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Influence of the crosslinks density on the crystallization of water in PAA gels

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It is shown that confinement of water in crosslinked PAA gels cannot be compared to that of water in solid porous materials. In crosslinked gels the ice melting temperature and the amount of non-crystallizable water is explained by the classical variations of the glass temperature and the ice dissolution temperature with the concentration of water. © 1997 Elsevier Science Ltd.

Water in porous solid materials and in gels presents some similar behaviour as far as the mobility of water and the ice melting temperature are concerned. In both materials at low temperature a certain amount of water does not crystallize. The properties of confinement dimension (radius of the pores) on the properties of water in porous materials are well-known[1–4]. In gels, often 'dynamic pores' are described to explain some permeation properties[5], but up to now the influence of the mesh size of the network, or in other words of the crosslink density, on the melting of ice formed at low temperature has not been studied. In this article one shows that the crosslink density has a weak influence on the melting properties of ice, and on the amount of non-crystallizable water, these properties are explained not in terms of confinement but by the phase diagram.

Various gels of polyacrylamide (PAA) have been synthesized by dissolving acrylamide (A) and biacrylamide (BA) monomers in water. Potassium persulfate (PP) and tetramethyl-ethylene diamine (TEMED) are added to initiate the polymerization. The concentration in weight are fixed: A = 40%; PP = 0.6%; TEMED = 0.03%. Only the concentration C_{CL} of crosslink agent BA is varied. The following table gives the characteristics of the gels, the M_c values are deduced from the concentrations C_{CL}. The samples have been removed from the moulds after 1 h and then washed in water to wash out residual monomers and initiator. The maximum swelling ratio is then measured, which permits us to calculate the molecular weight M_c^* between crosslinks according to the method of Flory–Rehner[6,7] and to compare with the calculated M_c values (*Table 1*).

The gels have been swollen at various ratios and studied by d.s.c. at various heating and cooling rates. The properties of the gels have been compared to the uncrosslinked PAA ($M_W = 200\,000$) and typical d.s.c. curves shown in *Figure 1*.

As in all uncrosslinked hydrophilic polymers, PVA, PVP, gelatine, etc. two regimes of concentration can be considered[8–12]. In the low concentration regime $c < c^*$ water does not crystallize whereas in the second regime $c > c^*$ a certain amount of water can crystallize at low temperature.

In the low concentration regime the glass temperature T_g has been measured at a heating rate of 5°C min^{-1}. *Figure 2* reports T_g of the crosslinked materials as a function of the water concentration c. The $T_g(c)$ curves of gels and swollen polymers cannot be distinguished. The figure shows the theoretical curve deduced from the Fox equation $T_g^{-1}(c) = cT_{gw}^{-1} + (1-c)T_{gp}^{-1}$; the glass temperature of pure water T_{gw} and pure polymer T_{gp} being respectively 135 K and 400 K. In conclusion the crosslink density has no conspicuous effect on the macroscopic mobility of water in such gels. It would be interesting to study the microscopic mobility of water in these gels by high frequency techniques such as quasi-elastic neutron scattering as reported for the gelatin–water system[14].

In the second regime $c > c^*$ water crystallizes partially and then the glass transition is not directly observed. As explained for non-crosslinked polymers the glass transition becomes constant and merges with the crystallization or ice melting peak[10–12], depending on the d.s.c. measurement in cooling or heating. This effect called the T_g regulation effect by ice formation is recalled in *Figure 3*. In this regime when the temperature is decreased the liquidus $T_m(c)$ is passed through before the glass temperature $T_g(c)$. For simplification one

Table 1

BA%	C_{CL}%	M_c	M_c^*
0.048	0.1	25 000	30 000
0.096	0.2	8 000	15 000
0.288	0.6	4 000	5 000
0.480	1	3 000	3 000

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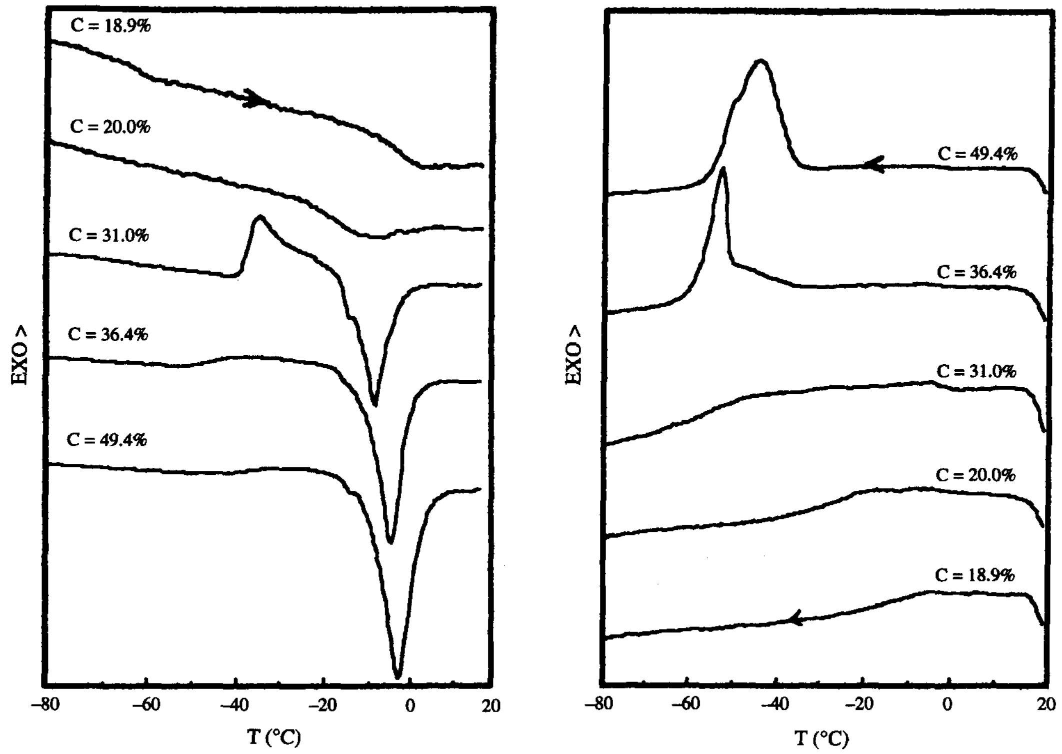

Figure 1 Heating and cooling d.s.c. curves of water-swollen (5°C $\min^{-1}$) PAA as a function of the water concentration

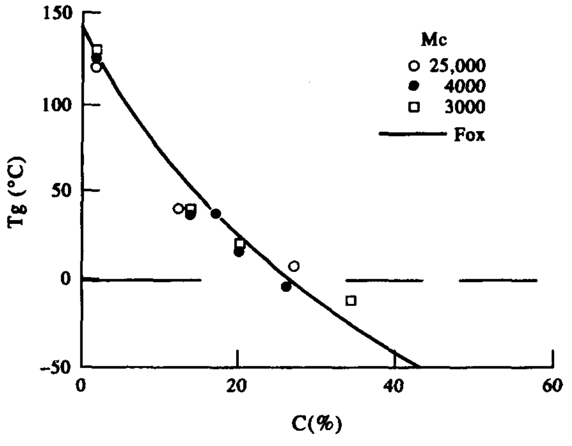

Figure 2 T_g of crosslinked PAA as a function of the water concentration and of the molecular weight M_c between crosslinks: heating rate 5°C $\min^{-1}$. The solid curve represents the Fox equation. T_g of homopolymers, not given in the figure for more clarity, also verifies the Fox equation

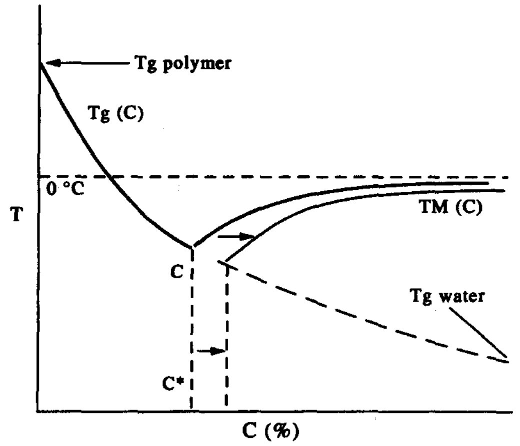

Figure 3 The T_g regulation effect in polymers. In the low concentration regime $0 < c < c^*$ water does not crystallize, for $c > c^*$ water crystallizes partially, during ice formation the concentration c and the T_g of the remaining amorphous phase increases and the ice melting temperature decreases; the process of ice formation stops when the two temperatures $T_m(c)$ and $T_g(c)$ become equal. The amount of non-crystalline water is equal to c^*. When the $T_m(c)$ curve is shifted from an amount Δc (dashed curve) the c^* value increases the same amount

assumes that there is no supercooling effect ($T_c \cong T_m$). When the temperature becomes equal to $T_m(c)$, ice forms and then the concentration of water in the remaining phase decreases, the T_g of this phase increases and the new crystallization temperature $T_m(c)$ decreases. Ice formation carries on, only if the temperature is lowered. Ice formation stops when the temperature becomes equal to T^*, that is to say when the glass and crystallization temperatures becomes equal. In melting experiments the same feature occurs. During melting there is a change of concentration in the remaining liquid, ice melting begins at T^* and ends up at $T_m(c)$. The melting peak is in fact a dissolution peak. This can be verified easily as demonstrated in *Figure 4a*. A true melting peak has a width which extrapolates to zero when the heating rate extrapolates to zero. In all crosslinked and non-crosslinked polymers swollen with water, the width $\Delta T(1/2)$ at half height of the melting peak is constant and of the order of $T^* - 273$ K.

In conclusion the melting peak of ice in gels has the same characteristics as the dissolution peak of ice in solution of polymers. In *Figure 4b* one reports the temperature T_m corresponding to the maximum of the endotherm of melting. Pure water is used as calibration. It is well known that the position of the d.s.c. melting

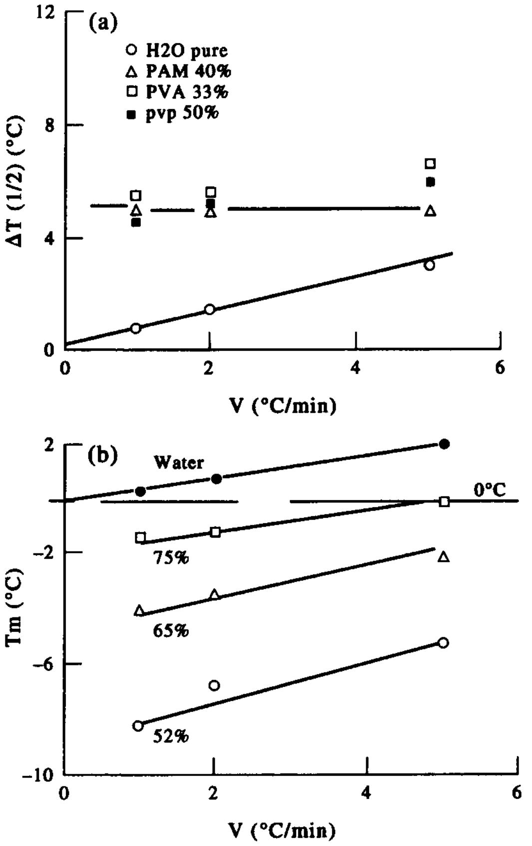

Figure 4 Melting of ice in swollen PAA. (a) Width $\Delta T(1/2)$ at half height of the ice melting peak, comparison with other polymers and with pure water; polyacrylamide (PAM), polyvinylalcohol (PVA), polyvinylpyrrolidone (PVP). (b) Dependence of the 'melting' temperature T_m with the heating rate and with the water concentration, comparison with pure water

peak depends on the weight of materials and on the heating rate. One compares in the figure materials with similar weight (2–4 mg) of crystallizable water as a function of the heating rate v. Extrapolation to $v = 0$ gives the true dissolution temperature $T_m(v = 0)$ as a function of the concentration. This procedure for determining T_m has been applied to all the PAA materials. In *Figure 5* extrapolated values of T_m are given for three series of crosslinked PAA and for the swollen polymer as a function of the water concentration.

From this figure one concludes that the crosslink density has a small effect on the dissolution curves $T_m(c)$ of ice in these PAA gels. The homopolymer and the gel with $M_c \sim 25\,000$ has similar $T_m(c)$ curves. In the most crosslinked PAA ($M_c = 4000$ and 5000), ice melting depression is more important, but the maximum value at $c \sim 50\%$ is only 2 to 3 degrees higher than for the corresponding homopolymer.

As noted for swollen PVA[10], the melting temperature T_m of ice can be predicted by the Flory–Huggins theory[7]

$$(T_m)^{-1} - (T_m^o)^{-1} = \frac{R}{\Delta H}(\log c + 1 - c + \chi(1 - c)^2) \qquad (1)$$

T_m^o being the melting temperature of the pure solvent (water), R the gas constant, ΔH the melting enthalpy of ice and χ the Flory interaction parameter. This equation applies also to ice of small dimensions embedded in a polymer–water matrix in the liquid state. In that case T_m^o is a function of the size r of ice crystallites and can be deduced from the Brun equation[15] (r in nm)

$$r(\text{nm}) = 0.57 + 65/\Delta T \qquad (2)$$

If one applies this equation to ice crystals of dimension $r = 10$ and 30 nm one obtains respectively ΔT values of 6.5 and 2°C.

The dimension of the crystals of ice in PAA gels with 40% of water have been determined by X-ray ($\lambda = 1.54\,\text{Å}$ with graphite monochromator) using a linear detector (resolution 0.01 Å); the dimension r deduced from the Scherrer formula gives $r = 31$ nm and the accuracy is about 6 nm. This technique does not allow us to observe differences between the low and high crosslinked PAA, but one notes however that a change of the dimension of ice from 30 to 20 nm can be possible when the concentration of crosslinks increases, and therefore producing a small additional depression of a few degrees.

Equation (1) applies to the series $M_c = 25\,000$ and the homopolymer with $\chi \sim 0.5$, and a similar fit was obtained for the PVA–water system[9]. There is no reason to believe that χ varies with crosslink density which is always small ($C_{CL} \leqslant 1\%$). Therefore the higher variation of $T_m(c)$ for the highly crosslinked PAA

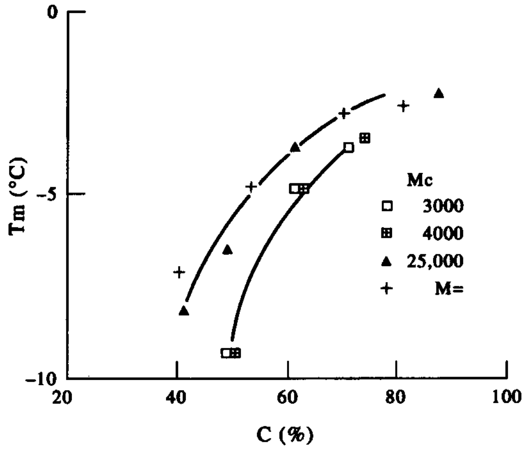

Figure 5 Variation of T_m (extrapolated at the heating rate $V = 0$°C min^{-1}) as a function of concentration c of water in swollen crosslinked PAA. T_m corresponds to the maximum of the dissolution peak

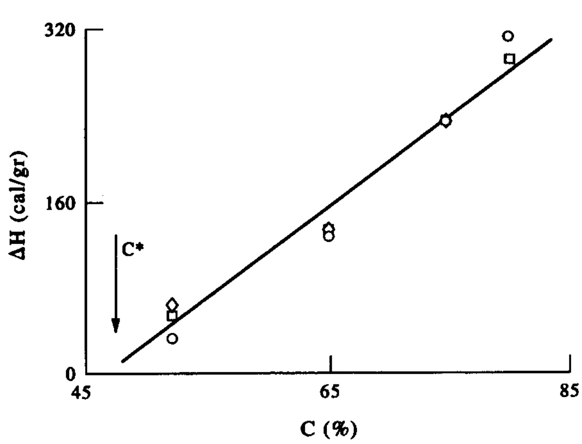

Figure 6 Melting enthalpy of ice in a swollen crosslinked PAA ($M_c = 4000$) for various heating rates. Extrapolation to $\Delta H = 0$ gives the critical concentration c^* of non-crystalline water

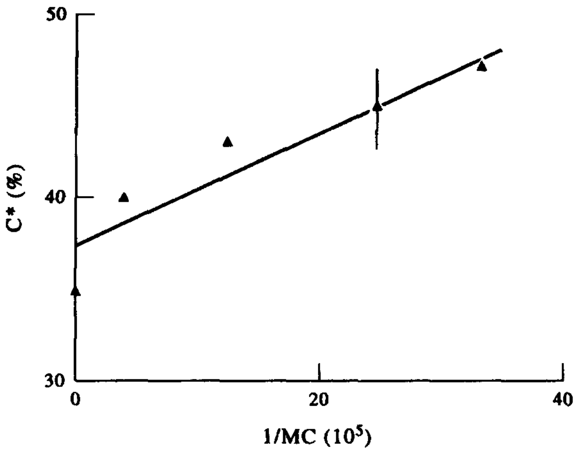

Figure 7 Variation of the critical concentration c^* in swollen PAA as a function of the inverse of the molecular weight M_c between crosslinks. The non-crystalline water concentration c^* is determined as shown in *Figure 6*

material would be due to the small dimension r of ice crystallites formed in this material.

In conclusion dilution effects explain the variation of the melting depression temperature of ice in polymer and gels; this depression can be of the order of 7°C for water concentration $c \sim 30\%$ and in highly crosslinked gel an additional depression of 2 to 3°C is supposed due to the dimension of the ice crystallites.

In *Figure 6a* one reports the enthalpy ΔH of the endotherm peak as a function of the water concentration c for the sample $M_c = 4000$. This procedure has been adopted for measuring the extrapolated value c^* of non-crystallizable water, in all the crosslinked materials. As is expected, values of ΔH and therefore of c^* do not depend on the heating rate. In *Figure 6b* the critical concentration of c^* is plotted as a function of the inverse of the molecular weight M_c from the results of *Figure 6*. One concludes that the concentration c^* increases with the crosslink density. This effect can be deduced from the variations of T_m reported in *Figure 5* and schematized in *Figure 3*. In this figure the T_g curve is common to all the samples (see *Figure 2*), only the melting curves are different. The concentration c^* corresponding to the intersection point C of the $T_g(c)$ and $T_m(c)$ curves increases by an amount of 10% when the curves $T_m(c)$ are shifted along the c-axis an equal amount; a similar effect of displacement of the critical concentration was observed in PVA–PVP blends swollen with water[13].

In conclusion, ice melting in crosslinked PAA is ruled by the dilution effect. A small influence of the crosslink density on the melting temperature and on the amount of non-crystallizable water is however observed. We think that in highly crosslinked materials crystallization appears at lower temperature than in the other materials. In general the density of germs increases with supercooling, therefore the dimension of ice crystallites decreases with supercooling. The decrease in dimension of the ice crystallites induces a supplementary depression of the ice melting curve via relations (1) and (2) and then a small shift of the solidus curve and of the critical concentration c^* of crystallizatable water. Finally it is worth noting that in highly crosslinked materials ($M_c = 3000$) the length of the chains having 42 monomers between crosslinks is about 6 nm, therefore the formation of ice crystals of 20–30 nm implies rupture of some chains. This is possible because the energy gained during formation of a crystal of 30 nm is of the order of 10^{-14} J ($\Delta H = 334\,\mathrm{J\,g^{-1}}$) this is four orders of magnitude greater than the energy 10^{-18} J for breaking one chain.

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