set value of f_e/f, equation (13) may be integrated to yield[15]:

$$f_n/\gamma_\zeta = (T/T_0)^{[1 - f_e/f]} \tag{14}$$

According to equation (14), for an ideal rubber ($f_e/f = 0$), f_n/γ_ζ will be proportional to absolute temperature. Were a rubber available in which the isovolumetric internal energy contribution to the force was far larger than the entropy contribution ($f_e/f = 1$), f_n/γ_ζ would be independent of temperature.

Figure 6 reports values of f_n/γ_ζ for the three tensile specimens. Also included are curves for f_e/f equal to 0, 0.78 and 1.0 plotted according to equation (14). No difference in behaviour between specimens is apparent and all the data show a close agreement with the theory in the form of equation (14) for $f_e/f = 0.78$. For this value of f_e/f equation (2) gives:

$$f_s = 0.22f \tag{15}$$

Equation (15) gives rise to two observations. First, the PHEMA gels conform to the concepts of the kinetic theory of rubber elasticity by displaying a positive entropic force component (f_s), corresponding to a decrease in network entropy upon stretching[12,21]. Secondly, however, the gels are anomalous in displaying an energy component of force (f_e) which is the larger proportion of the total tensile force.

The possibility of an energy component in the tensile force on elongated rubber was originally introduced as a fairly small proportion of the force predicted by the earlier theory of rubber elasticity[22]. The change in internal energy of a rubber stretched at constant volume is modelled in the theory by associating it with the rotation potentials of the bonds between units of the polymer chain. Different configurations of the chains are thereby permitted to have different internal energies and one result of this is that the chains, if cut free from their crosslink restraints, would show a temperature-dependence of their 'unperturbed' dimensions[16,21,22]. The internal energy contribution is thus modelled as an intramolecular phenomenon. Chain energetics of this kind are permissible within the theory so long as the polymer chains conform closely to the statistics of a Gaussian chain; the degree to which this condition is satisfied is dependent among other things on the relative magnitude of f_e and on the number of chain units between crosslinks[16].

For natural rubber f_e is known from a large number of reported experiments to be approximately 18% of the total force[21]. Large negative values have been reported for crosslinked polyethylene, of the order of 60% of the tensile force[22] but the authors know of no large positive values reported for any elastomers. Our observations therefore suggest that PHEMA is unique among elastomers studied in this way in showing a large positive value of f_e/f.

PHEMA differs from other elastomers for which f_e/f has been measured by being a highly hydrophilic polymer. The state of water within hydrogels is not well understood; a 'three-state' model has been regarded by some workers as necessary to describe the various aspects of the swelling behaviour of hydrogels[23], but whatever the state of water within the gels, we may be confident that the hydrophobic effect active in the presence of the amphiphilic molecules must give rise to some degree of local ordering or micelle formation not commonly found in natural rubber and its related elastomers[10,24]. It seems probable that a local ordering dictated by the hydrophobic effect would be a predominantly intermolecular phenomenon in strong contrast to the intramolecular behaviour usually associated with energy contributions to the force on a condensed network. The 'melting out' of ordered micelles or the exposure of groups of the polymer molecules to environments made energetically less favourable by the hydrophobic effect seem likely to give rise to an influentially large energy component of force. The measurement of f_e/f for hydrogels other than PHEMA would prove informative in this connection.

If the constraints upon chain mobility introduced by micelle formation are sufficiently severe to modify the chain statistics in such a way as to invalidate the Gaussian approximation, the statistical theory of rubber elasticity as usually applied will no longer be able to describe hydrogel elasticity. The thermoelastic measurements undertaken in this work are largely irrelevant to this question. Because γ_ζ differs so little from unity over the range of temperature we have studied, its contribution to equation (6) is almost negligible. This being the case, Gee's approximation can be applied in a form suited to the system, quite independently of any equation of state, as:

$$(\partial f/\partial T)_{p,\alpha,\zeta} \simeq (\partial f/\partial T)_{V,L,n} \qquad (16)$$

and the overall conclusion regarding f_e and f_s is established without recourse to the rubber elasticity theory.

The sample chosen by Warren and Prins[10] for thermoelastic measurements contained 2.4 x 10^{-5} mol of crosslinker per cm^3 of monomer. From *Table 1* it can be seen that this value is nearly central to the range we have investigated. Without evidence to the contrary we assume that Warren and Prins achieved polymerization using a chemical catalyst. The difference between such a procedure and our use of radiation polymerization is not thought to be important enough to prevent a meaningful comparison of results from the two thermoelastic experiments.

Warren and Prins observed the thermoelasticity of the *free*-swollen PHEMA gel. Under these conditions they observed a rise in load followed by a decrease in load upon increasing the temperature of a specimen held at constant length[10]. The load attained a maximum value at 55°C. Conversely a plot of the volume of the free-swollen undeformed gel against temperature was found to show a minimum. This minimum occurs at approximately 51°C. After using the latter data to take account of the free-swelling effect on the former data, of load as a function of temperature at constant length, f_e/f was calculated by Warren and Prins to rise from 0.30 at 30°C to a maximum of approximately 1.4 near 50°C, and then fall again to 0.19 at 80°C.

In the force–temperature data at constant length in *Figure 3*, where the constraint ζ corresponds to retaining constant molar uptake for the whole temperature cycle, no evidence of a force maximum is detected. This must lead us to suggest that the quite unexpected and erratic variation of f_e/f over the range 30°–80°C claimed by Warren and Prins[10] is not a reflection of any basic retractive mechanism of the molecular network, but arises from errors in the method adopted, which cause f_e to follow the peak in their force–temperature curve at constant length.

Two possible sources of error are apparent. First, if the kind of irreversibilities are present in chemically polymerized PHEMA as we have observed here, then a progressive error in the measured values of $(\partial f/\partial T)_{P,L,eq}$ after 12 h equilibrations might be large[10]. Other measurements required in the calculation of f_e/f using the Warren and Prins method would suffer similarly. Secondly, the numerical calculation of f_e/f involves handling differences between large numbers, which may give rise to serious deviations of the calculated value of f_e/f from the true value.

In view of the above we feel unable to accept the conclusion of Warren and Prins[10] that 'the molecular events occurring upon elastic deformation differ fundamentally from those occurring in a rubbery network of randomly coiling, homogeneously crosslinked chains. The increase in entropy upon stretching, which these authors were led to claim from their measurements of f_e/f greater than unity, is not confirmed by the present work. Thus, while recognizing the need to beware of applying the rubber elasticity theory (with its requirement for Gaussian chain statistics) to hydrogels in which micelle formation or 'microsyneresis' may dominate the substructure, our observations suggest that the deformation is accompanied by a *decrease* of entropy upon stretching. In this sense, PHEMA is found to conform to the common behaviour of all other known crosslinked polymeric networks.

Finally, we note that the irreversibilities we have observed in the water swollen PHEMA gel, together with the long equilibration times associated with the reversible solvent transport by diffusion, are properties which may have a disturbing influence upon the biomedical application of the gels immediately following on from manufacture. We have measured similar effects to those shown in the uptake curve of *Figure 1* in specimens manufactured over a wide range of crosslinking density and of proportion of water present at manufacture.

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