Comparison of the thermal behaviour of aqueous solutions and hydrogels of poly(N-methylol acrylamide)

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The intrinsic viscosity ($[\eta]$) in water of a sample of linear poly(N-methylol acrylamide) (PMAM) has been measured over the range 278–348 K and the swelling ratio (Q) in water of a sample of chemically crosslinked PMAM has been determined within the interval 278–353 K. The plots of $[\eta]$ and Q versus temperature (T) both exhibited a maximum. The viscometric behaviour is consistent with an analysis based on excluded volume theory, which indicates the existence of a critical solution temperature both below (263 K) and above (375 K) the maximum. The swelling data were analysed on the basis of the Flory–Rehner theory which yielded a predicted minimum in the dependence of the polymer–water interaction parameter (χ) with T, thus according with the observed maximum in Q versus T. Prolonged heating of linear PMAM and its xerogel yielded products, which were no longer soluble or swellable, respectively, in water. The induced crosslinking proposed as the cause has been confirmed by chemical and infra-red analysis.

INTRODUCTION

A hydrogel is a water-swollen, and commonly crosslinked, polymer the linear form of which may or may not be soluble in water, as typified by poly(N-vinyl-2-pyrrolidone) (PVP)[1] and poly(2-hydroxyethyl methacrylate) (PHEMA)[2], respectively. In studies on crosslinked organogels such as swollen rubber it is common practice to assign the same value of the polymer-swelling liquid interaction parameter χ as that known for solutions[3]. This procedure is clearly somewhat inexact, as χ is concentration dependent or effectively depends on the level of crosslinking in the gel. The latter statement has been corroborated for PVP networks in water[1]. Nonetheless, as evidenced by our findings on linear and crosslinked PHEMA in aqueous dioxan mixtures[2,4], certain analogies do exist between swollen gels and the corresponding solutions. It is this aspect which constitutes the main aim and theme of this paper.

The effects of temperature on the equilibrium swelling which have been noted to date are quite diverse[5–8], namely: (1) increased swelling with increase in temperature (T), i.e. an endothermic process; (2) decreased swelling with increase in T, i.e. an exothermic process; and (3) a combined effect of increased swelling followed at high T by decreased swelling. Examples of these types have been quoted previously[5]. The effects of temperature on the intrinsic viscosity ($[\eta]$) of a solution of a linear polymer also encompass several forms, which have been discussed and rationalized[9,10]. Hence we have sought a system whereby the swelling of a hydrogel over a wide range of T can be compared with the value of $[\eta]$ at different temperatures. Several of the hydrogels cited previously within the above types do not have water-soluble linear forms. The parallel between the behaviour of PVP hydrogels and the decrease in $[\eta]$ with increasing T for aqueous solutions of linear PVP is already known[11].

A preliminary search and relevant tests indicated that linear and crosslinked poly(N-methylol acrylamide) (PMAM) might well provide suitable systems, since the former is water soluble and the latter is capable of considerable water uptake at swelling equilibrium.

EXPERIMENTAL

Preparation of linear PMAM

The aqueous reaction mixture contained N-methylol acrylamide (MAM), ammonium persulphate (initiator) and isopropanol (chain transfer agent[12]) at overall concentrations of $0.4 \, \text{mol dm}^{-3}$, $3.5 \times 10^{-3} \, \text{mol dm}^{-3}$ and $8 \, \text{ml dm}^{-3}$, respectively. The water used was slightly acidified with HCl to pH = 6 in order to enhance solubility of the monomer[12]. After passage of gaseous nitrogen through the solution for 10 min, the vessel was sealed and reaction was carried out at 323 K for 14 min. The clear solution was then chilled to stop reaction and dialysed in a Visking bag against deionized water, which was changed twice daily. After 7 days the solution was concentrated in a rotary evaporator and freeze dried for 15 h. The resultant white powder was dried finally under vacuum at 303 K. The yield was 40%.

Preparation of PMAM hydrogels

The reaction mixture in water, which was slightly acidified as before, contained MAM, ammonium persulphate and methylene bisacrylamide (crosslinking agent) at overall concentrations of $2 \, \text{mol dm}^{-3}$, $6 \times 10^{-3} \, \text{mol dm}^{-3}$ and 0.5% of the weight of monomer, respectively. After outgassing with nitrogen for 5 min, the solution was injected into a mould consisting of two glass microscope slides separated by a peripheral polytetrafluoroethylene gasket. The assembly was held together by four bulldog clips. Polymerization was

carried out in a preheated oven for 2.5 h at 328 ± 1 K, after which the mould was left to cool to room temperature and opened. The hydrogel was removed and placed in distilled water.

To determine the conversion in the preparation of the hydrogel a parallel experiment under identical conditions was conducted on a small quantity of the reaction mixture in a small stoppered vial. After the reaction the resultant hydrogel disc was removed, washed with water and left for 4 days when a constant weight of swollen disc was obtained. The sample was then dried to constant weight in a vacuum oven at 313 K. The fractional conversion was calculated as the ratio of the weight of dried disc to weight of monomer in the initial reaction mixture. The conversion was found to be 92%.

Procedures

Fundamental characteristics. For solutions of linear PMAM in water the specific refractive index increment (dn/dc) and the weight average molar mass (M_w) were determined at 298 K and 633 nm employing apparatus and procedures described previously[13,14]. The partial specific volume ($\bar{v}_2$) of polymer in water was also measured as before[15]. The method of Cornet and van Ballegooijen[16] was used in conjunction with a previously adopted experimental technique[17] to determine the composition of a θ mixture at 298 K, the solvent and precipitant being water and ethanol, respectively.

Spectroscopy of linear and crosslinked polymer. Certain of the samples subjected to different treatments (see Results) were ground to a fine powder and dried thoroughly. Potassium bromide pellets containing ~ 1.5 wt% polymer were made and their spectra examined in a Perkin-Elmer 1710 IR Fourier transform spectrometer, the resolution and number of passes being $2 \, cm^{-1}$ and 20, respectively.

Intrinsic viscosity and swelling. The intrinsic viscosity [η] of the linear polymer in water was measured in an Ubbelohde viscometer, data being treated according to the standard Huggins[18] equation. Values were determined at eight temperatures within the interval 278–348 K. A separate solution, which had been maintained at the highest of these temperatures and then restored to 278 K, gave the same value of [η] as that obtained initially. In order to obtain the viscometric chain expansion factor (α) the value of [η] was measured also in the ethanol/water θ mixture at 298 K.

The crosslinked hydrogel produced in the shape of the mould was cut into a rectangular strip ($60 \times 12 \times 3$ mm). This was weighed, stored at ambient temperature in water to extract any unreacted monomer and/or uncrosslinked species and left to attain swelling equilibrium (72 h), when the surface dried specimen was reweighed. The swollen hydrogel was then immersed in distilled water in a beaker in a bath at 353 K. The weight of the swollen gel was determined at 15 min intervals until a constant value was reached (swelling equilibrium). Weighings were made in tared sample bottles after lightly surface drying with Whatman no. 1 filter paper. This procedure was repeated to obtain values of the equilibrium swelling at 5 K intervals down to 278 K. Then the sample was restored to 353 K when the same degree of swelling as that obtained initially was yielded. Degrees of swelling were expressed as a swelling ratio Q:

$$Q = W/W_0 \tag{1}$$

where W is the weight of hydrogel at equilibrium and W_0 is the weight of dry unswollen gel, which was obtained after completion of all swelling experiments by drying at 333 K for ~ 24 h and then to constant weight at 363 K.

RESULTS AND DISCUSSION

Primary characteristics

Certain properties of PMAM have not been reported elsewhere. The values obtained here for dn/dc (at 633 nm at 298 K) and $\bar{v}_2$ in water at 298 K were 0.151 and $0.714 \, dm^3 \, kg^{-1}$, respectively. The value of $\bar{v}_2$ is smaller than the value of $0.769 \, dm^3 \, kg^{-1}$ for polyacrylamide[19]. The θ mixture in aqueous ethanol at 298 K was determined from a plot of volume fraction of ethanol in the solvent mixture at the phase separation point *versus* log of the volume fraction of polymer. Extrapolation of the linear plot to pure polymer [i.e. to the log of the volume fraction of polymer = 0] yielded the θ composition as ethanol/water = 45.0/55.0 (v/v). For the linear sample of PMAM the value of [η] measured under θ conditions ([η]$_\theta$) was $225.1 \, dm^3 \, kg^{-1}$. Due to difficulty in effecting perfect clarification even after centrifugation at 1700 rev min^{-1} for 30 min, the light scattering measurements on aqueous solutions of PMAM could be obtained reliably only down to a scattering angle of 75°. Consequently the derived value of M_w can be quoted only as an approximate one of $2.5 \pm 0.3 \times 10^6 \, g \, mol^{-1}$.

Intrinsic viscosity at different temperatures

The values of [η] are not listed here, but are presented graphically as a function of T in *Figure 1A*, which shows two distinct regions, namely a sharp increase in [η] with T at low T and a gradual decrease in [η] with T at high T. A maximum occurs at $T \sim 298$ K.

As shown previously for other systems the variation of [η] with T can assume several forms. One of the factors dictating the precise form in any particular system is the proximity, or otherwise, of the working range of T to the upper and lower critical solution temperatures. References should be made to earlier papers[9,10] for details of the relevant derivations and further discussion of them. Essentially the general dependence of [η] on temperature is embodied in equation (2) in which K and L are defined
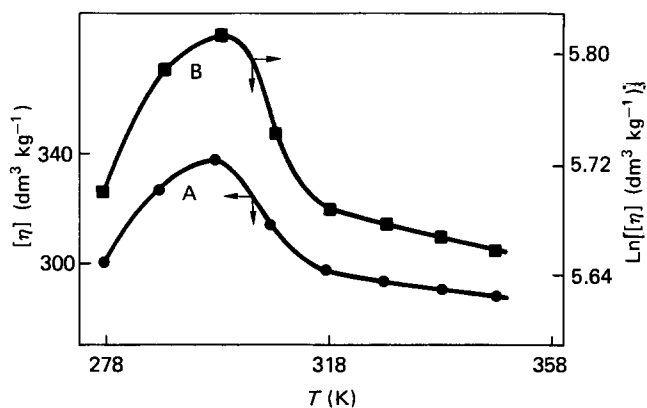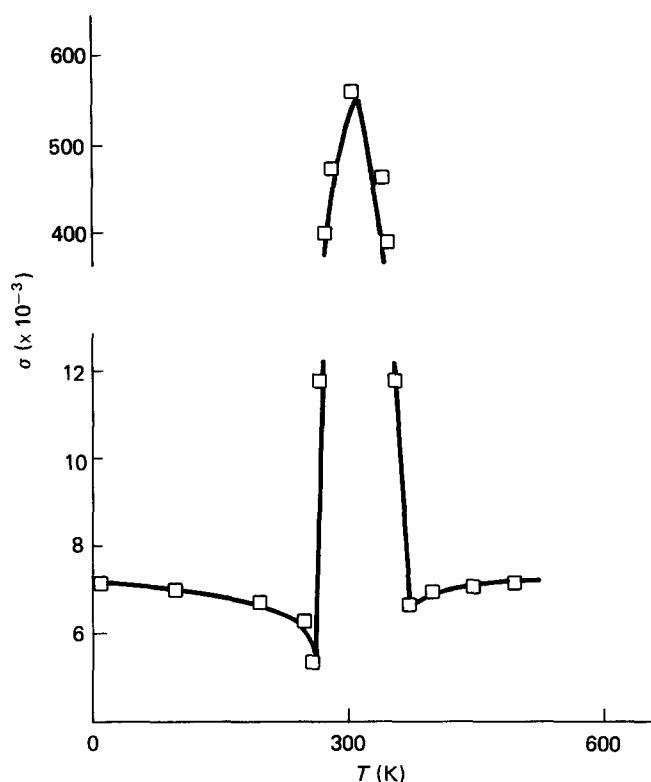

Figure 1 Variation with temperature of the intrinsic viscosity of linear PMAM expressed as (A) [η] *versus* T and (B) ln [η] *versus* T

Figure 2 Dependence of the standard deviation (σ) of the parameter λ as a function of selected θ temperature

by equations (3) and (4), respectively.

$$\lambda = \frac{1 - K[(T/\theta) - 1]}{L[(T/\theta) - 1]} \tag{2}$$

$$K = T(\mathrm{d}\ln[\eta]/\mathrm{d}T)(\omega/\gamma) \tag{3}$$

$$L = T[1 - (\omega/\gamma)] \tag{4}$$

Here γ is the dimensionless exponent in the general expression in equation (5) in which M is the molar mass of the polymer and the constant K_θ is defined in equation (6). A value of 3.0 is most commonly assigned[20-22] to γ and was used here.

$$[\eta] = K_\theta M^{1/2} \alpha^\gamma \tag{5}$$

$$K_\theta = \phi_0(\langle r^2 \rangle_0 / M)^{3/2} \tag{6}$$

In equation (6) ϕ_0 is the universal Flory constant and $\langle r^2 \rangle_0$ is the mean square end-to-end distance of the chain in the unperturbed state. The excluded volume parameter is proportional to a function $f(\alpha)$ of the chain expansion factor α and the parameter ω in equations (3) and (4) is defined[9] as

$$\omega = \mathrm{d}\ln f(\alpha)/\mathrm{d}\ln\alpha \tag{7}$$

The quantity λ in equation (2) is proportional to the temperature coefficient of the unperturbed dimensions:

$$\lambda = \mathrm{d}\ln K_\theta / \mathrm{d}T = (3/2)\mathrm{d}\ln\langle r^2 \rangle_0 / \mathrm{d}T \tag{8}$$

In previous studies[10] good accord was found between experimental and predicted values of λ and the θ temperature on the basis of analysis via the Fixman theory[23,24], which is adopted here:

$$f(\alpha) = \alpha^3 - 1 \tag{9}$$

From equation (7), this gives

$$\omega = 3\alpha^3/(\alpha^3 - 1) \tag{10}$$

Relevant values of α were obtained from the values of $[\eta]$ in conjunction with $[\eta]_\theta$ in the ethanol/water θ mixture:

$$\alpha = ([\eta]/[\eta]_\theta)^{1/3} \tag{11}$$

Note that for aqueous PMAM the values of K_θ, λ and the θ temperature, θ, are a priori unknown.

A plot of $\ln[\eta]$ *versus* T is given in *Figure 1B* and values of $\mathrm{d}\ln[\eta]/\mathrm{d}T$ were obtained at 29 temperatures separated by intervals of 2.5 K. Similarly, from *Figure 1A*, 29 values of $[\eta]$ at the same temperatures were obtained to enable the values of α to be calculated via equation (11). The following procedure was then adopted.

By assigning separately nearly 500 different values to θ at 1 K intervals between 5 K and 500 K for each θ, equation (2) was used to calculate the corresponding value of λ, that is, λ_i at 29 temperatures and hence also the mean of these values, $\bar\lambda$, as indicated in equation (12) where $n = 29$:

$$\bar\lambda = \sum_{i=1}^n \lambda_i / n \tag{12}$$

The standard deviation (σ) of λ_i calculated for each of the values assigned to θ can thus be calculated:

$$\sigma = \left[\sum_{i=1}^n (\lambda_i - \bar\lambda)^2 / n \right]^{1/2} \tag{13}$$

The minimum in σ must correspond to best compliance within equation (2). Treatment according to this procedure was effected by means of a computer program.

The values of σ at different selected values of θ are shown in *Figure 2*, which possesses the following features: (1) the maximum in σ occurs at a selected θ temperature ~ 298 K. Hence this temperature must be very different from the true θ temperature. This accords with *Figure 1A* which shows that 298 K is in fact the temperature of maximum coil expansion; (2) there are two minima, one at a selected $\theta = 263$ K and the other at a selected $\theta = 375$ K. Both of these are consistent with the trend towards decreasing $[\eta]$ at very low and also at very high temperatures in *Figure 1A*. The value of λ at the lower of these values of θ (263 K) is -8.75×10^{-3} K^{-1}, which corresponds [cf. equation (8)] to a temperature coefficient of the unperturbed dimensions of (2/3) $(-8.75 \times 10^{-3}$ K$^{-1}) = -5.8 \times 10^{-3}$ K^{-1}.

Swelling of hydrogel at different temperatures

The swelling ratio Q as a function of T is plotted in *Figure 3*. Although the range of Q is relatively small, the changes in the weights of the swollen sample were always
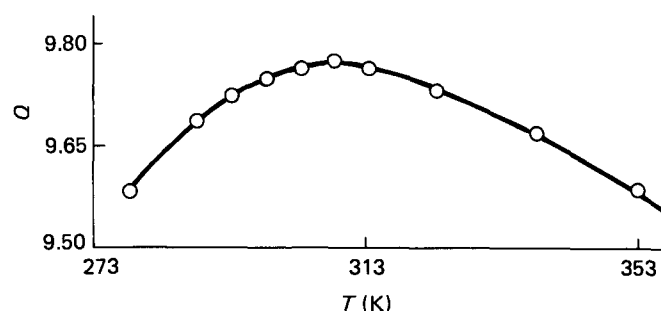
Figure 3 Variation with temperature of the swelling ratio Q for a PMAM hydrogel

in the first or second decimal place (in a total weight of $\sim 3.7\,g$). Hence the trend in *Figure 3* is a real one, i.e. an increase in Q followed by a maximum at $\sim 308\,K$ and then a decrease in Q. Depending on the temperature regime, therefore, the swelling of crosslinked PMAM can be endothermic, athermal or exothermic.

Neither the polymer–water interaction parameter χ nor the effective crosslinking density v_e is known. However, the following semi-quantitative treatment allows the general form of the temperature dependence of χ to be estimated. The Flory–Rehner theory[3] yields the condition at swelling equilibrium as:

$$\ln(1-\phi_2)+\phi_2+\chi\phi_2^2+v_e V_1(\phi_2^{1/3}-2\phi_2 f^{-1})=0 \quad (14)$$

where f is the functionality of crosslinker ($f=4$ for methylene bisacrylamide), V_1 is the molar volume of water and ϕ_2 is the volume fraction of polymer in the hydrogel. Values of ϕ_2 were calculated from Q at each temperature in conjunction with the density of water and $1/\bar{v}_2$. Equation (14) can be recast into the following form in which K_1 is a function of ϕ_2 only and K_2 is a function of ϕ_2, V_1 and f:

$$\chi=K_1+K_2 v_e \quad (15)$$

The nominal or theoretical crosslinking density v_t is known, namely $v_t=\text{mol}$ crosslinking agent/volume of (monomer + crosslinking agent) $=4.3 \times 10^{-2}\,\text{mol dm}^{-3}$. However, v_e rarely has exactly the same value as v_t. Values of v_e between $0\,\text{mol dm}^{-3}$ and $4.3 \times 10^{-1}\,\text{mol dm}^{-3}$ were assigned separately to calculate χ at each temperature via equation (15). The result was insensitive to the assigned value of v_e with regard to the resultant form of the calculated χ as a function of T. In each case the form was the same, namely a decrease in χ to a minimum at $T\sim 308\,K$ followed by an increase in χ at higher temperatures. The curve is thus an inverted form of the plot of Q *versus* T in *Figure 3*.

For the hydrogel, therefore, there is maximum swelling and minimum χ at a certain temperature, which in this case is 308 K. The maximum chain expansion of the linear polymer (*Figure 1A*) must correspond with a minimum in χ. Hence, there is corroboration with earlier findings in which χ was changed according to the swelling medium[2,4] rather than temperature, and a good parallel exists between the behaviour of the swollen gel and that of dissolved linear polymer. The fact, that the temperature of maximum chain expansion (298 K) and maximum swelling (308 K) do not coincide is perfectly reasonable, because the latter is affected by the level of crosslinking. In this connection we note that similar experiments on a PMAM hydrogel prepared at a higher [crosslinker]/ [monomer] ratio yielded a curve of a similar form to that in *Figure 3* but with lower values of Q and a maximum at 288 K.

Effect of heating on linear and crosslinked PMAM

Heating a sample of linear PMAM at 353 K for $> \sim 1\,h$ or at 333 K for $> \sim 6\,h$ produced materials which could not be redissolved in water. Similarly, when a swollen hydrogel was subjected to drying by heating at $> \sim 333\,K$, the resultant dry xerogel exhibited a zero degree of swelling in water. Both of these observations are indicative of a form of crosslinking introduced at high temperature. The nucleophilicity of the oxygen atom of the hydroxyl group tends to induce a displacement

reaction eliminating formaldehyde:
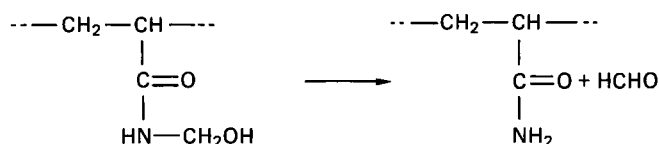
On this basis crosslinking in the polymer can occur by interaction between original methylol groups and the amide groups produced in the displacement process[25].
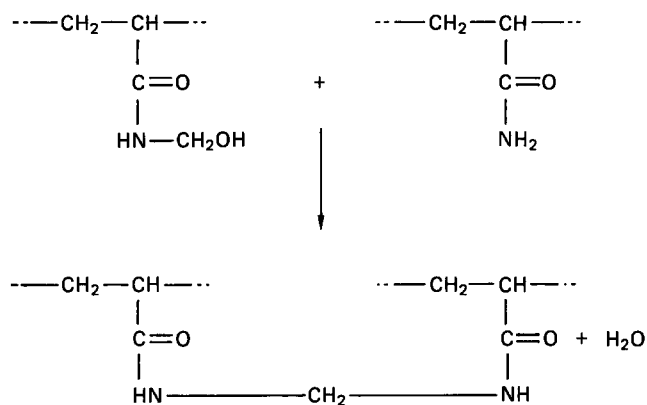
To confirm this mechanism a sample of linear PMAM was heated strongly in a small bent tube and the gas evolved was absorbed directly into a smaller receiver containing 1 ml methanol. Freshly prepared Brady's reagent was then added to the methanol and the mixture was boiled for 1 min and left to cool. The appearance of a yellow precipitate confirmed the presence of formaldehyde[26].

Further examination of the temperature induced crosslinking was made by Fourier transform infra-red spectroscopy on the following samples: (a) linear PMAM; (b) linear PMAM slightly heated (2 h at 323 K); (c) linear PMAM strongly heated (2 h at 363 K); (d) hydrogel of PMAM strongly heated (2 h at 363 K). The corresponding spectra, which are given in *Figures 4a–d*, respectively, exhibit the following main absorption peaks[27] at the wavenumbers (v, cm^{-1}) indicated: $v=3409$, OH stretching; $v=2926$, CH_2 stretching; $v=1664$, $C=O$ stretching; $v=1546$, secondary amide deformation. We have chosen the peaks due to OH stretching (i.e. group at which decomposition occurs) and $C=O$ stretching (as reference group at which no reaction occurs) to compare the relative absorbances. After taking the appropriate base line the ratio of absorbance (OH stretching)/absorbance (CO stretching) was obtained as 1.42, 1.20, 0.97 and 0.97 for samples a–d, respectively.

These findings indicate clearly the partial loss of OH groups on heating. Thus, although sample c became completely insoluble, sample b, which had been subjected to a milder thermal treatment, swelled without dissolution. The value of the absorbance ratio for sample c was the same as that for the heated hydrogel, sample d, and hence the degrees of crosslinking are similar. However, there was already some deliberately introduced chemical crosslinking (via methylene bisacrylamide) in sample d and hence the heating time to induce complete lack of swellability in it was probably more than was actually necessary. Moreover, the proposed intermediate stage in the crosslinking is verified by the appearance of the
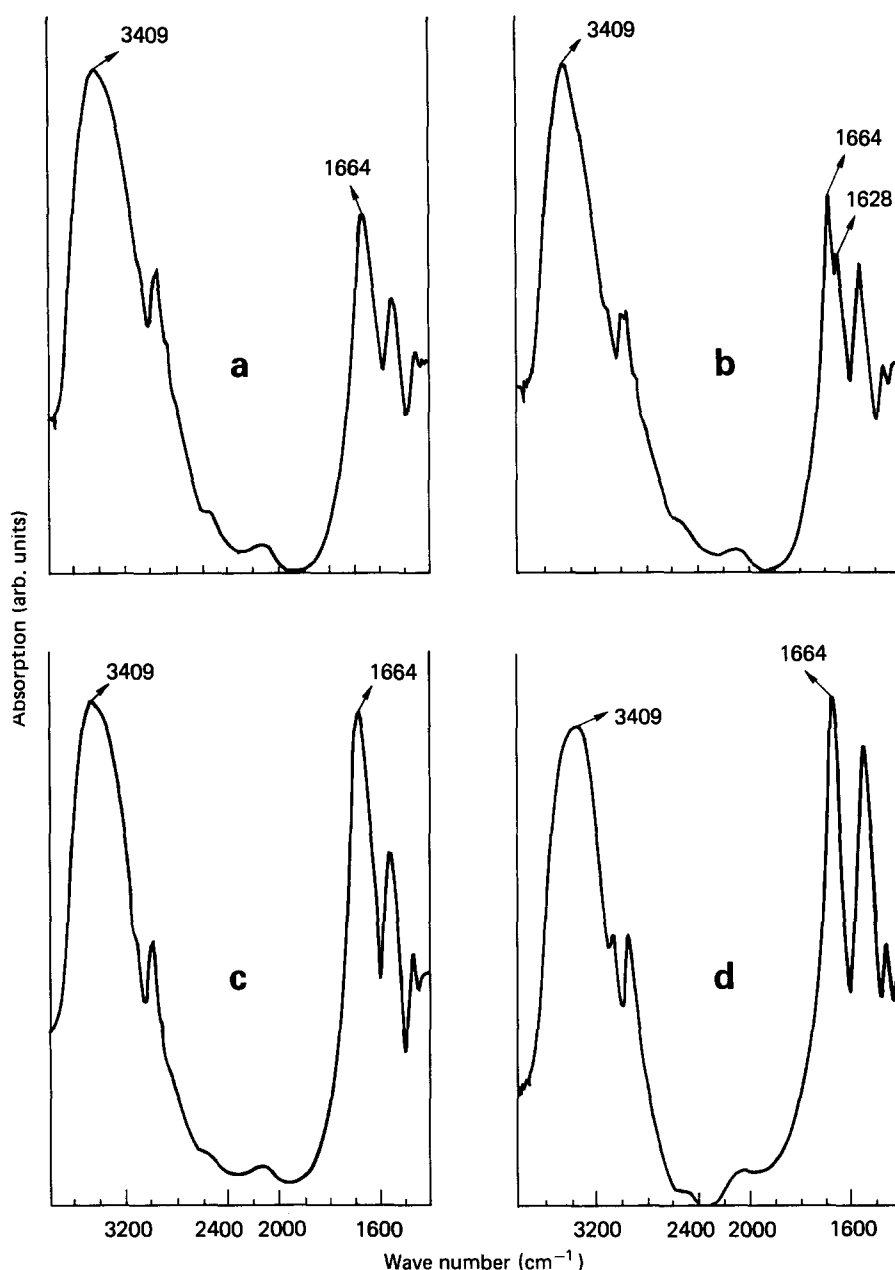
Figure 4 Infra-red absorption spectra for (a) sample a, (b) sample b, (c) sample c and (d) sample d. For details of thermal treatments of linear PMAM (samples a, b and c) and hydrogel (sample d) see text

primary amide deformation peak at $v = 1628 \, cm^{-1}$ (*Figure 4b*).

Finally it is of interest to note recent related work by Mayen and Drouin[28], who applied somewhat different theoretical concepts in their studies on the relation between the swelling of a network and $[\eta]$ of its linear precursor. A linear correlation between Q and $[\eta]$ was predicted and was tested mainly by the use of several different solvents. The correlation was only moderately satisfactory. Of closer similarity to the present work was their use of temperature to effect changes in Q and $[\eta]$ in one liquid, which was water. The temperature range employed was similar to the present one. These authors obtained a decrease, but not the predicted linear one, in both Q and $[\eta]$ with increase in T. This reflects the behaviour of PMAM/water found here, but only partially, since we have also noted the opposite trend at lower temperatures.

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