

Application of Dielectric Spectroscopy and DSC to the Study of Relaxations in Some Copolymeric Hydrogels

MANSOR BIN AHMAD,^{1,*} JOHN P. O'MAHONY,^{2,†} MALCOLM B. HUGLIN,¹ THOMAS P. DAVIS,^{3,‡} and ADAM G. RICCIARDONE³

¹Department of Chemistry & Applied Chemistry, University of Salford, Salford M5 4WT, ²ICI C&P LTD., Runcorn Technical Centre, PO Box 8, The Heath, Runcorn, Cheshire WA7 4QD, United Kingdom, and ³Department of Polymer Science, School of Chemical Engineering & Industrial Chemistry, University of New South Wales, Sydney, NSW, 2052, Australia

SYNOPSIS

The nature of water in copolymeric *N*-vinyl pyrrolidone/methyl methacrylate hydrogels has been investigated using dielectric thermal analysis (DETA) and differential scanning calorimetry (DSC). Dielectric $\tan \delta$ measurements are reported over a frequency range 500 Hz–20 kHz and a temperature range of -140 to $+20^\circ\text{C}$. The observed complex relaxations were attributed to the mobility of water and the relaxation processes of the copolymer matrix. In addition DSC was used to measure the melting endotherm of water in gels partially swollen to a pseudoequilibrium. The resultant data were fitted to a two-phase approximation model. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The nature of water in synthetic hydrogels has attracted considerable research interest over the past two decades. The impetus for this has come from the field of biomedical materials where polymer/blood compatibility is seen as an important issue. In 1973 Andrade et al.¹ published a short overview on "Water as a Biomaterial" and included in their conclusions the following statements:

1. Water is now known to be structured, organized, and influenced by a variety of solutes and surfaces, including many hydrogels.
2. The structure of water is of importance in a wide range and variety of biological phenomena; it is reasonable to hypothesize that it may also play a role in cardiovascular interfacial phenomena."

Water in hydrogels has generally been categorized into three groupings: bound, interfacial, and free water.^{2,3} Evidence to justify these generic groupings includes data from nuclear magnetic resonance (NMR),⁴ dilatometry,⁵ specific conductivity,⁵ X-ray and neutron scattering,^{6,7} and differential scanning calorimetry (DSC).^{8,9} The last of these techniques is more widely used because the instrumentation is readily available in many laboratories. However, there are a number of pitfalls that are often made in this type of analysis, most commonly, neglect of the contribution of the heat of polymer/water mixing when the melting endotherm is recorded. It is also common to overinterpret DSC data, which in reality can only provide information on the melting/freezing transition of water. This in itself is insufficient to support a case for the generic groupings suggested above. Thus DSC needs to be used in tandem with other techniques to allow conclusions to be drawn on the detailed structure of water in hydrogels. DSC is also insensitive to secondary and tertiary thermal transitions that have been shown to exist by NMR studies.¹⁰

Much of the work in this area has been concentrated on poly(2-hydroxyethyl methacrylate) (PHEMA) gels.^{11,12} Recently Pathmanathan and Johari¹³ ap-

* Current address: Jabatan Kimia, Universiti Pertanian Malaysia, 43400 UPM Serdang, Selangor, Malaysia.

† Current address: School of Chemical Engineering, University of Queensland, Brisbane 4072, Australia.

‡ To whom correspondence should be addressed.

plied dielectric thermal analysis (DETA) to the study of thermal transitions in PHEMA xerogel and hydrogel. This work showed DETA to be a sensitive means of identifying secondary and tertiary transitions in PHEMA gels below 0°C.

Less work has been done on methyl methacrylate/*N*-vinyl-2-pyrrolidone (MMA/VP) hydrogels, although three studies merit reference. Takizawa et al.¹⁴ used DSC and drew conclusions on the importance of hydrophobic interactions on water structure. Quinn et al.¹⁵ used pulsed NMR relaxation data and concluded that three types of water were present: bound water that could be resolved into two groupings characterized by relative molecular mobility, and free water. When these NMR data were combined with DSC data, five thermal equilibrium states were postulated in MMA/VP copolymeric hydrogels. Yokota et al.¹⁶ used NMR to study MMA/VP gels swollen in both water and chloroform, which highlighted the heterogeneity of these copolymers. This heterogeneity has its origins in the kinetics of the free-radical synthesis used for their preparation.^{17,18}

It is our intention to apply DETA together with DSC to investigate the thermal transitions in MMA/VP hydrogels, a copolymer system of considerable importance in contact lens manufacture, for example. This article represents our initial foray into the use of DETA for the study of water structure in hydrogels and demonstrates the complex nature of the polymer/water interaction not entirely revealed by DSC measurements alone.

EXPERIMENTAL

Materials

All monomers were obtained from Aldrich Chemical Co. VP and MMA were dried over anhydrous mag-

nesium sulfate and vacuum distilled in the presence of cuprous chloride. Ethylene glycol dimethacrylate (EDMA) was used as supplied.

Procedure

Monomer mixtures were made up gravimetrically, transferred into ampoules, and outgassed by freeze-thaw cycles. The glass ampoules had been siliconized previously to facilitate subsequent removal of the solid rods of copolymer. After sealing, the ampoules were subjected to a total dose of 1 Mrad (10 kGy) of γ -irradiation from the ⁶⁰Co source at Salford University. Solid polymerized rods were removed, oven cured at 105°C for 24 h, and cut into thin discs as described elsewhere. Dry xerogel discs were subjected to Soxhlet extraction with boiling water for 24 h to remove any sol fraction, and then dried to a constant weight in a vacuum oven at 45°C. Hydrogels were obtained by swelling the xerogel discs in deionized water to equilibrium at 25°C. The notation for composition of the xerogels was the same as that defined earlier.¹⁷ The equilibrium water content (EWC) expressed as a percentage was obtained as

$$\text{EWC} = 100$$

$$\times \frac{\text{weight of hydrogel} - \text{weight of xerogel}}{\text{weight of hydrogel}}$$

Details of the hydrogel compositions and EWC values are given in Table I.

Differential Scanning Calorimetry (DSC)

A Mettler DSC 30 was utilized for the measurements. The xerogel was swollen to equilibrium in deionized water in a thermostated bath at 25°C. The resultant hydrogel was then removed, surface dried with filter paper, and about 10 mg of the water-

Table I Sample Compositions and EWCs of P(VP-MMA) Hydrogels

Sample No.	Nominal Composition VP/MMA/EDMA	EWC (wt %)	Tru Composition ^a VP/MMA/EDMA	Corrected EWC ^a (wt %)
1	85/15/1	77.3	83.1/16.9/1	75.9
2	70/30/1	64.5	66.9/33.1/1	63.8
3	55/45/1	48.1	52.6/47.4/1	47.6
4	40/60/1	32.9	37.8/62.2/1	30.4
5	25/75/1	16.1	24.5/75.5/1	15.2

^a As some PVP is extracted on swelling; the actual composition of the gels is slightly different from that expected from the monomer ratios.

swollen hydrogel was sealed in an aluminum pan. DSC measurement of the sealed sample was performed by cooling the sample to -75°C and holding at this temperature for 2 min prior to heating from -75 – 25°C . Two different rates of heating were applied: $5^{\circ}\text{C min}^{-1}$ and $2.5^{\circ}\text{C min}^{-1}$. Samples were also partially swollen and allowed to equilibrate in small sealed plastic bags to reach pseudoequilibrium swelling prior to measurement.

Dielectric Analysis

Dielectric measurements were carried out using a Dielectric Thermal Analyser (Polymer Laboratories Ltd., Loughborough, UK). Two types of experiments were conducted. Samples swollen to their EWC were cooled to -140°C , stabilized for 5 min, and then heated to room temperature at $2^{\circ}\text{C min}^{-1}$. Measuring frequencies of 0.5, 1.0, 5.0, and 20.0 kHz were used. Sample 3 was dried in an oven to a water content of 20.4% and then treated as above. The dimensions of the hydrogel discs were measured using calipers and a micrometer.

RESULTS AND DISCUSSION

DSC

One of the commonly adopted procedures for obtaining the nonfreezing water content of hydrogels is to integrate the melting endotherm at (or around) 0°C to obtain the total enthalpy change. This value is then divided by the heat of fusion of water to obtain the mass of freezing water. The total water content of the gel is known and so the nonfreezing water content can be calculated by difference.

This analysis has a major assumption, namely that the heat of fusion of water in the gel is the same as that derived under standard conditions. The discrepancy between the heat of fusion for water in a hydrogel and bulk water has been discussed by Pouchly et al.⁹ The basic argument is that when crystals of ice in the hydrogel matrix melt, then the resulting additional water is absorbed or “dissolved” in the hydrophilic polymer matrix. This dissolution process liberates a heat of mixing thus reducing the measured endothermic transition. This heat of mixing may be quite significant as can be demonstrated using PHEMA hydrogels as an example. The heat of mixing per unit volume, $\Delta H_m/V$, for a polymer/solvent pair can be calculated from

$$\Delta H_m/V = (\delta_1 - \delta_2)^2 \phi_1 \phi_2,$$

where V = the volume of the mixture, δ_i = the solubility parameter of component i , and ϕ_i = the volume fraction of component i . The solubility parameters of water and PHEMA are 47.9 and 29 (kJ dm^{-3})^{1/2}, respectively.¹⁹ For PHEMA at equilibrium swelling, $\phi_{\text{polymer}} = 0.575$. These combine to give

$$\Delta H_m/V = 87 \text{ J/mL}.$$

The density of a PHEMA hydrogel at EWC is 1.17 kg dm^{-3} . This gives a value of $\Delta H_m/\text{wt} = 102 \text{ J/g}_{(\text{hydrogel})}$. The measured heat of fusion, ΔH_f , of water in the bulk is 329 J/g , thus it would appear that ΔH_m can be a significant factor. Of course this rudimentary analysis relies on a number of approximations and assumes that all the water in the gel melts at 273K . This may not be the case and therefore the actual heat of mixing will be less than that calculated above. However, it will still remain a significant factor.

Thus

$$\Delta H_f (\text{measured}) = \Delta H_f (\text{ice}) + \Delta H_m,$$

where $\Delta H_f (\text{ice})$ is the true specific enthalpy of fusion for water in the hydrogel matrix. In order to account for this Quinn et al.¹⁵ proposed a simple two-phase model for water in hydrogel systems.

The following assumptions are made.

1. Water can exist in the two states, “bound” non-freezing and freezing.
2. Water preferentially occupies those sites that result in a bound state of water.
3. There is a finite upper limit to the amount of bound water that can exist in a hydrogel matrix. This means that above a certain upper limit, any additional water added will be freezable.
4. The freezable water has a heat of fusion independent of water content.

These assumptions appear to be consistent with experimental observation, namely;

1. below a certain water content no freezing water is observed;
2. if the amount of freezing water is defined as the difference between the total water content and the upper bound to the nonfreezing water content, then the heat of fusion divided by the freezing water content is observed to be a constant.

The model can be used to analyze DSC data to obtain the effective specific heat of fusion of water in the hydrogel matrix and the bound water content. The equations are obtained by normalizing all the quantities (except the effective specific heat of fusion for ice in the hydrogel matrix) to unit dry polymer weight.

Thus for 1 g of dry polymer let: w_b = the upper limit to the weight of nonfreezing water per unit dry polymer weight (g/g); w = the total water content in grams water per grams dry polymer weight (g/g); ΔH_f = the measured heat of fusion divided by the dry polymer weight (J/g); $\Delta H_{f(\text{eff.ice})}$ = the effective specific heat of fusion for ice in the hydrogel matrix in joules per gram of freezing water (J/g). This is the same as ΔH_f (measured) referred to earlier. If $w < w_b$ then there is no freezing water and ΔH_f is zero. If $w > w_b$ then the weight of freezing water is $w - w_b$ and the predicted heat of fusion is simply the weight of freezing water multiplied by its effective specific heat of fusion. Thus

$$\begin{aligned} \Delta H_f &= 0 && \text{if } w < w_b \\ \Delta H_f &= (w - w_b) \cdot \Delta H_{f(\text{eff.ice})} && \text{if } w > w_b. \end{aligned}$$

A graph of ΔH_f vs. w has slope equal to $\Delta H_{f(\text{eff.ice})}$ and w_b can be determined from the intercept. This model was adopted for use on three different VP/MMA hydrogels. The resultant plots are shown in Figures 1–3, and the derived parameters w_b and ΔH_f are given in Table II. As predicted by the model, only those samples with water contents exceeding the bound region exhibited detectable endothermic transitions. It is evident that the proposed linear model adequately represents the experimental data.

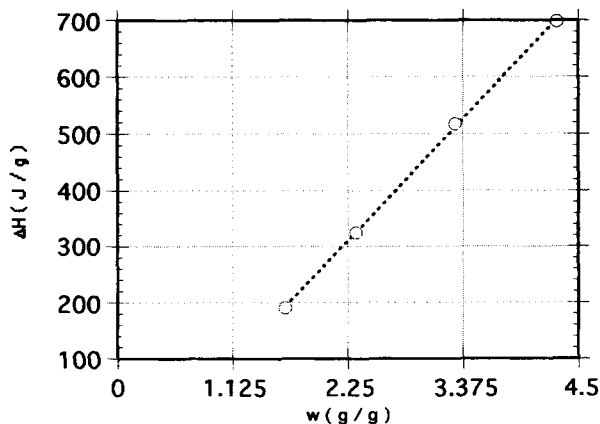


Figure 1 Plot of heat of fusion vs. total water content for VP85/MMA15/EDMA1.

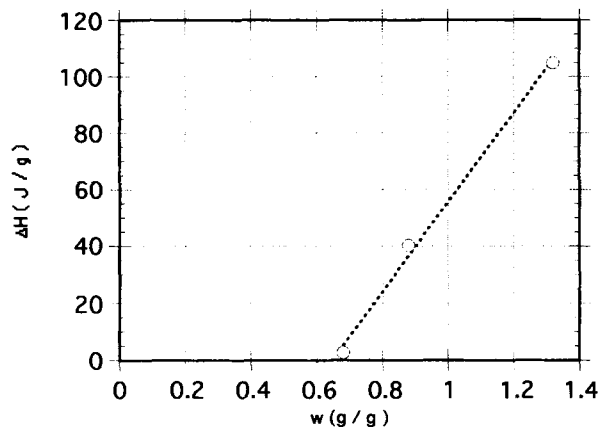


Figure 2 Plot of heat of fusion vs. total water content for VP70/MMA30/EDMA1.

However, the interpretation is not straightforward as the expected trends were not observed. If the model is based on a correct premise then the value for ΔH_f should be derived from the sum of the heat of fusion of ice (329 J/g) and the ΔH_m for the copolymer in water. As the difference in solubility parameter between the water and the polymer increases, then ΔH_m should increase and lead to a corresponding fall in the measured heat of fusion in the hydrogel matrix (as ΔH_m is negative and ΔH_f is positive). On the basis of the results reported here this trend is not obeyed, although the reason for this cannot be determined on the basis of DETA or DSC data alone. Further studies are in progress to ascertain whether the observations reported here are generally true and also the precise origin of the effect.

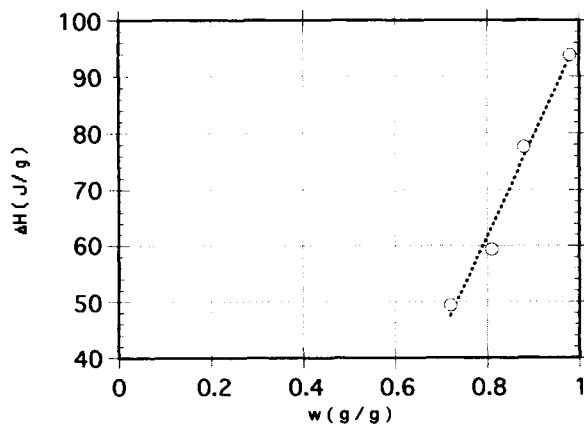


Figure 3 Plot of heat of fusion vs. total water content for V60/MMA40/EDMA1.

Table II Upper Limit to Weight of Bound Water (w_b) and Effective Specific Heat of Fusion ($\Delta H_{f(\text{eff.ice})}$) for Water in Hydrogels

Hydrogel Sample VP/MMA/EDMA	w_b (g/g)	$\Delta H_{f(\text{eff.ice})}$ (J/g)	Linear Correlation Coefficient (R)
85/15/1	0.64	192	1.00
70/30/1	0.65	158	1.00
60/40/1	0.48	196	0.99

This model assumes that water exists in two distinct thermodynamic states within the gel. This was questioned initially by Pouchly et al.⁹ and more recently by Roorda et al.^{8,11} who have reported evidence that the phenomenon of nonfreezing water is purely a kinetic effect, with the polymer matrix (below the glass transition) inhibiting the mobility of the water molecules thereby preventing nucleation. It is the glass transition of the system that gives the appearance of an upper limit to the "bound" water. This work implies that the frequently used classifications of bound, interfacial, and free water, as designated by thermal analysis, may have no physical meaning. A proportion of the imbibed water is associated with the polymer chains through hydrogen bonding but this polymer-water interaction is not necessarily the basis for the observation of nonfreezing water.

Dielectric Analysis

Figure 4 shows a plot of $\tan \delta$ vs. temperature for the five hydrogel samples (at equilibrium swelling). All the samples display at least three relaxations except sample 5 which has the lowest water content. All of the hydrogels exhibit a single relaxation at ca. -110°C . The second relaxation region is displayed by samples 1-4 at -60°C . The third relaxation region occurs within the range -40 to $+10^\circ\text{C}$ for samples 1-4. This relaxation region is complex, with sample 3 displaying three significant features.

Relaxation Regions

Samples 2-5 show a strong relaxation at -110 to -100°C . This relaxation can be assigned to the glass transition of water in the hydrophilic copolymer matrix. Pathmanathan and Johari¹³ made a similar observation for water imbibed in PHEMA. This transition in sample 1 appears at a higher temperature. The reason for this is not immediately apparent, although work by Hofer et al.¹² on PHEMA swollen in water/ethylene glycol mixtures has indicated that the T_g of water in the hydrogel is partly dependent on the history of the sample. The transition shifts to higher temperatures and has a better resolution for higher annealing temperatures.

Samples 1-4 display a relaxation at -60°C . Again this observation concurs with the results obtained by Johari and Pathmanathan¹³ for PHEMA hydrogels. This transition is associated with a number of

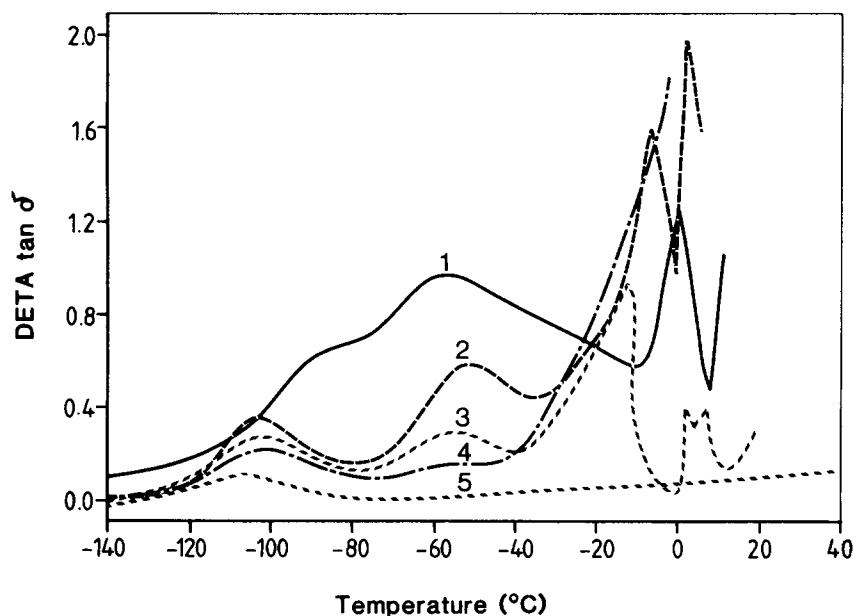


Figure 4 Plot of $\tan \delta$ vs. temperature for the five hydrogel samples (at EWC).

interconnected processes, namely the freezing of this mobile water into cubic ice and the γ -relaxation of the copolymer matrix in the presence of water. It is pertinent to note that Johari and Pathmanathan¹³ found that cross-linking density was not a factor in determining the location of these transitions, the sole governing factor being the water fraction in the hydrogel. The hydrophobic component in the MMA/VP hydrogels can be regarded as a physical cross-linking point (in the presence of water). The results here support the view of Johari and Pathmanathan as copolymer composition does not appear to affect the location of these transitions (at any specific frequency). The absence of any features for sample 5 can be ascribed to the fact that despite the increased mobility of the water it is still unable to crystallize. This hydrogel sample remains glassy and no relaxation is observed. A corollary of this is that the polymer matrix will still be insufficiently plasticized to allow the water to nucleate (on the time scale of the experiment). As this is proposed to be a kinetic phenomenon, it should be dependent on the rate of heating, i.e., if the rate of heating were sufficiently slow, then the formation of cubic ice may well occur. Further experimentation would be required to clarify this point.

Samples 1–4 display multiple features at temperatures approaching 0°C. In contrast sample 5 exhibits no features. DSC analysis of sample 5 shows no melting endotherm; the explanation is linked to

the discussion for relaxation regime 2. Because this hydrogel contains only a small amount of water, then the polymer chains can still be regarded to be in a glassy state and thus all the water is constrained even at 0°C. Therefore no crystalline ice is present and no melting endotherm is recorded by DSC. The other samples all contain some crystalline ice. These relaxations can be attributed to the formation and interchange between different crystalline forms. Indeed in some DSC thermograms a small but significant exotherm is recorded prior to the melting endotherm, which can be assigned to crystallization processes occurring as the vitreous water becomes mobile and able to nucleate. Hofer et al.¹² have shown using X-ray diffraction data that cubic ice transforms to hexagonal ice at -5°C.

Effect of Frequency

Relaxation regimes 1 and 2 were subjected to further analysis by multifrequency scanning. A typical DETA trace for the 70% N-VP hydrogel (sample 2) is shown in Figure 5. The activation energies for these transitions were determined. The first transition ascribed to the T_g of water has a constant activation energy of 58 kJ/mol for samples 1–4. This provides strong evidence that this transition is independent of the polymer matrix. However, this relaxation for sample 5 appears to have a lower activation energy of ~ 44 kJ/mol. Jain and Johari²⁰

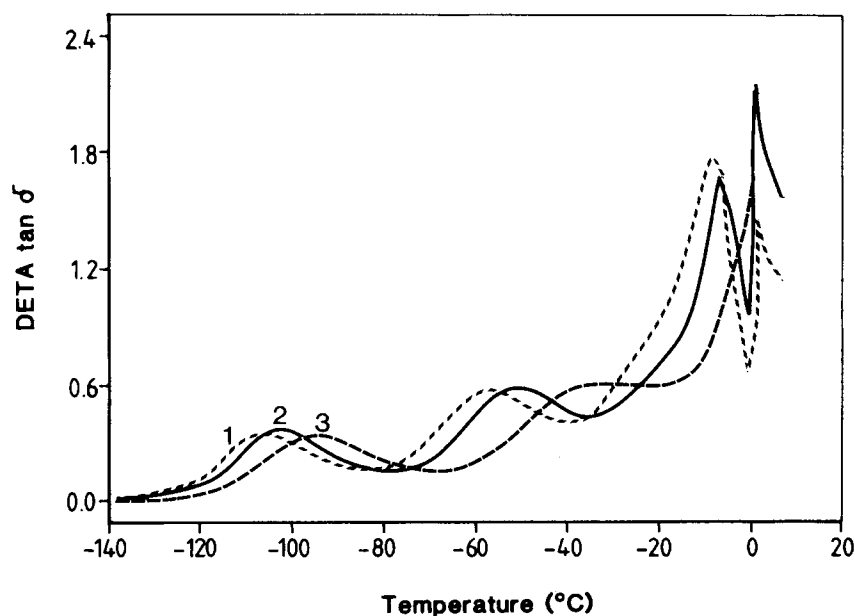


Figure 5 Plot of $\tan \delta$ vs. temperature for sample 2 at the following frequencies: (1) 500 Hz, (2) 1.0 kHz, (3) 5.0 kHz.

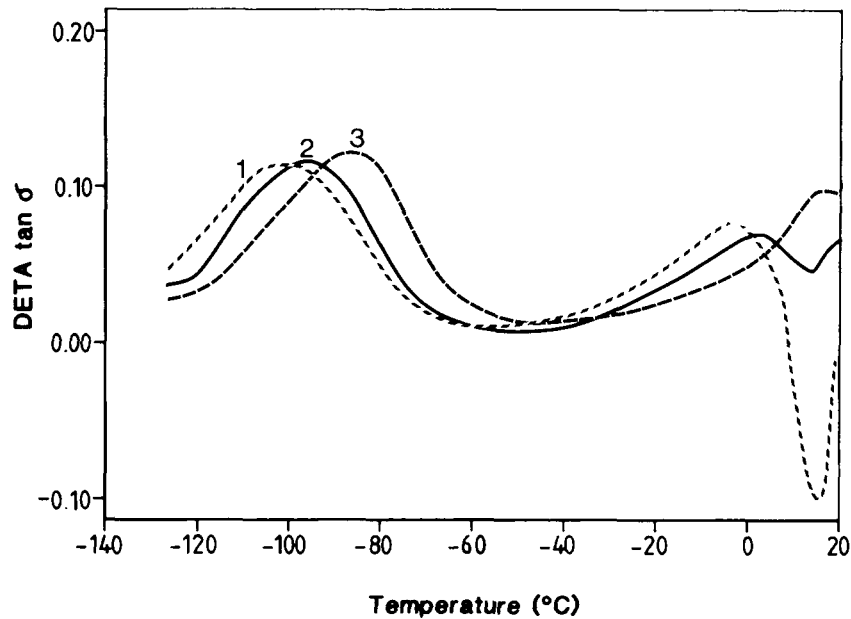


Figure 6 Plot of $\tan \delta$ vs. temperature for sample 5 at the following frequencies: (1) 500 Hz, (2) 1.0 kHz, (3) 5.0 kHz.

obtained 46 and 53 kJ/mol for pure PVP and 50% (wt/wt) PVP-water. They point out that their pure PVP sample probably did contain a small amount of water because it is very difficult to eliminate all water from hygroscopic polymers. They suggest that this relaxation has two contributions, one deriving

from the increased mobility of the water molecules and the other from "micro-Brownian motion of the PVP chains." In the samples containing large amounts of water, the former relaxation dominates whereas in samples containing only small quantities of water the latter relaxation becomes more signif-

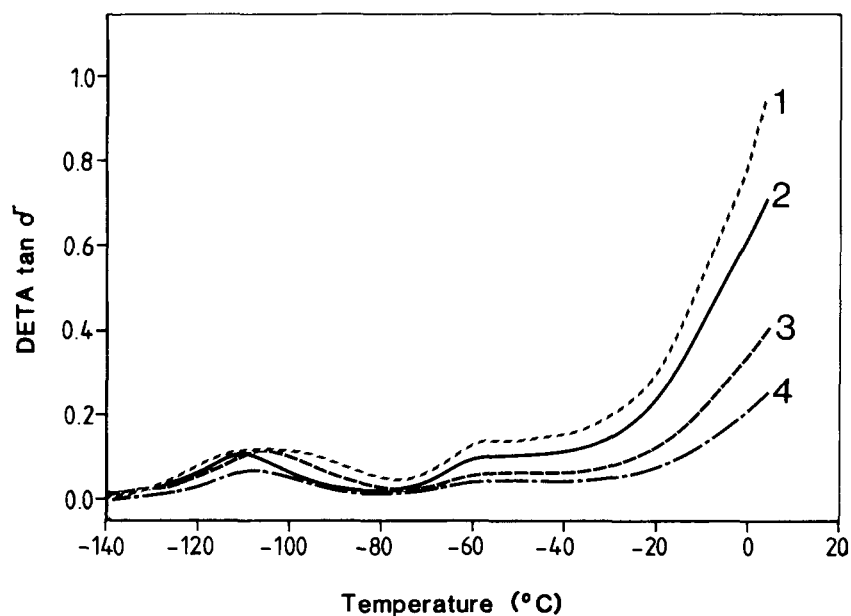


Figure 7 Plot of $\tan \delta$ vs. temperature for sample 3, partially swollen to 20.4 wt %, at the following frequencies: (1) 500 Hz, (2) 1.0 kHz, (3) 5.0 kHz, (4) 20 kHz.

icant. The same explanation would appear tenable for this work, and is supported to some extent by the results of Quinn et al.¹⁵ who reported a relaxation associated with the α -CH₃ in MMA at -103°C .

The second relaxation region at ca. -60°C was treated similarly. In this case the activation energies for samples 1–3 are all similar at 46 kJ/mol, whereas sample 4 has an activation energy of 84 kJ/mol. Clearly three data points are the minimum necessary for this type of analysis and more would have been desirable. Nonetheless the difference appears significant. The transitions occurring at -60°C are suggested to be complex in that they derive from the following contributions: the increased mobility as vitreous water becomes mobile, crystallization of water into cubic ice, increased mobility of polymer chains due to plasticization by the water, and finally decreased mobility of the chains as crystallites form. All of these phenomena are interdependent and thus it is difficult to make general statements. However one point that can be asserted is that this dielectric relaxation is expected to be partially dependent on the polymer composition. It does appear that between water contents (EWC) of 33–48 wt % there is sufficient water present to significantly plasticize the polymer chains at -60°C resulting in a lower activation energy for the observed (composite) transition. As shown in Figure 6, it is difficult to discern a significant relaxation at -60°C for sample 5.

Sample 3 was dried out to a water content of 20.4 wt % and then scanned over the same temperature range. The resulting DETA trace is shown in Figure 7. The low temperature relaxation remains in the same location with the same activation energy. In contrast the second relaxation is no longer present (cf. sample 5).

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