polymer papers

Wide-band dielectric spectroscopy of hydrated poly(hydroxyethyl methacrylate)

Huan Xu and J. K. Vij
Department of Microelectronics and Electrical Engineering, Trinity College, Dublin 2, Ireland

and V. J. McBrierty*
Department of Pure and Applied Physics, Trinity College, Dublin 2, Ireland
(Received 29 January 1993; revised 11 May 1993)

This paper examines the role of water in hydrated poly(2-hydroxyethyl methacrylate) (PHEMA). Dielectric complex permittivity measurements are reported over an extended range of frequency (0.1 Hz–1 GHz) and temperature (77–353 K) with water content as a disposable parameter. Data are correlated with the results of earlier relaxation experiments, notably nuclear magnetic resonance, to provide insight into water–polymer interactions at the molecular level. Three relaxations are detected in the dry polymer, whereas, in the hydrated system, a fourth relaxation is identified and attributed to a low-temperature phase transition of the water itself. Relaxation processes of the host polymer are strongly influenced by the presence of water.

(Keywords: PHEMA; dielectric relaxation; hydration)

INTRODUCTION

Poly(2-hydroxyethyl methacrylate) (PHEMA) and its copolymers constitute a category of hydrogels that are extensively used in medicine and pharmacy[1–3]. Some current applications include contact lenses, ocular inserts for controlled release of antibiotics and artificial liver support systems. As their classification suggests, these polymers can support sizable amounts of water, which can exist in a number of different environments or states ranging from normal bulk-like water to water that is hydrogen-bonded to hydrophilic groups of the polymer chain. Recall that normal water condenses to hexagonal ice at 272 K and this form is known to be retained down to at least 133 K[4]. In contrast, water in emulsions (small droplets) crystallizes to hexagonal ice only at $T<230$ K during cooling[5] and hyperquenched glassy water turns to cubic ice at 152 K ($\sim$16 K above its glass transition temperature T_g of $\sim$132 K) during heating[6].

Water in the hydrogel is known to be more stable than normal water, and can be studied in their deeply supercooled and glassy states when substantial amounts of water are present. These studies reveal a number of different macroscopic water structures or states, the range and relative contribution (occupancy) of which are found to depend on water concentration and on temperature. Their detection and quantification depends on the sensitivity of the technique used and on the thermal history of the sample[7–9].

N.m.r. measurements on hydrated PHEMA show that a significant part of the water is bound, comprising two distinguishable types described as tightly bound and loosely bound, both of which can be quantified[7,8]. For samples with high water content, near-normal water that freezes in the vicinity of 273 K is also present. A number of further observations are relevant.

(i) The greater portion of the water in PHEMA, which is tightly bound, is rendered mobile at about 170–180 K, the lower temperatures referring to material with larger water contents.

(ii) Samples with lower water contents exhibit a broader distribution of correlation times reflecting a preponderance of the motional constraints on water molecules.

(iii) Bound water above its T_g induces local plasticization at low temperatures, up to 260 K, after which plasticization becomes progressively more ubiquitous, especially for high water contents. Typically, the premature onset of general motions of polymer chains is observed at ca. 310 K in T_2 linewidth data, which is at least 100 K lower than for dry PHEMA.

(iv) N.m.r. and d.s.c. data confirm the formation of ice (devitrification) between 230 and 260 K when a sample, initially quenched to liquid-N_2 temperatures, is progressively heated to ambient temperatures. Pathmanathan and Johari[10] argue that water crystallization sets in at about 207 K and is detectable as a second dielectric loss peak at ca. 230 K.

More recent d.s.c. measurements by Hofer and coworkers[11] show that PHEMA undergoes two second-order glass transitions, one at 132 K in the form of an extremely weak endothermic step and a second at 152 ± 2 K, which is also endothermic. The first is at the same temperature as quenched emulsified water, whereas the second is assigned to the 'freezable' water present because it disappears upon its crystallization. Pathmanathan and Johari[10] carried out complex permittivity measurements on 39 wt% PHEMA hydrogel in the frequency range 12 Hz–200 kHz and temperature range 77–273 K. They observed two dielectric relaxation

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* To whom correspondence should be addressed

0032-3861/94/020227-08

processes attributed to the α relaxation of supercooled water and to the crystallization of loosely bound water at higher and lower frequencies respectively.

In this paper, we extend the dielectric upper limits in both frequency and temperature and report complex permittivity measurements from 77 to 353 K over a frequency range of 0.1 Hz–1 GHz. We also investigate the dielectric behaviour of different forms of water in PHEMA ranging from the quenched, partially frozen to the fully frozen forms of water in the hydrogel mixture. Similar measurements are also reported on dry PHEMA and PHEMA immersed in ethanol, in which the direct effect of ice on relaxation is excluded. The object of this paper is therefore to gain further insight into the various forms of water in hydrogel systems through an understanding of the different dielectric relaxation processes observed over the extended range of frequency and temperature.

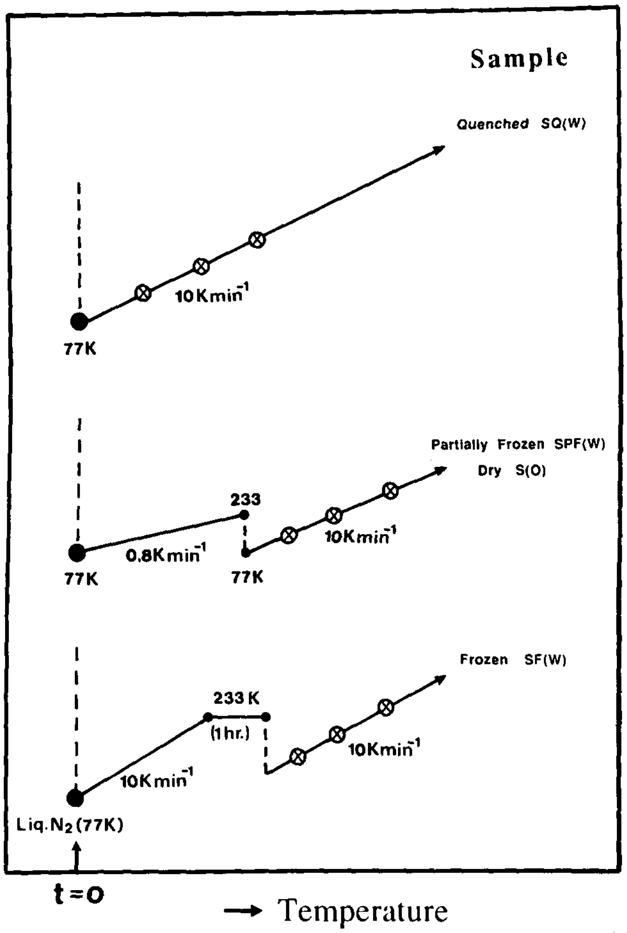

Figure 1 Modes of heating of the samples indicated. The points ⊗ denote the temperatures at which measurements are taken

EXPERIMENTAL

Sample preparation

PHEMA monomer with minor additives[8] is sandwiched between two parallel-plane glass plates and is then polymerized by exposure to u.v. light in the absence of oxygen for 30 min. After 12 h the thin film of polymer, of thickness ~87 μm, is separated from its substrate by immersion in distilled water. To prepare a dry PHEMA sample, the water-released film is sandwiched between two pieces of plastic sheet under moderate pressure and left in a vacuum oven at 333 K for 8 days. Hydrogels with different water contents were prepared by immersing the PHEMA films in freshly distilled water for different periods of time. The equilibrium water content (W) is measured as follows:

$$W=\frac{\text{weight of water in gel}}{\text{weight of dry PHEMA}}\times 100\%$$

Water contents (W) are shown in parentheses in the sample designations (S(0), SQ(W), SPF(W), SF(W)) described in *Figure 1*, which portrays the different thermal histories of the samples studied. Rapid quenching to liquid-nitrogen temperatures is the initial step in all cases. Most of the measurements are reported on hydrated samples for a maximum water saturation level in the polymer corresponding to $W=54\%$. Measurements on samples with $W=4$, 24, 32 and 51% are also discussed.

Experimental methods and analysis

Complex permittivity measurements are made in the frequency range $f=0.1$ Hz–1 GHz using a frequency response analyser (Solatron, Schumberger 1254) along with Hewlett-Packard HP4192A and HP4191A impedance analysers. Here $f=\omega/2\pi$ is the frequency of the applied electric field. A three-terminal dielectric cell for low frequencies was constructed using a design similar to that of Kremer and coworkers[12]. For high frequencies, the sample was placed in a gap in the inner conductor of a coaxial line. Measurement and calibration procedures will be described elsewhere. An automatic temperature-control system (Novocontrol GmbH, Germany) used with home-made cryostats controlled sample temperature to an accuracy of ±0.1 K over the entire temperature range. The real and imaginary parts of the complex permittivity, ε' and ε'', were determined to accuracies of ±2% and ±4%.

For a single, broad, dipolar relaxation process, the complex permittivity data are fitted to the Havriliak and Negami equation[13]:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1+(i\omega\tau)^\beta]^\gamma} \tag{1}$$

Recall that ε' is a measure of the energy stored in the dielectric while ε'' monitors the energy dissipated per cycle of the alternating field. If $\gamma=1$, equation (1) reduces to the Cole–Cole expression[14]. The parameter β is a measure of the distribution of relaxation times, ε_s is the static permittivity, ε_∞ is the permittivity at a frequency where the dipoles are unable to follow the alterations of the electric field, and τ is the most probable relaxation time of the perturbed electric dipoles.

For materials exhibiting a number of distinct relaxation regimes in the frequency domain, the complex permittivity data can be fitted to the following equation:

$$\varepsilon^*(\omega) - \varepsilon_\infty = \sum_{i=1}^{n} \frac{\Delta\varepsilon_i}{1+(i\omega\tau_i)^{\beta_i}} \tag{2}$$

Here n is the number of peaks (at most temperatures, data can be fitted up to three peaks); $\Delta\varepsilon_i$ and τ_i correspond to the relaxation amplitude (or dielectric strength) for the ith process; and β_i is the corresponding dielectric distribution parameter with the most probable relaxation time τ_i.

From the Kirkwood–Fröhlich theory[15,16], $\varepsilon_s - \varepsilon_\infty = \alpha N g \mu^2 / kT$ to a first approximation, where N is the number density of dipoles with moment μ, g is the Kirkwood short-range correlation factor and α is a proportionality constant. Within this approximation, the amplitude of the relaxation process can then be interpreted in terms of the number density of dipoles and/or the factor g.

RESULTS AND DISCUSSION

An understanding of hydrated polymers is bedevilled by subtle and complex interactions between water and its host polymer. Water, for example, may act as a plasticizer or antiplasticizer, thus altering, often dramatically, the characteristic molecular motions of the polymer. In analysing the dielectric data recorded as a function of temperature, frequency and water content, it is helpful to construct transition maps of $\log \nu_c$ *versus* inverse temperature, where ν_c is the correlation frequency, which characterizes specific molecular motions. Here, ν_c is identified as the frequency, $f_m = (2\pi\tau)^{-1}$ at which maxima of resolved relaxation processes occur in the plot of ε'' *versus* frequency or temperature.

Representative spectra

Consider the principal features of PHEMA dielectric spectra for the following representative cases. In the dry material (*Figure 2a*), the temperature dependence of the high-frequency peak is clearly evident between 373 and 443 K, whereas below 433 K the lower-frequency peak rapidly moves out of the frequency range of our measurements. The half-width of the peak centred at 10^5 Hz at 233 K (*Figure 2b*) is 3.5 decades, which exceeds the half-width of the Debye peak characterized by a single relaxation time (1.14 decades) by a factor of 3. A similarly broad frequency dispersion is evident in the plot of ε' *versus* frequency. The dielectric distribution parameter β can be determined by fitting the ε' and ε'' data to equation (1) as described later.

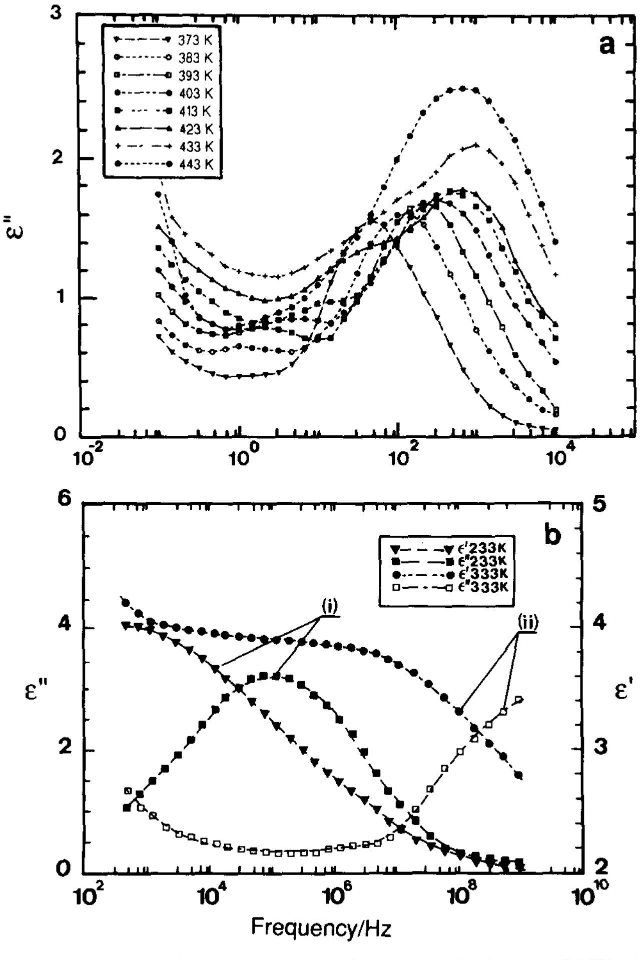

Figure 2 Plots of ε' and ε'' vs. log(frequency/Hz) for dry PHEMA, S(0): (a) between 373 and 443 K and (b) between 233 and 333 K; (i) and (ii) correspond to the measurements at 233 and 333 K, respectively

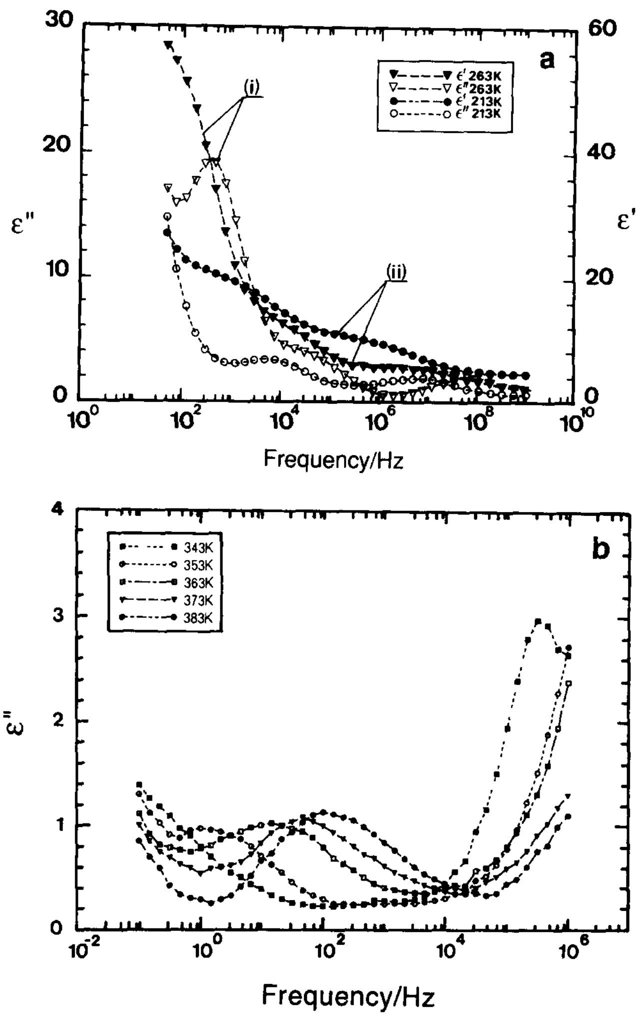

Figure 3 Plots of ε'' vs. log(frequency/Hz) for SQ(54): (a) at temperatures of 213 and 263 K and (b) between 343 and 383 K. Spectra of ε' vs. log(frequency/Hz) are also shown in (a), where (i) and (ii) correspond to measurements at 263 and 213 K, respectively

Spectra of ε'' *versus* frequency for the hydrated sample SQ(54) contain three resolved dispersions at low temperatures (*Figure 3a*), in contrast to the high-temperature region where two are detected between 10^{-1} and 10^6 Hz (*Figure 3b*). Spectra of ε' *versus* frequency (*Figure 3a*) provide complementary insight. In an alternative representation, three resolved dispersions are also detected in $\log \varepsilon''$ *versus* T at 10 kHz (*Figure 4*). Sensitivity to thermal history is typically revealed in the observation of only two ε'' maxima in the frozen hydrogel SF(54) (*Figure 5*), which, in turn, is supported in the corresponding ε' *versus* frequency data.

Before considering the suite of data, the results of one further experiment are introduced. The complex permittivity for SQ(54) above 273 K was measured by minimizing the effect of d.c. conductivity in the polymer,

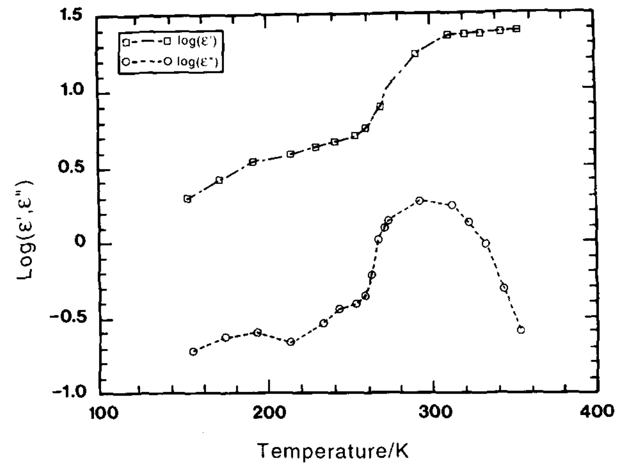

Figure 4 Log ε' and log ε'' vs. temperature for SQ(54) at 10 kHz and in the temperature range 153–353 K

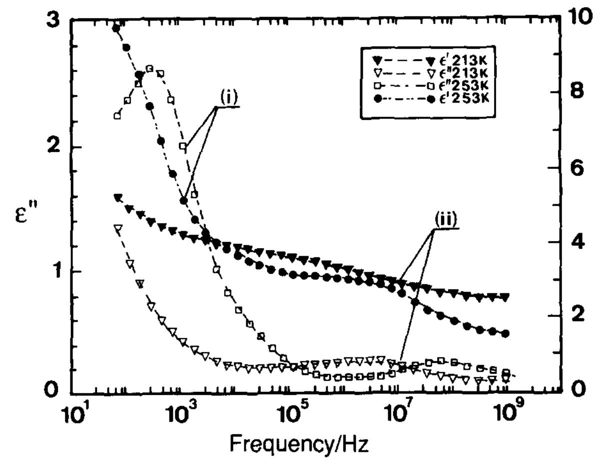

Figure 5 Plots of ε' and ε'' vs. log(frequency/Hz) for SF(54) at 213 and 253 K. (i) and (ii) correspond to the measurements at 253 and 213 K, respectively

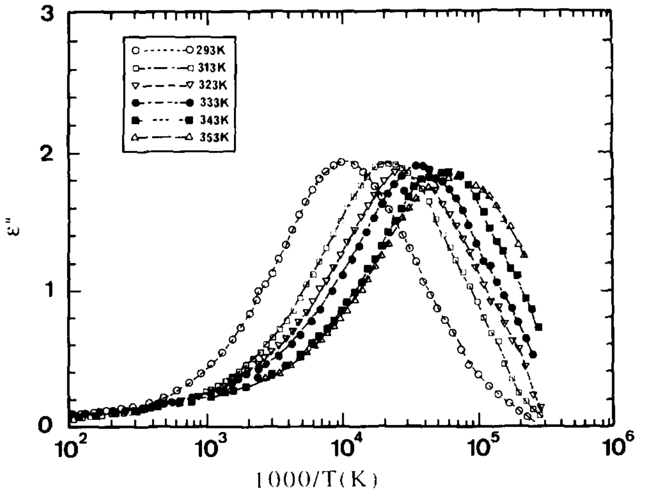

Figure 6 Plots of ε'' vs. log(frequency/Hz) for SQ(54) between 293 and 353 K. Spectra are corrected for the inserted Teflon spacer (see text)

which tends to distort the results. This was achieved by blocking the flow of ions from the bulk water in the hydrogel to one electrode by inserting a thin film of Teflon between the sample and the electrode. The effect of the Teflon spacer on the measured spectra was corrected for in the analysis of experimental data (*Figure 6*).

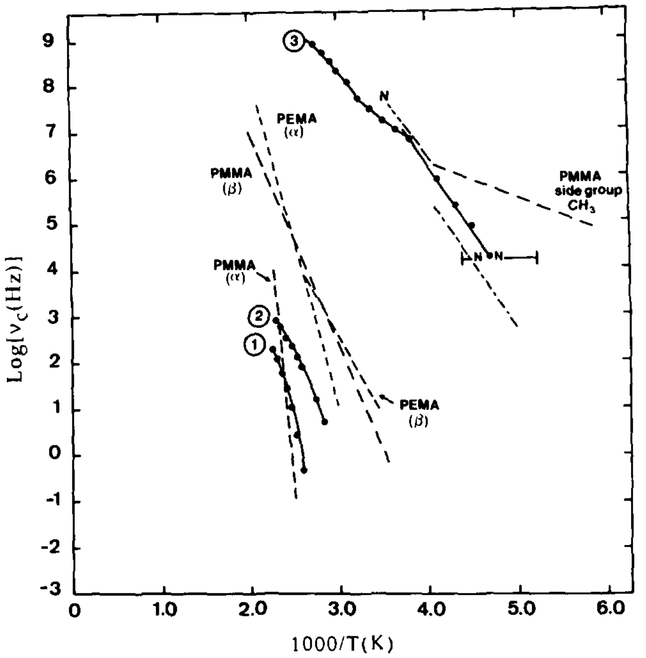

Figure 7 Transition map for dry PHEMA, S(0). Relaxation data for PMMA and PEMA are included for comparison. The dielectric data (●) equate f_m with ν_c. N denotes n.m.r. relaxation data from ref. 8. The loci 1–3 are discussed in the text. The chain line (-·-·-) denotes dielectric data taken from ref. 10

Transition maps

The transition map in *Figure 7* presents the available dielectric relaxation data for the dry polymer. N.m.r. results recorded earlier[8] are also included along with relaxation loci for the related polymers, poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA)[17]. The α-methyl group relaxation in PMMA and PEMA, which is dielectrically inactive, is omitted for clarity of presentation. Overall, the dielectric results correlate well with n.m.r. data, and three relaxation processes, labelled 1, 2, 3 in order of decreasing temperature, are clearly identified.

The map for the quenched hydrated polymer SQ(*W*) is rather more complex (*Figure 8*). In this case there are four *regions* of relaxation, labelled 1 to 4, where each region encompasses variations due to water content for the relaxation in question. The pattern of water behaviour over the heating cycle elucidated in n.m.r. and d.s.c. measurements[8] is portrayed schematically on the diagram as an aid to interpretation. That water is progressively driven off as the temperature is increased above room temperature, thus diminishing the effects of plasticization on relaxation, is borne out in the thermogravimetric (t.g.a.) data for saturated PHEMA shown in *Figure 9*. While the t.g.a. experiment does not precisely replicate sample conditions in the dielectric cell, the experiment does illustrate the ease with which water is driven off as the temperature is increased.

RELAXATION ASSIGNMENTS

Dry PHEMA

Prior assignments in dry PMMA and PEMA serve as a guide in analysing relaxation in PHEMA. The α relaxation in PMMA and PEMA is ascribed to the onset of general motions of the main chains, and it is reasonable to suppose that the dielectric peak at the highest temperatures (locus 1) is the corresponding α relaxation

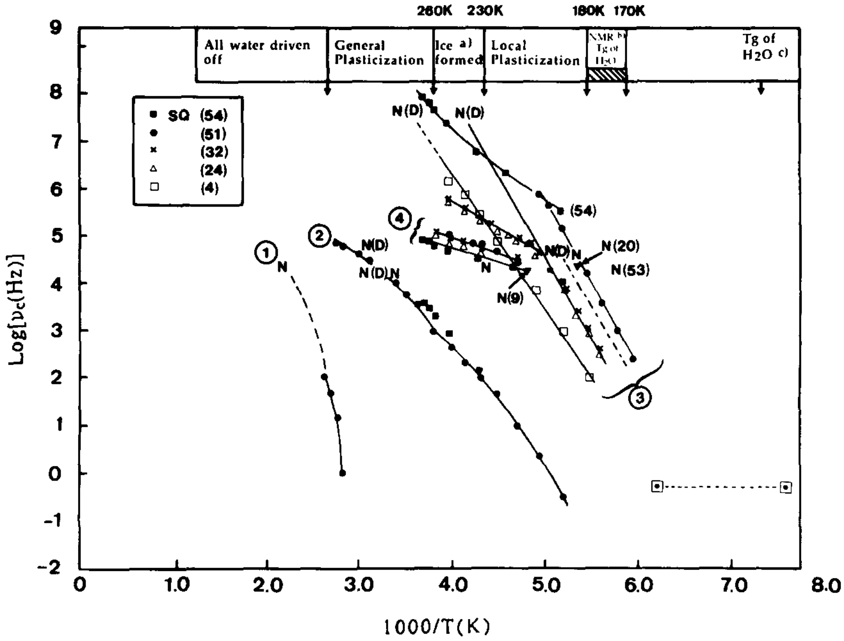

Figure 8 Transition map for hydrated PHEMA with different water contents. Again, the dielectric data points equate f_m with ν_c and N denotes n.m.r. relaxation data from ref. 8. N(D) are for PHEMA/D_2O systems. The dielectric transition temperatures (⊡---⊡) are taken from ref. 11. Water behaviour portrayed in the different temperature regimes along the top of the diagram is carried over from ref. 8: (a) ice formation on the heating cycle due to devitrification; (b) glass transition for tightly bound water at n.m.r. linewidth frequencies (10^4–10^5 Hz); (c) quasi-static glass transition for tightly bound water. Loci 1–4 are discussed in the text. The chain line (–·–·–) denotes dielectric data for PHEMA with 38.6 wt% water taken from ref. 10. In all cases, numbers in parentheses denote water content

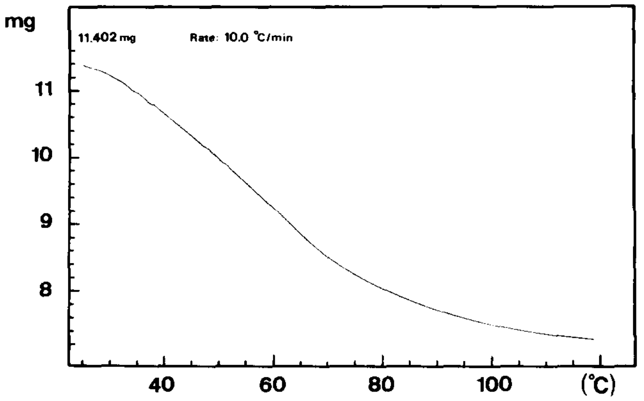

Figure 9 Thermogravimetric (t.g.a.) trace for a typical hydrated sample

in PHEMA. Assignment of the β relaxation to the motion of the complete side group also carries over to dry PHEMA (locus 2). As mentioned above, methyl group motion is dielectrically inactive and there is no corresponding analogue in the dielectric response of PHEMA. Note, however, that the relaxation assigned to side-chain methyl group motion in PMMA tends to merge with locus 3 for PHEMA at higher temperatures (*Figure 7*), indicating that the low-temperature relaxation in PHEMA is associated with the end-group of the ester side chain, that is, rotation of the terminal OH group, perhaps in consort with internal rotations of the polar groups around the C–O and O–C bonds of the polymer. This is termed the γ relaxation in PHEMA.

Hydrated PHEMA

Analysis of the data for the hydrated polymer is best approached through consideration of each relaxation in *Figure 8* in order of decreasing temperature.

Locus 1. To understand the source of this relaxation in the hydrated polymer, note that the bulk of the water is driven out of the sample at temperatures where these data appear. Reference to *Figure 7* confirms that this locus approaches the α transition for the dry polymer and it is so interpreted.

Locus 2. The relative dielectric strength and the shape of the peak for the truly hydrated material (peak 2) depends on temperature and thermal history. Typically, at 263 K, ε''_{max} for SQ(54) is 19.5 and occurs at 400 Hz (*Figure 3a*), whereas $\varepsilon''_{max}=2.7$ in SF(54) at comparable frequencies and temperatures (*Figure 5*). This peak is not well resolved in SPF(54). Note also that the frequency for which ε'' is maximum is two decades higher than for the corresponding peak in dry PHEMA at the same temperature. This locus clearly signifies the onset of general motions in the heavily hydrated and plasticized polymer, in keeping with its designation as the α relaxation. That the n.m.r. point N(D) corresponding to PHEMA plasticized with D_2O falls on locus 2 reinforces this viewpoint. It is also possible that the β relaxation assigned to motion of the ester side group in dry PHEMA merges with the α relaxation in the plasticized polymer.

In analysing the shape of locus 2, recall the various temperature regimes portrayed in *Figure 8*, which delineate different types of water behaviour in the polymer. A minor discontinuity in locus 2 coincides with the onset of ice formation (devitrification) of part of the water rendered mobile at ca. 170 K followed by a more

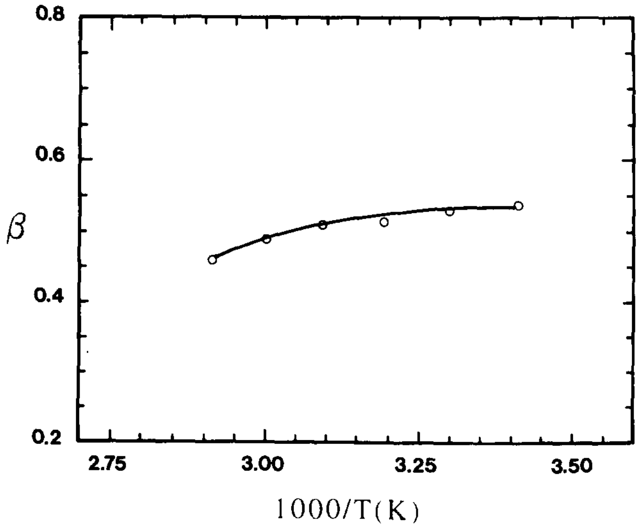

Figure 10 Dielectric distribution parameter β vs. $1000/T$ for locus 2

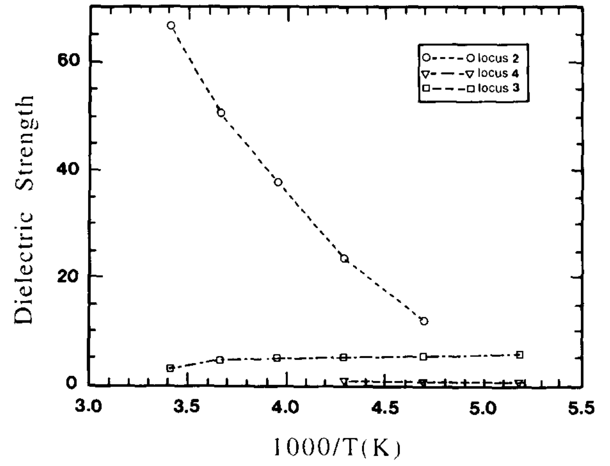

Figure 11 Dielectric strength vs. $1000/T$ for SQ(54) for loci 2–4 between 193 and 270 K

defined discontinuity at higher temperatures associated with the onset of bulk plasticization. A number of interesting observations can be drawn from the data:

(i) Below 260 K, the dielectric data monitor the onset of the α relaxation in the presence of ice and mobile water.

(ii) The activation energy (slope of the curve) in the region of devitrification (230–260 K) is less than the activation energy in the temperature regime below 230 K, indicating that the bound water that survives devitrification continues to be effective in plasticizing the polymer matrix as the temperature is increased.

(iii) The peak intensity in SQ(32) is a factor of 10 lower than for SQ(54) at the same temperature, indicating the prominent contribution of water to the relaxation process. As expected, the onset of bulk plasticization above 260 K is accompanied by a further progressive decrease in the activation energy.

(iv) Above 273 K, the half-width of the dielectric peak increases with increase of temperature (*Figure 6*) where, typically, at 293 K it is nearly twice the width of a Debye dielectric described by a single relaxation time. This is reflected in a gradual drop in the value of the dielectric distribution parameter with increasing temperature (*Figure 10*). The broad dielectric dispersion pinpoints significant structural and motional heterogeneity in hydrated PHEMA.

(v) The activation energy of ca. 30 kJ mol^{-1} in the high-temperature regime is 1.6 times higher than for free bulk water but is considerably lower than for the α relaxation of the dry polymer. This is again consistent with plasticization.

(vi) The strength of the dielectric peak for SQ(54) and SF(54) increases with increasing temperature, which is contrary to the expected behaviour for a dipolar system comprising a fixed number of non-interacting dipoles (*Figure 11*). Either the number density of dipoles increases or an immobile dipolar system becomes more mobile. The latter interpretation is again consistent with the enhanced effects of plasticization with increase in temperature.

(vii) In the high-temperature regime, the shape of the curve is defined by a number of factors: the usual increased vigour of motion with increase in temperature; the effects of bulk plasticization by water all of which is fully mobile at these temperatures; and the progressive removal of water out of the polymer matrix, which retards motion and heralds a progressive return to conditions prevailing in the dry polymer, ultimately leading to a resolved peak for dry PHEMA (locus 1). While the shape of the curve might also reflect Williams–Landel–Ferry (WLF) behaviour for a single process[18], a definitive assignment cannot be made in light of the factors listed above.

In summary, the prediction that locus 2 denotes the α relaxation in the truly hydrated polymer arising from the onset of general motions is confirmed. The significant shift of this relaxation to lower temperatures upon hydration precludes resolution of an analogous β relaxation in hydrated PHEMA.

Locus 3. The dielectric peaks described by locus 3 are observed in all samples irrespective of thermal history and water content. On the frequency scale for both hydrated and dry polymer, the ε'' peaks are almost three decades wider than predicted by the simple Debye model. The dielectric distribution parameter β for both cases is much less than unity, as shown in *Figure 12*, where, it is recalled, $\beta = 1$ corresponds to a single relaxation. The parameter β is found to vary from 0.14 to 0.35 and 0.42 to 0.60 for SQ(54) and S(0), respectively. The broader distribution of relaxation times in the hydrated system is a further indication that the presence of water has a

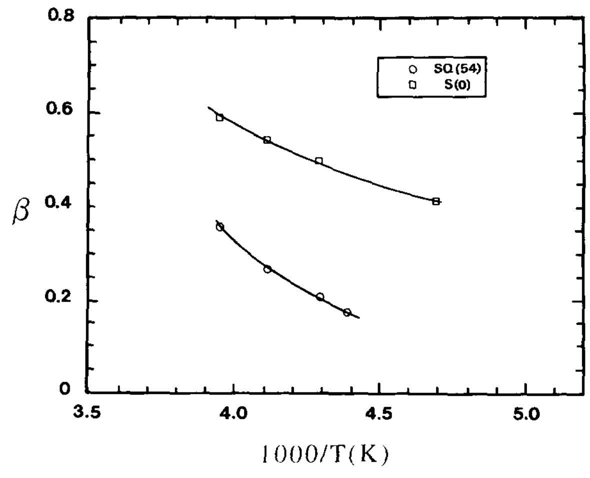

Figure 12 Dielectric distribution parameter β vs. $1000/T$ for locus 3 in SQ(54) and S(0)

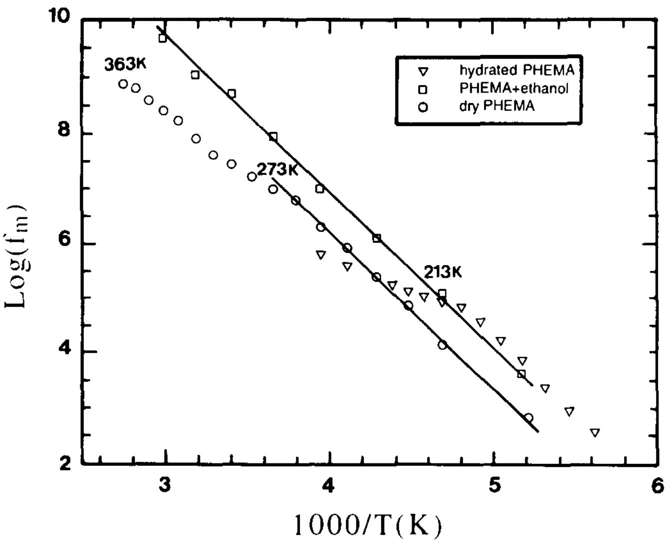

Figure 13 Log(f_m/Hz) vs. 1000/T for the γ relaxation peak (locus 3) for dry PHEMA, hydrated PHEMA SQ(32) and PHEMA with ethanol

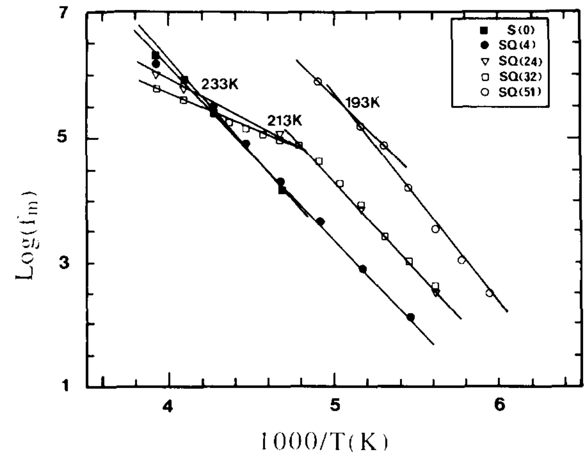

Figure 14 Log(f_m/Hz) vs. 1000/T for locus 3 in samples with different water contents. Note the dependence of the temperature at which devitrification begins to set in (the break in the locus) on water content

profound influence on the motion of polar groups in the side chain, arising in part from hydrogen bonding between the OH polar end-groups and bound water.

The complex interplay between bound water and the polymer, alluded to earlier, involves different modes of interaction. In an effort to clarify the effects of the low-temperature phase transition of the bound water, dielectric data for PHEMA saturated with ethanol are compared with results for the dry material and PHEMA saturated with water in *Figure 13*. Recall that the freezing point of ethanol is 156 K, which ensures that it is in the liquid phase over the entire temperature range of this study. A number of interesting conclusions can be drawn. First, the activation energies ΔH for the dry sample and PHEMA saturated with ethanol are of comparable magnitude although the two sets of data are shifted in frequency. Secondly, both ethanol and mobile water plasticize the polymer matrix. Thirdly, the curve for water-saturated PHEMA changes slope abruptly at ca. 213 K. For the dry polymer there is a slight change in slope at 273 K. The fact that a similar change in slope does not occur in the material saturated with ethanol clearly associates the change in slope with water behaviour. More specifically, reference to *Figure 14* shows that the temperature at which this abrupt change occurs depends on water content and is closely allied to the relaxation behaviour of the bound water itself as discussed in detail in the next section.

Regarding possible underlying mechanisms, consider the relative activation energies either side of the break in the curves. Typically, at lower temperatures ΔH is 59 kJ mol^{-1} for the dry PHEMA and 61 kJ mol^{-1} for SQ(32) below 213 K; above 213 K, ΔH for SQ(32) is 31 kJ mol^{-1}. A number of scenarios come to mind. At low temperatures, the higher activation energy may be due to hydrogen bonding of the ethoxy group to water molecules, in which case the relaxation process either involves reorientation of the fully hydrated moiety or requires the breaking of hydrogen bonds, reorientation of the polar group and re-forming of the hydrogen bonds again. Above the transition point where devitrification is prevalent, the fact that reorientation of the terminal polar group requires less energy implies that it is unlikely to be hydrogen-bonded to ice and rotates without constraint; alternatively, the OH group may be associated with the mobile phase of water that survives devitrification in a way that enhances end-group motion. Note that the low-temperature relaxation observed by Pathmanathan and Johari[10] is consistent with locus 3. The intimate relationship between localized end-group motion and water is explored further in the analysis of locus 4, the appearance of which coincides with the abrupt change in slope of locus 3.

Locus 4. The dielectric peak giving rise to locus 4, that is, the peak centred at approximately 10 kHz in *Figure 3a*, is observed in SQ(W) and SPF(W) but not in SF(W) samples. As noted above, the temperature at which the peak is first detected depends on the total water content W, typically 193 and 213 K for SQ(54) and SQ(32), respectively (*Figure 14*). The peak frequency, ε''_{max}, systematically decreases from quenched, to partially frozen and presumably frozen samples. Its absolute magnitude is a factor of 10 greater in SQ(54) compared to SPF(54). The fact that the dielectric strength of the peaks corresponding to locus 4 also increases with a decrease in temperature (*Figure 11*) can be explained by assuming that either the total number of dipoles or its low-frequency permittivity increases with a decrease in temperature. This is quite plausible in view of the suggestion made by Pathmanathan and Johari[10] that there is a change from a partial crystallization of supercooled water to the cubic form of ice in this temperature region. The devitrification that shows up in our earlier n.m.r. and d.s.c. measurements[8] surely reflects the same phenomenon.

The process is found to be Arrhenius with $\Delta H = 25$ kJ mol^{-1}, which is a factor of 2 lower than for known phases of ice (50 kJ mol^{-1}) but it is almost twice that calculated for normal bulk water (12.6 kJ mol^{-1}). Of course it is feasible that supercooled water and cubic ice coexist, albeit in different regions of the hydrogel. Recall too that the larger the amount of loosely bound water, the lower is the temperature for which the mobility and partial crystallization of a bound water component begins to set in. In summary, locus 4 can be unambiguously assigned to a phase transition of the water itself. It is equally certain that this water behaviour profoundly affects the γ relaxation in the hydrated polymer.

SUMMARY

As in many other host matrix systems, the role of water in PHEMA is exceedingly complex. This dielectric relaxation study on samples that have undergone different thermal histories reveals four relaxation processes in the hydrated polymer, the details of which are further clarified through a correlation of the extended range of dielectric data reported herein with the results of other relaxation experiments, notably n.m.r.

ACKNOWLEDGEMENTS

We thank Dr A. Kocot of the University of Katowice, Poland, for the help rendered in designing the two cryostats and the gas heater used in the temperature-control system. Dr F. Kremer of the Max Plank Institute for Polymer Science, Mainz, kindly provided access to the Solatron Schumberger 1254 frequency response analyser for dielectric measurements at very low frequencies. The research was carried out in cooperation with Bausch and Lomb (Ireland) under the Programme for Advanced Technology (PAT) funded by the Irish Government.

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