

The effect of water on the glass transition temperature of poly(methyl methacrylate)

L. S. A. Smith

Department of Applied Physical Sciences, Coventry Lanchester Polytechnic, Priory Street, Coventry CV1 5FB, UK

and V. Schmitz

Fachbereich 3 Chemieingenieurwesen, Fachhochschule Aachen, Kurbrunnenstrasse 22, 5100 Aachen, FRG

(Received 14 January 1988; accepted 11 April 1988)

Poly(methyl methacrylate) (PMMA) has been brought to equilibrium with water vapour of different activities at 23°C. The sorption isotherm was found to belong to the BET type III classification, confirming previous measurements. At saturation 1.92 g water per 100 g PMMA were sorbed. The glass transition temperature (T_g) was measured. It was depressed at saturation by about 20 K. The variation of T_g with water content was modelled best by the Kelley–Bueche equation, using appropriate constants. The Couchman–Karasz equations also fitted the data well provided a variable fraction, f , of sorbed water was taken to be active in depressing T_g . The data could be fitted to the form of the Fox equation, but with arbitrary constants.

Models of the structure of H₂O in PMMA were reviewed and the model used to interpret the isotherm (random solution followed by clustering) was contrasted with that used to interpret the variation of density with water content (dual-mode sorption in microvoids). Insofar as the equations describing the variation of T_g with composition have a structural content, it appears that our results support a simple random solution model best, although a dual-mode treatment of the Couchman–Karasz equations fared well.

A model involving hydrogen-bonded crosslinking of the PMMA chains by the H₂O molecules was discussed and found to have several points of contact with the dual-mode model.

(Keywords: water; poly(methyl methacrylate); glass transition; sorption; isotherm; density; structure)

INTRODUCTION

The influence of water on the thermal and mechanical properties of polymers has received considerable attention and the general interaction of water with polymers has been reviewed^{1–5}. The work to be described here is a development of earlier studies with poly(methyl methacrylate) (PMMA) and water⁶ in which those earlier ideas are somewhat modified in the light of new experimental results. Our interest is in the physical structure of the water sorbed in the polymer matrix and in the relationship between this and the thermal and mechanical properties of the mixture. Water and macromolecules interact in a wide variety of ways^{1–5,7}. A water molecule may be encompassed by a defining sphere of diameter about 3 Å, small enough to fit into typical microvoids or holes which comprise the structural free volume. Even highly hydrophobic polymers like polystyrene (PS) absorb small quantities of water⁸ and this affects their mechanical properties⁹. At this low level of sorption the results can be seriously affected by small quantities of impurities in the polymer structure¹⁰. Hydrophilic impurities are more effective than hydrophobic ones, and water-soluble impurities can give rise to osmotic flows with very damaging mechanical results^{10,11}. When the polymer backbone contains hydrophilic groups then the sorption of water is enhanced and may result, for example, in hydrogen bonding to

specific backbone sites detected by spectroscopic means¹². Such specific interactions result in exothermal sorption characterized by considerable rises in temperature, as is the case with cotton and wool. A sufficiently numerous population of strong hydrophilic groups tips the hydrophilic–hydrophobic balance and results in a water-soluble system in which water and polymer are miscible in all proportions^{4,5}.

Water can also form a separate phase. In the case of polyethylene¹³ and polystyrene^{4,15} and epoxy drum lacquers¹⁴ this is associated with a high-temperature aqueous treatment close to the melting point or glass transition temperature of the polymers. If water is more soluble in the polymer at high temperature the phase separation may result from the excess water being rejected from solution as the temperature falls. Some polymers, however, contain a structural group that is sensitive to chemical attack by water, and in these cases a high-temperature treatment with water will result in hydrolysis. In the case of polyesters^{16,17} and polyamides the chain degradation results in embrittlement and loss of strength. In PMMA the hydrolytically sensitive ester linkage is a side group and hydrolysis results in the formation of backbone mer units of methacrylic acid (without backbone chain scission) and also of methanol. Methanol is a well known plasticizer and swelling agent for this polymer^{18,19}. Methanol is also strongly hydrophilic and has the effect of greatly increasing the

apparent solubility of water in the polymer. Thus specimens of PMMA which have been boiled for a long time in water absorb water continuously without coming to equilibrium^{20,21} and on cooling to room temperature become hazy due to phase separation. Hydrolysis is thus a danger if high temperature is used to accelerate the approach to equilibrium of PMMA and H₂O. It is certainly significant at 80°C²² and probably so at 60°C^{6,22}. The effect of hydrolysis is thus to cast doubt on the significance of mechanical and thermal measurements made after a high-temperature pretreatment since the results are bound to be affected by the methanol. In this study we have deliberately brought our specimens to equilibrium with water vapour at room temperature in order to minimize the influence of hydrolysis.

Evidence for the structure of water dissolved in polymers comes from the interpretation of a variety of different experiments. Here we will only discuss measurements of the isotherm, glass transition and density. The relevant models will be briefly reviewed, and the published results for the PMMA/H₂O system will be surveyed. Some anomalies will appear when the results are seen as a whole and we will consider whether our results can resolve the difficulty revealed.

Sorption isotherm

Isotherm analysis^{1,2,23} depends strongly on structural models. A linear increase of the mass absorbed with the activity of the vapour (Henry's law) is not often found in polymer/water systems and is associated with very dilute solutions in which the dissolved water molecules are sufficiently few and far apart for the system to behave as if ideal, i.e. as if a simple random mixture. If the system were in fact ideal, Raoult's law would be obeyed, and water and polymer would be infinitely miscible.

An isotherm that is linear at low activities and curves upward more rapidly than predicted by Henry's law is a type III isotherm in the BET classification²⁴ and is sometimes called a Flory-Huggins isotherm²⁵⁻²⁸. Inherent in the Flory-Huggins statistics is the idea that at higher water contents there will be some clustering of the water molecules. Clustering was studied specifically by Zimm and Lundberg^{29,30}, who developed the cluster integral as a method of measurement of non-random mixing.

Whilst the PMMA/water system does not exhibit a dual-mode sorption isotherm, it is important to discuss the dual-mode here because it has been applied to PMMA/H₂O to explain changes in density with humidity. The dual-mode model considers sorption into microvoids, i.e. into the excess of free volume existing in the glass state³¹⁻³³. The sorption can be thought of as occurring in two stages, the results of which are added together. At low activities water molecules dissolve in the glass and are preferentially sorbed and arrested in the microvoid structure. The microvoids ultimately reach saturation. This stage is described by a Langmuir tight-binding model and a Langmuir isotherm equation. The shape at low activity is described as a 'toe'. Exposure to higher activities leads to further simple random solution, described by Henry's law. The isotherm is thus the sum of a Langmuir and a Henry's law isotherm. Support for this model of polymer/water interaction has come from many workers^{34,35}.

Other types of isotherm exist but they and their sorption models are not relevant to this discussion.

Glass transition temperature

The effect of a plasticizer is to lower the glass transition temperature of a polymer, and several equations have been proposed to describe this effect³⁶. In many cases the Fox equation³⁷, which is a simple empirical inverse rule of mixtures, describes the effect of water on the T_g of glassy polymers^{38,39}. This equation is given by:

$$T_g^{-1} = w_1 T_{g1}^{-1} + w_2 T_{g2}^{-1} \quad (1)$$

where T_g is the glass transition temperature of the mixture and $T_{g1,2}$ the value for the pure components; $w_{1,2}$ is the weight fraction of each component in the mixture.

A thermodynamic theory for the compositional dependence of T_g has been proposed by Couchman and Karasz⁴⁰⁻⁴². The model assumes that mixing entropy is continuous during the transition from glass to rubbery state. For polymer blends in which the T_g values of the components are not far apart, it is a reasonably good assumption that increments of heat capacity $\Delta C_p = C_p^l - C_p^g$, where l and g refer to liquid and glass state respectively, are independent of temperature. For such systems T_g is predicted by:

$$\ln T_g = \frac{w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \quad (2)$$

where $T_{g1,2}$ is the glass transition temperature of each component and $\Delta C_{p1,2}$ is the increment of the heat capacity at T_g of each component in the mixture. The theory was successfully applied to polymer blends^{41,42} and, somewhat modified, to the effects of plasticizer on the T_g of poly(vinyl chloride)⁴³.

For systems in which the T_g values of the components are well separated, as in PMMA/H₂O, it is not satisfactory to assume that the ΔC_p values are independent of temperature. Instead Ellis and Karasz⁴⁴ made the assumption that ΔC_p is inversely proportional to the temperature and found that this led to reasonable agreement between predicted and observed T_g values in the epoxy/H₂O system. With this assumption equation (2) becomes:

$$T_g = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \quad (3)$$

The Kelley-Bueche theory⁴⁵ for the compositional dependence of T_g makes two assumptions: first, that the free volume contributed by the diluent may be added to that of the polymer; secondly, that at T_g the system reaches a critical free volume fraction of 0.025. Small molecules such as water introduce relatively large amounts of free volume and thus depress T_g effectively. The Kelley-Bueche equation is:

$$T_g = \frac{\Delta \alpha T_{g2} \phi_2 + \alpha_1 T_{g1} \phi_1}{\Delta \alpha \phi_2 + \alpha_1 \phi_1} \quad (4)$$

Here $\phi_{1,2}$ is the volume fraction of diluent and polymer, respectively, α_1 is the coefficient of cubic expansion of the diluent and $\Delta \alpha$ the change in the coefficient of cubic expansion of the polymer at T_g (for which the WLF 'universal' value ($4.8 \times 10^{-4} \text{ K}^{-1}$) is often used). This equation has been applied to the epoxy/water system⁴⁶ and less rigorously by us to poly(ether sulphone)/water^{47,48} and PMMA/water⁶.

Published results for the PMMA/H₂O system

The PMMA/H₂O isotherm belongs to the BET type III class. Applying cluster analysis to the PMMA/water isotherm, Starkweather^{49,50} calculated average cluster sizes, finding that they increased as the humidity increased. Up to about 50% r.h. (or 0.9% (w/w) water content) he found the water molecules to be more or less randomly absorbed with possibly a slight tendency towards clustering. From this point on, first one and then a second water molecule form a bridge between two initially uncorrelated water molecules to give an average cluster size of four near saturation. In liquid water the average cluster size is about five. These clusters can be thought of as the precursors to the phase separation that occurs when the structure becomes saturated with water: they are the response which the polar water molecules make to their hydrophobic environment.

Thermodynamic analyses of how the solubility of H₂O in PMMA varies with temperature have produced some interesting results. Thomas⁵¹ used the BET sorption equation to calculate the entropy change during the sorption of water into PMMA. At low activity he found the entropy of sorption to be $-17.14 \text{ J mol}^{-1} \text{ K}^{-1}$, the negative sign indicating an increase in order due to sorption. Thomas noted that the entropy change from water to ice was $-21.95 \text{ J mol}^{-1} \text{ K}^{-1}$ and suggested that the molecules of sorbed vapour at low r.h. are in a state of order nearly but not quite the same as the molecules in ice. This therefore suggests that water molecules cluster together in an ice-like structure during the early stages of sorption.

Measurements of the PMMA/H₂O isotherm at different temperatures by Barrie and Machin^{52,53} enabled them to calculate the limiting Henry's law solubility coefficient as the vapour activity tended to zero. Using the van't Hoff equation they calculated ΔH_s° , the limiting heat of sorption for the transfer of 1 mol of water from the vapour phase into the polymer. They found ΔH_s° to be close to the latent heat of condensation of water (i.e. -44 kJ mol^{-1}) and suggested that this represented the heat of condensation of water into microvoids in the system. This is an early application of dual-mode ideas to the PMMA/H₂O system. We should note however that this interpretation is at variance with the isotherm model. The isotherm is consistent with the Flory-Huggins, Zimm and Lundberg models of random solution followed Zimm clustering rather than the dual-mode model associated with hole filling.

Dual-mode sorption, as we have seen, leads to an isotherm having a 'toe' shape at low activity and the PMMA/H₂O isotherm shows no sign of this. The thermodynamic results both suggest that the early stages of sorption are associated with condensed structures in which water-water interactions are significant. Molyneux¹ pointed out that water-water interactions were statistically unlikely in the regime where Henry's law was obeyed. He suggested that the limiting heat-of-sorption data of Barrie and Machin were consistent with a model in which one water molecule effectively crosslinked two polymer chains by forming a hydrogen bond to an oxygen moiety in each of two ester side groups. He suggested that 44 kJ mol^{-1} was a reasonable enthalpy change to be associated with the formation of two hydrogen bonds. Thus we have a further model to consider which involves hydrogen-bonded crosslinking of

the glass. The model is not inconsistent with the thermodynamic data and allows for the water molecules to be widely dispersed in the polymer matrix as required by Henry's law. All the evidence for it thus far comes from a study of the isotherm.

Density measurements of the PMMA/H₂O system^{27,54} have been interpreted along dual-mode lines^{22,55,56}, with sorption in the microvoids at low activities followed by random solution at high activities, in contrast to the isotherm analysis. Quantitative assessments of the sorption data for PMMA/H₂O have been made by Turner^{55,56}, who calculated the 'fraction of the total water uptake which is accommodated without any expansion of the sample in microvoids'. Turner calculated $(W_{w,t} - W_{w,0}) / (W_{a,t} - W_{a,0})$, where W_a and W_w are the weight of the sample in air and water respectively, and the subscripts 0 and t refer to time. It is possible to show that this fraction is $1 - [\Delta v_t / v(w)_t]$, where $v(w)_t$ is the volume of water that has been sorbed by the polymer at time t and Δv_t is the difference in volume between the dry polymer at $t=0$ and the volume of the solution at $t=t$; Δv_t may be positive (as in the case of PMMA/H₂O), zero or negative. In order to equate Turner's experimental result to the 'fraction of total water accommodated in microvoids' it is necessary further to assume that a fraction (absorbed in the microvoids) makes no contribution to the volume change and the remainder goes into (ideal) solution with conservation of volume. The model has frequently been used and the 'fraction accommodated in the microvoids' found to lie between 0.4 and 0.6. Turner applied a similar approach to values of the density of the PMMA/H₂O system as measured by Ender⁵⁴. He assumed a fraction f of the water contributes to an increase in volume (or $(1-f)$ is accommodated in the microvoids). Masi *et al.*⁵⁷ used a least-squares regression analysis to fit f to Ender's density data, finding f to vary from 0.2 to 0.6 as the water content varied from 0 to 2.5%. Their result thus agrees with Turner's. Masi pointed out that f is the partition coefficient for the water in the two modes of sorption and is constant with temperature but varies with pressure of the water vapour.

We have seen that in the early stages of sorption the linear isotherm is consistent with a dilute random solution model whereas the density measurements are best explained by hole filling, so it is reasonable to ask whether the model based on hydrogen-bonded crosslinking might reconcile these opposing views. Molyneux¹ proposed that one H₂O molecule should form two hydrogen bonds (thus linking two polymer chains to each other) in order to be consistent with the measured heat of solution. This imposes no particular stoichiometry on the system and the chance of successful crosslinking must be connected with the random chance of ester groups positioning themselves appropriately on neighbouring chains. Inasmuch as this is a random process, the H₂O molecules will be randomly distributed in the glass, as required in a system that obeys Henry's law. Now suppose that the crosslinking reaction removes some of the excess free volume associated with the small H₂O molecule, and also some associated with the freely rotating ester side group, and it is then feasible to propose that crosslinking would be associated with a reduction in total volume and an increase in density, as found in practice. Thus far the model appears to be helpful. If however we turn again to the isotherm and ask what influence the hydrogen bonding might be expected to

exert on the vapour pressure (or escaping tendency) of the H_2O molecules we must conclude that the H_2O molecules would be more tightly bound to the structure than if in free solution and that this 'negative deviation from Raoult's law' would suggest that the isotherm would form a 'toe' at low activities, as in the dual-mode model. In fact the H_2O molecules, acting as crosslinking agents, are not in free solution (although they may be widely separated from each other) and we should not expect Henry's law to be obeyed. The crosslinking model thus appears to be a particular case of dual-mode sorption where the crosslinking constitutes the 'Langmuir tight-binding process'—rather than sorption into microvoids—and saturation occurs when the available crosslinking sites are all occupied. As such we would expect this model to agree with the density results rather than those of the sorption isotherm.

It was in the hope of throwing some light on this situation that we carried out measurements of T_g of the PMMA/ H_2O system at different water contents. We hoped to make some progress along these lines in spite of the absence of specific structural details from the theories governing the influence of diluents upon T_g .

EXPERIMENTAL

Specimen preparation

All specimens were made from commercial-grade PMMA sheets ('Perspex', ICI Ltd) of nominal thickness 1 mm, and were machined with the protective paper in place. The discs used for d.s.c. measurement were cut with a diameter of about 2.5 mm and had a mass of approximately 15 mg. The specimens used for water absorption measurements were stripped of protective paper, gently washed with hot soapy water, washed in distilled water and polished using a soft cloth. From this point forward the specimen surfaces were not touched by hand.

After cleaning, the specimens for mechanical testing were dried at 60°C under vacuum of about 1 mmHg until their mass no longer decreased. This took about 1 week. Then the specimens were normalized by heating to 140°C (i.e. above T_g) to remove all locked-in polymerization, casting and machining strains. The normalizing programme followed a formula laid down by the manufacturer. During normalizing there was an increase in thickness of about 3.5% and a decrease of length and width of 1.5–2.5%. The specimens were now clean, dry and relaxed of locked-in stress and the glass structure should have been close to its equilibrium state.

Measurements

The measurements of water absorption were made at $23 \pm 1^\circ\text{C}$. Specimens were stored in different sealed containers at various humidities until they reached sorption equilibrium. Sorption was followed by weighing dummy specimens periodically. Equilibrium of 1 mm thick specimens was reached in 6–7 weeks. The humid atmospheres were produced using saturated salt solutions. The thickness of the solution layer above the salt was 2–4 mm. The humidity was checked with a Vaisala HMP14 humidity probe and found to agree with the published values within $\pm 3\%$ r.h.: the experimentally measured humidity was the one used in subsequent calculations.

After reaching equilibrium, the dummy specimens were dried under vacuum at 60°C to determine their weight loss and water content (in g/100 g dry polymer) in order to construct the sorption isotherm.

Glass transition temperatures were measured using a Perkin-Elmer DSC-1B. The specimens were sealed in volatile sample pans against vapour loss and then heated at 64 K min^{-1} (sensitivity 8 mcal s^{-1}). This high rate of heating gave the best instrumental response, the most reproducible results and reduced to a minimum the amount of water evaporated from the sample into the empty space of the sample pan when the temperature was raised above the boiling point of water. Samples were normally scanned in the range $20\text{--}150^\circ\text{C}$, but a number of samples were chilled to -80°C using a liquid-nitrogen cryostat and scanned to $+100^\circ\text{C}$.

RESULTS AND DISCUSSION

Isotherm

Figure 1 shows our sorption results plotted as an isotherm at $23 \pm 1^\circ\text{C}$. The same figure shows the isotherm published by Kawasaki and Sekita²⁷, which they found to be independent of temperature in the range $25\text{--}49.5^\circ\text{C}$. Both isotherms are very similar and have the BET type III shape: there appears to be no suggestion of the 'toe' at low humidities which is characteristic of the dual-mode isotherm. Our results are almost identical to Kawasaki's up to about 60% r.h., and thereafter our isotherm curves upwards less strongly and reaches 1.92% (w/w) at saturation. This saturation concentration is in the mid-range of values reported in the literature (from about 1.6%⁵⁸ to 2.2%⁵⁹). The initial linear portion of the isotherm extends to about 35% r.h. and from this we can obtain the limiting Henry's law gradient (0.0115% (w/w)/% r.h.). As we have mentioned previously, this type of isotherm is modelled by a process in which simple random solution at low activities is followed by clustering (up to about four H_2O molecules per cluster) at high activities.

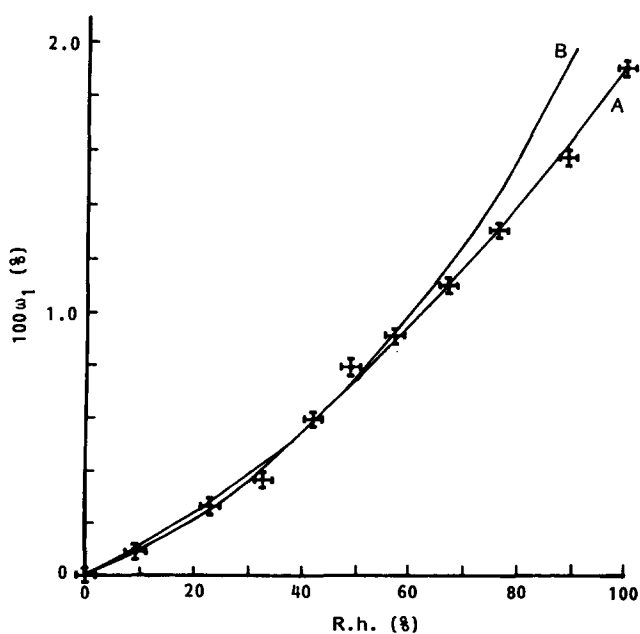


Figure 1 The sorption isotherm of H_2O in PMMA: A, experimental measurements at $23 \pm 1^\circ\text{C}$; B, result due to Kawasaki and Sekita²⁷

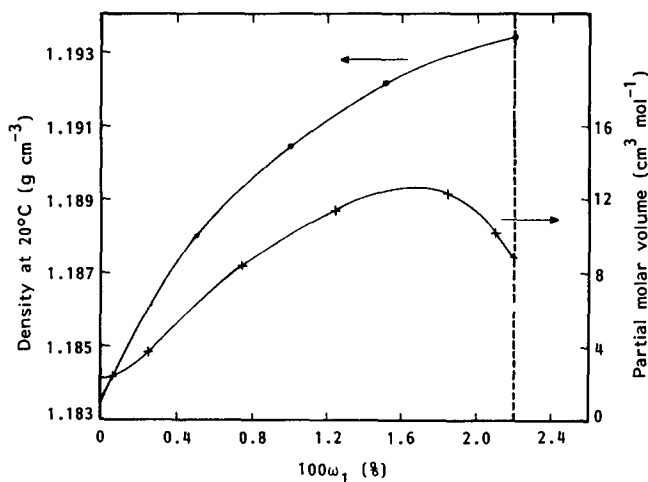


Figure 2 The variation of the density of PMMA/H₂O mixtures with water uptake (l.h. scale; data taken from Ender⁵⁴; and the partial molar volume of H₂O dissolved in PMMA²²) (r.h. scale; based on Ender's measurements)

For the crosslinking model we should consider the stoichiometry of the reaction proposed. This can be predicted from the molar mass of the chain repeat unit C₅H₈O₂ ($M = 100.1178 \text{ g mol}^{-1}$) and of H₂O ($M = 18.0154 \text{ g mol}^{-1}$) respectively. In the mixture let x chain repeat units be associated with one molecule of H₂O when the water uptake is $w_1/\%$ (w/w). Then $w_1 = 17.994/x$. Thus if two backbone mer units are to be associated with one crosslinking H₂O molecule, the predicted water uptake when the crosslinking reaction is complete would be $w_1 = 8.997\%$, roughly 4–6 times the experimental value. In practice, the published range of measured values for w_1 at saturation is 1.6–2.2% for which x varies from 8 to 12. We found $w_1 = 1.92\%$ at saturation so that each H₂O molecule is associated with 9.37 backbone mer units. If crosslinking occurs then only about one site in five is active. The reason why every ester side group is not involved in hydrogen-bonded crosslinking must lie in the details of the random chain conformations. The isotherm approximates to Henry's law up to $w_1 \sim 0.4\%$, at which point one H₂O molecule is present for about 45 backbone mer units. Similar results have been given by Thomas⁵¹.

Density: partial molar volume

The partial molar volume of H₂O ($\bar{v}(\text{H}_2\text{O})$) in solution may be defined by:

$$\bar{v}(\text{H}_2\text{O}) = (\delta v / \delta n_1)_{n_2, T, P}$$

where n_1 is the number of moles of H₂O in solution. The density data of Ender⁵⁴ are plotted in Figure 2 together with the partial molar volume calculated from them²². Ender found the density of dry PMMA to be 1.1835 g cm^{-3} at 20°C, rising to 1.1939 g cm^{-3} when 2.185% H₂O had been sorbed at saturation. This process involves an increase in volume of 1.36%. If volumes were additive the final volume would be almost twice as large, namely 2.66%. Reference to Figure 2 shows that the partial molar volume of H₂O is very small (about 2–3 cm³ mol⁻¹) during the first 10% of the water uptake and in this range the density rises almost as if the water made no contribution to the total volume. This was first pointed out by Kawasaki and Sekita²⁷. With increasing

sorption $\bar{v}(\text{H}_2\text{O})$ rises to a maximum of about $12 \text{ cm}^3 \text{ mol}^{-1}$. If the water actually occupied the free volume in the glassy matrix without any expansion of volume, then $\bar{v}(\text{H}_2\text{O})$ would be zero. In liquid water at 25°C a mole of H₂O occupies about 18 cm^3 , so that at no stage of sorption is the structure of the solution expanding as much as demanded by ideal mixing. It seems reasonable to suggest that sorption in microvoids would be accompanied by an increase in configurational order and a decrease in entropy, and similarly the action of crosslinking the chains via hydrogen bonding to the ester side groups would certainly result in an increase in configurational order. Hence at this stage we can summarize the position as follows:

(a) Isotherm analysis suggests a process in which monomeric water dissolves in PMMA at low activities and forms clusters at higher activities.

(b) Density analysis and the calculation of $\bar{v}(\text{H}_2\text{O})$ in Figure 2 are consistent with two models, which are inconsistent with the isotherm analysis:

- a conventional dual-mode sorption, first into microvoids then into simple solution at higher activities;
- a crosslinking reaction in which one H₂O molecule links together ester sidegroups in neighbouring chains, the stoichiometry being controlled in some way so that most of the reaction is completed in the early stages of sorption.

Glass transition temperature

We carried out calorimetric measurements in the hope that we would throw more light on this problem. A number of fully saturated samples were scanned in the d.s.c. from -80 to $+100^\circ\text{C}$. No freezing exotherm was observed on cooling and no melting endotherm observed on heating through the ice point. In the case of a phase-separated mixture of H₂O in polystyrene¹⁵ the water froze at about 220 K and melted at $273 \pm 2 \text{ K}$. Our results therefore show that no phase-separated water was present in our specimens and supports our contention that in carrying out the sorption at 23°C we have avoided any significant hydrolysis of the ester side group. Side-group hydrolysis leads to the formation of methanol and is associated with phase separation and optical haze⁶.

Each value of T_g is the mean of three measurements. For the dry specimens of PMMA we found $T_g = 393.5 \text{ K}$ and for the water-saturated specimens $T_g = 373.7 \text{ K}$. This drop of about 20 K is about 5%. In earlier measurements²² on PMMA we obtained $T_g(\text{dry}) = 380 \text{ K}$ and $T_g(\text{wet}) = 367 \text{ K}$, a drop of about 13 K and 3%. In those earlier measurements, however, the PMMA had not been normalized before sorption, and more significantly a much slower heating rate was used (5 K min^{-1}) so that both results are compatible. Our results for the variation in T_g with water content are shown in Figure 3, together with their estimated experimental uncertainties.

When treated according to the Fox equation (equation (1)) Figure 4 is obtained. Here the reciprocal of the experimentally determined T_g (from Figure 3) is plotted against the uptake, w_1 . The straight line is a least-squares fit to the data ($r = 0.9958$) with gradient $7.08 \times 10^{-3} \text{ K}^{-1}$. If we recast equation (1) in the form:

$$T_g^{-1} = (T_{g1}^{-1} - T_{g2}^{-1})w_1 + T_{g2}^{-1} \quad (5)$$

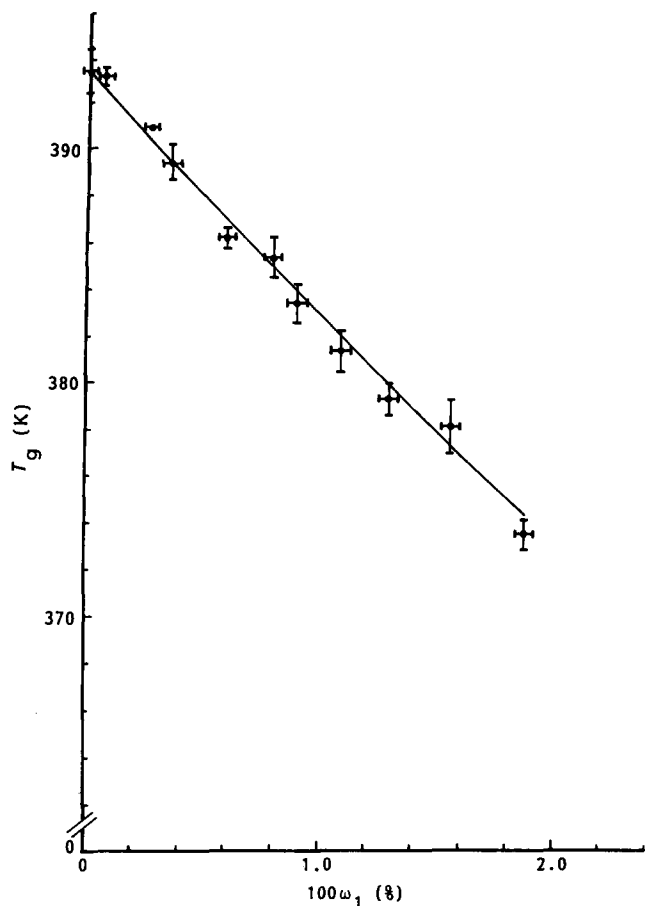


Figure 3 The variation of the T_g of PMMA/H₂O mixtures with water uptake (measured at d.s.c. scan rate of 64 K min⁻¹); full curve shows results predicted by equation (4) using $\alpha_1(\text{H}_2\text{O}; 110^\circ\text{C}) = 8.4 \times 10^{-4} \text{ K}^{-1}$ and $\Delta\alpha(\text{PMMA}) = 2.45 \times 10^{-4} \text{ K}^{-1}$

we can calculate the expected gradient of Figure 4. Taking $T_{g1} = 135 \text{ K}$ for water⁶⁰ and for dry PMMA our experimental value, $T_{g2} = 393.5 \text{ K}$, then the expected gradient is $(T_{g1}^{-1} - T_{g2}^{-1}) = 4.87 \times 10^{-3} \text{ K}^{-1}$. The gradient of Figure 4 is thus some 45% larger than expected and the Fox equation does not sufficiently estimate the experimentally measured reduction of T_g due to sorption. If we wish to make the equation fit our results we must take an unacceptable value for the glass transition of H₂O, namely, $T_g = 104 \text{ K}$, some 31 K below its measured value. Thus although equation (5) has the right form, it does not predict the correct gradient and as it does not represent any particular model, there seems to be no way of improving on this position.

In an earlier publication⁶¹ we have compared our results with the logarithmic form of the Couchman-Karasz equation (equation (2)) appropriate to polymer blends. There, one of us showed that with reasonable values of C_{p1} (for H₂O) and C_{p2} (for PMMA), the equation considerably overestimates the fall of T_g with water uptake. However, because equation (2) overestimates the reduction of T_g , the application of 'dual-mode' concepts (in which only a fraction, f , of the water is active in affecting T_g), can be used to fit data. Following Turner⁵⁵ we took $f = 0.5$ so that in equation (2) we used $w_1 = w_1(\text{exp})/2$ (where $w_1(\text{exp})$ is the experimental water uptake) and $w_2 = (1 - w_1)$. With these data we found a good fit to the experimental results. Even so, equation (2) consistently overestimated the reduction

of T_g by an average of 1.4 K per measurement point. We now develop Turner's suggestion, as modified by Masi *et al.*⁵⁷, and propose the use of f as a variable partition coefficient for use with the second of the Couchman-Karasz equations, which is more appropriate to small-molecule mixtures, i.e. equation (3). If f is the fraction of water that is active in reducing T_g , then equation (3) may be written:

$$T_g = \frac{fw_1\Delta C_{p1}T_{g1} + w_2\Delta C_{p2}T_{g2}}{fw_1\Delta C_{p1} + w_2\Delta C_{p2}} \quad (6)$$

and we may obtain f as the subject of this equation as follows:

$$f = \frac{w_2\Delta C_{p2}(T_{g2} - T_g)}{w_1\Delta C_{p1}(T_g - T_{g1})} \quad (7)$$

In equation (7) we put for H₂O, $\Delta C_{p1} = 1.94 \text{ J g}^{-1} \text{ K}^{-1}$ (ref. 44) and for PMMA, $\Delta C_{p2} = 0.318 \text{ J g}^{-1} \text{ K}^{-1}$ (ref. 62), and (as earlier) $T_{g1} = 135 \text{ K}$, $T_{g2} = 393.5 \text{ K}$. Figure 5 shows how the fraction $(1 - f)$ varies with water uptake: $(1 - f)$ is the fraction referred to by Turner⁵⁵ and by Masi *et al.*⁵⁷ as 'sorbed in the microvoids'. The value of $(1 - f)$

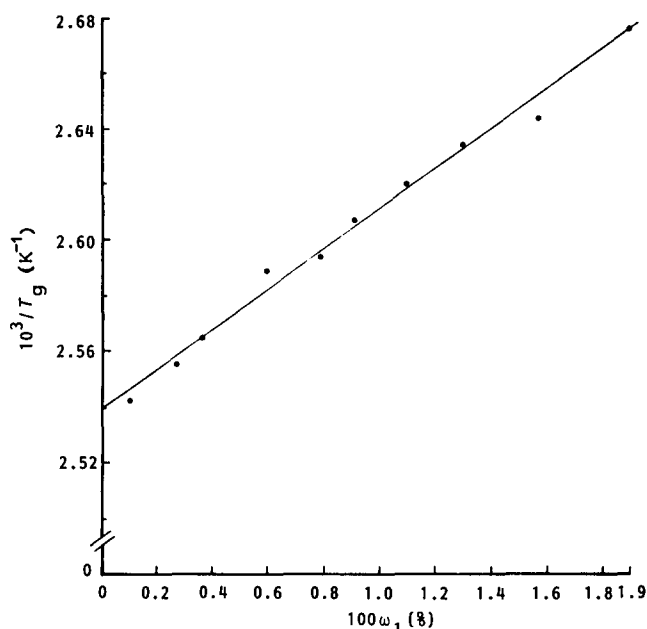


Figure 4 The variation of the reciprocal of T_g of PMMA/H₂O mixtures with water uptake, plotted according to equation (5), the Fox equation; full line shows least-squares fit to the data, with gradient = $7.08 \times 10^{-3} \text{ K}^{-1}$

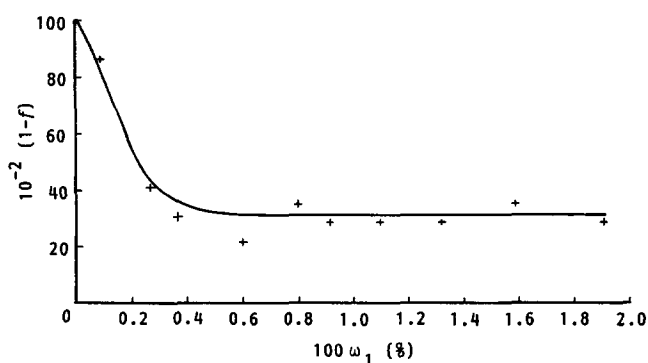


Figure 5 The fraction of water $(1 - f)$ that is inactive in affecting T_g as it varies with water uptake according to equation (7)

falls sharply from about 0.8 to about 0.3 at 0.4% water uptake and then stays roughly constant. The curve flattens at a water uptake which corresponds to an equilibrium r.h. (Figure 1) of about 35% or the end of the Henry's law process. In fitting the fraction f to the density versus water uptake measurements of Ender⁵⁴, Masi *et al.*⁵⁷ calculated that $(1 - f)$ varied from 0.8 to 0.4, results which are consistent with our treatment of T_g given here. In summary, then, our work with the two Couchman-Karasz equations has made use of the idea that only a fraction of the water uptake is active in diminishing T_g and it has been possible to do this in practice because both of the unmodified equations overestimate the reduction in T_g . To this extent, this part of the work supports the dual-mode sorption theories, and yields results for f which agree with those of other workers based on density measurements^{49,55}.

The Kelley-Bueche⁴⁵ equation (4) assumes that the free volumes of polymer and diluent are additive and that the glass transition is an iso-free-volume process. To fit the equation we must choose two constants: α_1 , the coefficient of thermal expansion of the diluent, and $\Delta\alpha$, the increment of the expansion coefficient of the polymer at T_g . For lack of detailed knowledge of the latter the WLF 'universal' value ($4.8 \times 10^{-4} \text{ K}^{-1}$) is often used. Earlier we took this course⁶¹ and chose $\alpha_1 = 2.1 \times 10^{-4} \text{ K}^{-1}$, the coefficient of expansion of water at 23°C. With these constants, equation (4) seriously underestimated the fall in T_g due to sorption of water, predicting $T_g = 391 \text{ K}$ at saturation, only 2.5 K below T_g for the dry PMMA, whereas experiment showed a fall of 20 K. In the event of equation (4) underestimating the depression of T_g it was clear that considering only a fraction of the dissolved water to contribute free volume at T_g (i.e. to use a dual-mode model) was not going to help fit the data. Such an assumption would result in an even smaller predicted fall in T_g . We then considered that the value of $\alpha(\text{H}_2\text{O})$ increases considerably as the temperature rises, and that the appropriate value would be one taken at the experimental T_g of the PMMA/ H_2O system. We therefore extrapolated published values of $\alpha(\text{H}_2\text{O})$ ⁶³ to predict a value of $\alpha(\text{H}_2\text{O})$ at 383 K (i.e. above the normal boiling point of H_2O , and the mean of the measured T_g values). We chose $\alpha(\text{H}_2\text{O})$ at 383 K = $8.4 \times 10^{-4} \text{ K}^{-1}$, four times larger than the room-temperature value. We also abandoned the 'universal' value of $\Delta\alpha$ ($4.8 \times 10^{-4} \text{ K}^{-1}$) in favour of a specific value obtained from dilatometric measurements by Rogers and Mandelkern⁶⁴. They measured the T_g of their sample to be 378 K and for the change in α at T_g they obtained $\Delta\alpha = 2.45 \times 10^{-4} \text{ K}^{-1}$, or about half the 'universal' value. The use of these more realistic constants in equation (4) gave an excellent fit to the data. The results of this calculation are compared with the experimental results and plotted as a full curve in Figure 3, where the correspondence is seen to be very good and the mean difference between experimental and calculated results is $\pm 0.52 \text{ K}$ per measurement point. We arrived at this result by a process of using reasonable values of $\alpha(\text{H}_2\text{O})$ and $\Delta\alpha(\text{PMMA})$ which were appropriate to the changes taking place at T_g . The result showed that a free-volume theory could account for the depression of the T_g of PMMA due to water sorption.

As we have previously stated, the theories governing the influence of diluents upon T_g do not have explicitly structural components. Perhaps their authors assumed

that mixing would be random and that T_g would be more significantly affected by other factors, such as free volume or entropy, and the indefinite concepts of 'order' associated with them. The use by Masi of the partition factor, f , in modelling the density measurements is based on the physical picture of a water molecule occupying a pre-existing hole and thus being sorbed without increase in the total volume. Our use of f with the Couchman-Karasz equation does not lead to any simple picture like this. We regard f as a curve-fitting parameter only, although the similarity in the magnitude of f obtained from T_g and density measurements is suggestive.

The Kelley-Bueche treatment is similarly silent about structure but the fact that the free volumes of polymer and diluent are simply added together, with no allowance for excess volume, suggests that random mixing is probably appropriate. If this is the case, then the satisfactory agreement between the equation and our measurements leads us to a fourth contending model for the structure of H_2O in PMMA, namely a simple random solution. Insofar as random solution is used to explain the isotherm shape at low activities, these results support that model rather than the dual-mode model.

Finally we consider how the crosslinking hypothesis might be applied to the glass transition. If this model describes the progressive saturation of available crosslinking sites followed by random solution which ultimately ends in phase separation, then its important feature is the loss of free volume consequent upon the rise in the 'effective molar mass' of the chains. Theories for the effect of molar mass on T_g have been published by Fox and Flory⁶⁵ and by Couchman⁶⁶ and predict that T_g rises as molar mass increases. If crosslinking were all that occurred on sorption, we would expect an increase in T_g , rather than a decrease. If a portion of the water is also going into solution, however, this would cause T_g to fall, and the net result would depend upon the balance of these two processes. Again it seems that a partition factor might be used to model the process. We suggest therefore that the crosslinking model would predict results parallel to our partition function treatment of the Couchman-Karasz equation and that this would benefit from being tested more quantitatively.

CONCLUSIONS

The model that has been used to understand the effect of humidity on the solubility of H_2O in PMMA is in conflict with that used to understand the corresponding volume and density changes. Measurements of the variation of T_g with water content have shown the following:

(1) A linear inverse mixing rule is followed but with a gradient substantially different from that of the Fox equation.

(2) The Couchman-Karasz equations overestimate the effect of diluent on T_g but use of the variable partition factor f fits the data, yielding values of f that are similar to those derived from a parallel treatment of the density measurements. This is a type of dual-mode model.

(3) If reasonable values of the constants are taken which describe the system at T_g , the Kelley-Bueche equation fits the data best of all. The structural implications of this are uncertain but it is suggested that a random solution structure is implied. This is a model that fits neither the isotherm nor the density measurements.

A model in which H₂O acts in part as a hydrogen-bonded crosslinking agent is discussed qualitatively and it is suggested that this would predict results similar to those given by the dual-mode model.

ACKNOWLEDGEMENTS

We would like to acknowledge many valuable discussions with Professor J. A. Sauer and Professor O. Lorenz.

REFERENCES

- 1 Molyneux, P. in 'Water: A Comprehensive Treatise', (Ed. F. Franks), Plenum, New York, 1975, Vol. 4, Ch. 7
- 2 Barrie, J. A. in 'Diffusion in Polymers', (Eds. J. Crank and G. S. Park), Academic Press, New York, 1968, Ch. 8
- 3 Rowland, S. P. (Ed.) 'Water in Polymers', ACS Symp. Ser. 127, American Chemical Society, Washington DC, 1980
- 4 Molyneux, P. 'Water Soluble Synthetic Polymers', CRC Press, Boca Raton, FL, 1983, Vols. 1 and 2
- 5 Finch, C. A. (Ed.) 'Chemistry and Technology of Water Soluble Polymers', Plenum, New York, 1983
- 6 Smith, L. S. A. and Sauer, J. A. *Plast. Rubber Proc. Appl.* 1986, 6(1), 57-65
- 7 Sauer, J. A. and Smith, L. S. A. *Trans. Inst. Marine Eng. (C)* 1985, 97 (Conf. No. 2), 95-102
- 8 Day, A. G. *Trans. Faraday Soc.* 1963, 59(485), 1218-24
- 9 Smith, L. S. A., Chen, C. C. and Sauer, J. A. *Polymer* 1982, 23, 1540-3
- 10 Muniandy, K. and Thomas, A. G. *Trans. Inst. Marine Eng. (C)* 1985, 97 (Conf. No. 2), 87-94
- 11 Ghotra, J. S. and Pritchard, G. *Trans. Inst. Marine Eng. (C)* 1985, 97 (Conf. No. 2), 15-22
- 12 Toprak, C., Agar, J. and Falk, M. J. *Chem. Soc., Faraday Trans. I* 1979, 75, 803
- 13 Bair, H. G. and Johnson, G. E. *Anal. Calorim.* 1977, 4, 219
- 14 Pogany, G. A. *Polymer* 1976, 17, 690-4
- 15 Smith, L. S. A. *Polymer* 1981, 22, 822-8
- 16 Gardner, R. J. and Martin, J. R. *J. Appl. Polym. Sci.* 1979, 24, 1269
- 17 Long, T. S. and Sokal, R. J. *Polym. Eng. Sci.* 1974, 14(12), 817-22
- 18 Andrews, E. H., Levy, G. M. and Willis, J. J. *Mater. Sci.* 1973, 8, 1000
- 19 Thomas, N. L. and Windle, A. H. *Polymer* 1981, 22, 627-39
- 20 Sweeney, W. T., Brauer, G. M. and Schoonover, I. C. *J. Dental Res.* 1955, 34, 306-12
- 21 Brauer, G. M. and Sweeney, W. T. *Mod. Plast.* 1955, 32, 138
- 22 Smith, L. S. A. *PhD Dissertation CNAA*, 1977
- 23 Brunauer, S. 'The Adsorption of Gases and Vapours', Vol. 1, 'Physical Absorption', Oxford University Press, Oxford, 1945
- 24 Brunauer, S., Emmett, P. H. and Teller, E. *J. Am. Chem. Soc.* 1938, 60, 309-19
- 25 Brown, G. L. in 'Water in Polymers', ACS Symp. Ser. 127 (Ed. S. P. Rowland), American Chemical Society, Washington DC, 1980, p. 441
- 26 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953, pp. 512-14
- 27 Kawasaki, K. and Sekita, Y. *J. Appl. Phys. Japan* 1957, 26, 678-80
- 28 Bueche, F. J. *Polym. Sci.* 1954, 14, 414
- 29 Zimm, B. H. *J. Chem. Phys.* 1953, 21, 934
- 30 Zimm, B. H. and Lundberg, J. L. *J. Phys. Chem.* 1956, 60, 425
- 31 Meares, P. *Trans. Faraday Soc.* 1958, 54, 40
- 32 Michaels, A. S., Vieth, W. R. and Barrie, J. A. *J. Appl. Phys.* 1963, 34, 1 and 13
- 33 Barrer, R. M., Barrie, J. A. and Slater, J. J. *Polym. Sci.* 1957, 23, 315-29
- 34 Chan, A. H. and Paul, D. R. *Polym. Eng. Sci.* 1980, 20, 87
- 35 Ranade, G., Stannett, V. and Koros, W. J. *J. Appl. Polym. Sci.* 1980, 25, 2179
- 36 Pezzin, G. Conf. 6th Conv. Ital. Sci. Macromol. (ATTI), 1983, Vol. 1, pp. 27-40
- 37 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, 1, 123
- 38 Sauer, J. A. and Smith, L. S. A. Conf. Macromolecules '86, R. Soc. Chem., Oxford, Sept. 1986, p. 144
- 39 Sauer, J. A. and Smith, L. S. A. 5th Int. Conf. Polymers in Medicine and Surgery, PRI and Biol. Eng. Soc., Leeuwenhorst, Holland, Sept. 1986, p. 9/1
- 40 Couchman, P. R. and Karasz, F. E. A. *Macromolecules* 1978, 11, 117-19
- 41 Couchman, P. R. *Macromolecules* 1978, 11, 1156
- 42 Couchman, P. R. *Polym. Eng. Sci.* 1984, 24, 135-43
- 43 Fried, J. R., Lai, S. Y., Kleiner, L. W. and Wheeler, M. E. *J. Appl. Polym. Sci.* 1982, 27, 2869-83
- 44 Ellis, T. S. and Karasz, F. E. A. *Polymer* 1984, 25, 664-9
- 45 Kelley, F. N. and Bueche, F. J. *Polym. Sci.* 1961, 50, 549-56
- 46 Browning, C. E. *Polym. Eng. Sci.* 1978, 18, 16
- 47 Cole, E. *PhD Dissertation CNAA*, 1985
- 48 Cole, E. and Smith, L. S. A. *Trans. Inst. Marine Eng. (C)* 1985, 97 (Conf. No. 2), 149-55
- 49 Starkweather, H. W. *Polym. Lett.* 1963, 1, 133-8
- 50 Starkweather, H. W. *Macromolecules* 1975, 8, 476-9
- 51 Thomas, A. M. *J. Appl. Chem.* 1951, 1, 141-58
- 52 Barrie, J. A. and Machin, D. *Trans. Faraday Soc.* 1971, 67, 244-56
- 53 Barrie, J. A. and Machin, D. *Trans. Faraday Soc.* 1971, 67, 2970-8
- 54 Ender, R. H. *DSc Dissertation MIT*, 1967
- 55 Turner, D. T. *Polymer* 1982, 23, 197-202
- 56 La Barre, E. E. and Turner, D. T. *J. Polym. Sci., Phys. Edn.* 1982, 20, 557-60
- 57 Masi, P., Nicodemo, L., Migliaresi, C. and Nicolais, L. *Polym. Commun.* 1984, 25, 331-3
- 58 Soderholm, K. J. and Calvert, P. D. *J. Mater. Sci.* 1983, 18, 2957-62
- 59 Moore, R. J. and Flick, J. R. in 'Water in Polymers', ACS Symp. Ser. 127, American Chemical Society, Washington DC, 1980, pp. 555-69
- 60 Kambour, R. P., Gruner, C. L. and Romagosa, E. E. *J. Polym. Sci., Polym. Phys. Edn.* 1973, 11, 1879-90
- 61 Schmitz, V. Diplomarbeit, Fachhochschule, Aachen, W. Germany, 1985
- 62 Naito, K., Johnson, G. E., Allara, D. L. and Kwei, T. K. *Macromolecules* 1978, 11, 1260-5
- 63 Nuffield Chemistry, 'Book of Data', Longmans/Penguin Books, London, 1968, pp. 38-9
- 64 Rogers, S. and Mandelkern, L. *J. Phys. Chem.* 1957, 61, 985
- 65 Fox, T. G. and Flory, P. J. *J. Appl. Phys.* 1950, 21, 1581
- 66 Couchman, P. R. *J. Appl. Phys.* 1979, 50, 6043