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Molecular complex formation in the system poly(vinyl methyl ether)/water

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Abstract

The behaviour of poly(vinyl methyl ether) (PVME) in water has been studied in detail. A molecular complex with maximum two molecules of water per repeating unit is formed. The glass transition temperature of this complex is −58°C. Additional water plastisises and hydrates the complex. This conclusion is based on the detailed analysis of the concentration dependence of the glass transition of the system and melting behaviour of water. A similar behaviour is found with the chemical networks, obtained by radiation cross-linking. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl methyl ether); Water; Molecular complex

1. Introduction

Poly(vinyl methyl ether) (PVME) is a water-soluble polymer that demixes from aqueous solutions on heating. This lower critical solution temperature behaviour (LCST-behaviour) is more complex than what can be expected from “classical” theoretical considerations. The corresponding LCST-demixing curve is bimodal and the two minima show a different molecular mass dependence [1]. The minimum in the low concentration range shifts towards lower concentration and temperature as expected for a “classical” Θ-behaviour, while the one at higher polymer concentration is molecular mass independent. Such a behaviour has been discussed recently [1]. The phenomenological analysis could distinguish between three types of limiting critical behaviour for water-soluble systems in general. Type I, the “classical” demixing behaviour, is characterised by a limiting critical concentration, for infinite molar mass, $\phi_L = 0$ (volume fraction). With type II, a single off-zero limiting critical concentration, $\phi_L \neq 0$, occurs at non-Θ-conditions. Type III is characterised by two off-zero limiting critical concentrations and one zero limiting critical concentration.

The swelling behaviour of the corresponding cross-linked analogues is directly related to the type of demixing [2]. Type I demixing results in a continuous swelling behaviour. The unusual Type II and Type III demixing behaviour lead to discontinuous swelling behaviour, a problem that has attracted much attention in recent literature [3–8].

These three types of behaviour can be theoretically predicted by the introduction of a strongly concentration dependent interaction function in the expression of the Gibbs free energy of mixing [1].

Several molecular reasons for the use of this concentration dependent interaction function may be advanced, such as:

- disparity in size and shape among solvent molecules and repeat units in the polymer chains;
- change of free volume with concentration;
- non-uniform segment density at low concentration;
- distribution of free solvent molecules among self-associated complexes and solvated polymer segments.

The system PVME/water shows this Type III demixing behaviour and the corresponding chemical networks show discontinuous temperature-dependent swelling behaviour.

From the structural considerations, it is obvious that in the system PVME/water complex formation between the water molecules and the ether functions of the repeat units may be responsible for the non-classical phase behaviour. Experimental evidence was already brought by Maeda et al. [9]. The formation of a stable molecular complex with 2.7 molecules water per chain repeat unit was proposed. At higher overall water content, a higher degree of hydration was suggested with up to five water molecules per repeat unit.

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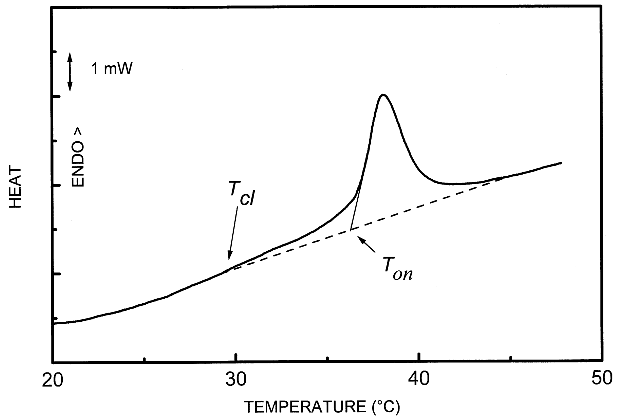


Fig. 1. DSC thermogram of the system PVME/water; $w_2 = 0.2$, heating rate 2°C/min.

The purpose of this paper is to bring further experimental evidence for such specific intermolecular interactions through the study of the behaviour of water in these solutions and the concentration dependence of their glass transition temperature.

2. Experimental

2.1. Materials

PVME was purchased from Aldrich. The average molar-masses and their distribution were determined by GPC in THF as the solvent and polystyrene as the calibration standard. This determination resulted in a weight average $M_w = 60.5$ kg/mol and a number average of $M_n = 20.5$ kg/mol, leading to a polydispersity $M_w/M_n = 3$. Deionised water was used as the solvent.

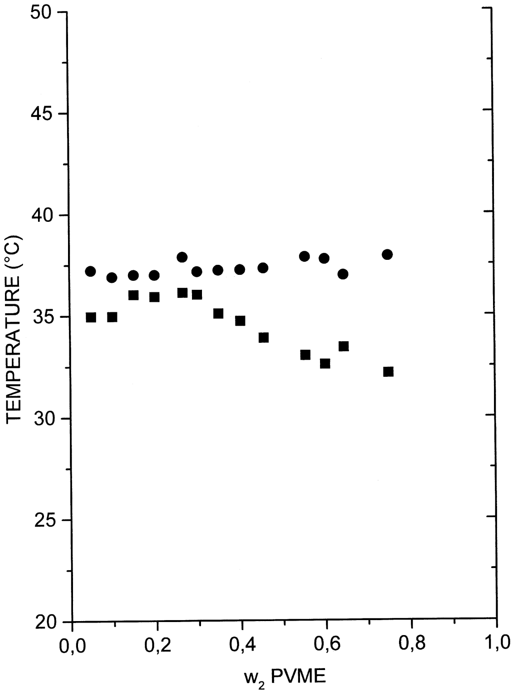


Fig. 2. Temperature–concentration diagram of the system PVME/water (●: T_{on}, ■: T_{cl}).

2.2. Cross-linking of PVME

Cross-linking of PVME was performed by irradiation of a 10 wt% PVME/water solution with high energetic X-radiation (80 kGy). A detailed description of this method can be found in an earlier publication [2]. Uncross-linked polymer is extracted with acetone in a Soxhlet apparatus for 2 weeks and then dried under vacuum. The networks swollen with water will be called gels.

2.3. Calorimetric measurements

Homogeneous solutions or homogeneously swollen gels were prepared by adding the appropriate amount of water to the dry polymer in a DSC sample pan. Concentrations are given in polymer weight fraction, w_2. A Perkin–Elmer 7 differential scanning calorimeter was used at a scanning rate of 2°C/min unless otherwise stated.

3. Results

3.1. Demixing behaviour of the system [linear PVME]/[water]

The liquid–liquid demixing behaviour (L–L demixing) of the samples used in this work was investigated by calorimetry. This was described in previous papers [1]. The samples were heated from 20 to 50°C. The demixing is endothermic and the corresponding heat of demixing is obtained from the integration of the area of the corresponding DSC signal. A typical thermogram is represented in Fig. 1. The endotherm is composed of two interfering peaks. The one at low temperature is small and relatively broad. The high temperature one is sharp. The temperature at the first deviation from the baseline at low temperature corresponds to the temperature at which the demixing sets in at the scanning rate used. This temperature corresponds to the cloud point and the temperature will be represented by T_{cl}. The onset of the second sharp peak cannot be localised in the same way because of the overlapping with the previous signal. Therefore, the onset as calculated by the DSC will be used. The corresponding temperature is called T_{on}. These temperatures are plotted in Fig. 2 as a function of the polymer concentration w_2. The concentration dependence of T_{cl} is in agreement with previously reported data. The transition temperature T_{on} is invariant because of the coexistence of three phases [1].

3.2. Demixing behaviour of chemically cross-linked PVME

The swelling behaviour of cross-linked PVME samples is also studied by calorimetry. The exact amount of water

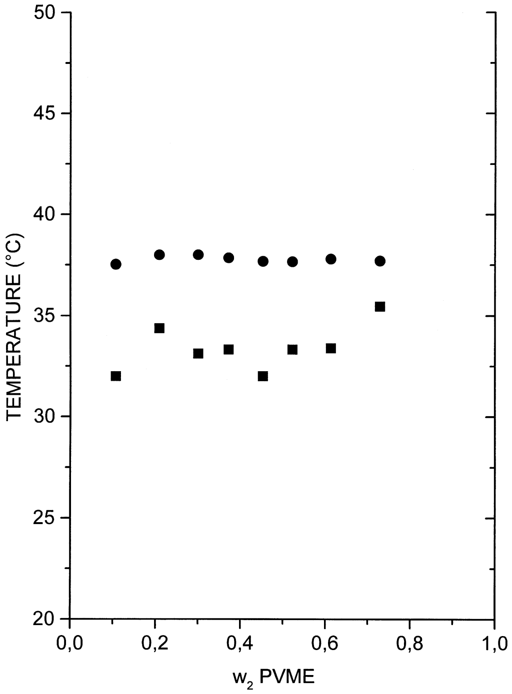


Fig. 3. Temperature–concentration diagram of the system cross-linked-PVME/water (●: T_{on}, ■: T_{cl}).

necessary to reach the correct ratio network/water (or overall concentration) is added in the sample pan and the sample is allowed to equilibrate at room temperature. The samples are heated from 20 to 50°C. The experimental data were analysed in a similar way as was reported in a previous paper [2]. The temperature at the first deviation from the baseline is taken as the cloud point, T_{cl}. The onset of the signal as calculated by the DSC (T_{on}) is taken as the reference temperature for the second transition. The results of these measurements are represented in Fig. 3 in a temperature–concentration diagram. The onset temperature, T_{on}, is shown little concentration dependence in the concentration range investigated. This transition temperature can therefore be considered as invariant. Such an equilibrium establishes a three-phase equilibrium between water and the two phases with different concentration inside the demixed network. The concentration dependence of the T_{cl} delimits the LCST miscibility gap.

3.3. Melting behaviour of water in the system PVME/water

3.3.1. Concentration dependence of the melting point of water

The melting behaviour of water in the system [linear PVME]/[water] was investigated over the whole concentration range. On the basis of the results of this investigation, the temperature–concentration diagram has to be divided into two parts. At $w_2 \geq 0.61$, only a glass transition is observed whatever is the thermal treatment given to the sample. Even long time annealing below 0°C but above the glass transition, T_g, of the solution does not induce any crystallisation.

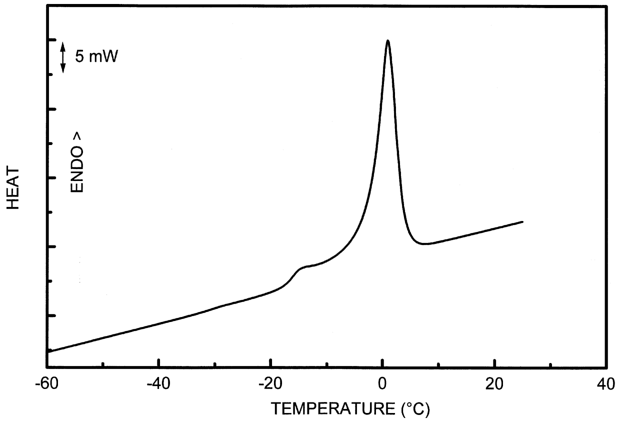


Fig. 4. DSC thermogram of the system PVME/water; $w_2 = 0.2$, heating rate 10°C/min.

At lower polymer concentration ($w_2 < 0.61$) water crystallises during a cooling–heating cycle between 20 and −80°C at 10°C/min. An endothermic signal is observed on heating. A typical thermogram is given in Fig. 4. The endothermic signal consists of a small pre-transition followed by a large peak. Owing to this complex shape, the maximum of the peak was taken as the melting point and corrected for the broadening of the signal due to the dynamic character of the measurement. These melting temperatures are plotted as a function of concentration in Fig. 5. The decrease of this melting point with increasing polymer content cannot only be ascribed to the increase in polymer concentration. If this was the case, then the decrease should be much less pronounced because of the colligative character of the phenomenon. Therefore, factors as crystal size have to be taken into account. Such phenomena have been reported in the literature [10,11]. The same melting point depression is observed in the PVME gels. Water does not crystallise anymore at $w_2 \geq 0.68$. These data are represented in Fig. 6.

3.3.2. Concentration dependence of the heat of melting

The heat of melting of water in the samples is obtained from the integration of the area under the melting peak. The heat of melting of pure water is $\Delta H_w^0 = 330$ J/g. In the solutions and in the gels, the experimentally obtained heat of melting decreases with increasing polymer content and becomes zero at $w_2 = 0.61$ in the solutions and at $w_2 = 0.68$ in the gels. These observations lead to two important conclusions. The behaviour of the solutions will be considered first.

The fact that water cannot crystallise under any circumstances at polymer concentrations $w_2 > 0.61$ means that all the water in these samples is strongly bound to the polymer chains. This observation confirms the formation of a

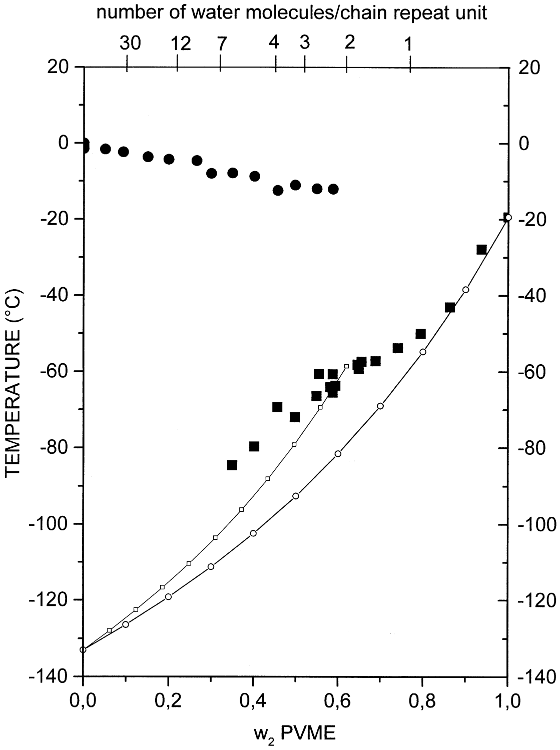


Fig. 5. Temperature–concentration diagram of the system PVME/water (●: melting temperature of water, ■: T_g experimental, -○-: calculated T_g (Fox) between T_g of pure polymer (−19°C) and T_g of water (−133°C), -□-: calculated T_g (Fox) between T_g of polymer complex (−58°C) and T_g of water (−133°C).

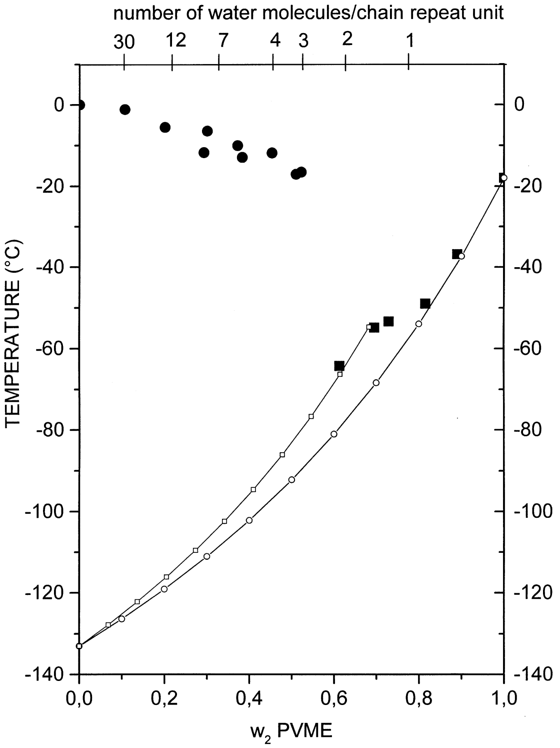


Fig. 6. Temperature–concentration diagram of cross-linked-PVME/water (●: melting temperature of water, ■: T_g, -○-: calculated T_g (Fox) between T_g of pure polymer (−17°C) and T_g of water (−133°C), -□-: calculated T_g (Fox) between T_g of polymer complex (−55°C) and T_g of water (−133°C).

molecular complex as already suggested in an earlier publication [9]. Also in the lower concentration range in which crystallisation of water can take place, a certain fraction of water is also not able to crystallise. If in this concentration range all the water in excess to the amount bound to the polymer chains would crystallise, then the heat of melting per gram solution would decrease in a linear way as given by the following equation:

$$\Delta H_{\mathrm{exp}} = \Delta H_{\mathrm{w}}^{0}[1 - (w_2/0.61)] \tag{1}$$

From Fig. 7, it is evident that the experimental data deviate systematically from the calculated linear behaviour. The best agreement is observed at $0.40 < w_2 < 0.61$. This difference can be slightly reduced by long time annealing at temperatures up to −10°C. However, the obtained heat of melting will never reach the calculated values represented by the straight line.

This concentration dependence of the heat of melting was also investigated for the gels. The data are represented in Fig. 8. This heat of melting becomes zero at $w_2 = 0.68$. In the lower concentration range ($w_2 < 0.68$), the difference between the experimentally obtained values and the theoretically calculated ones is much less pronounced than in the polymer solutions. This linear relationship

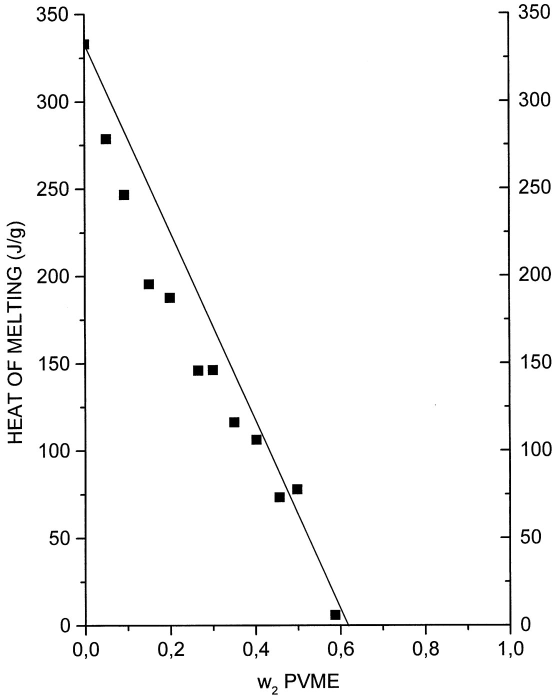


Fig. 7. Heat of melting of water per gram solution of PVME/water (solid line: calculated, squares: measured).

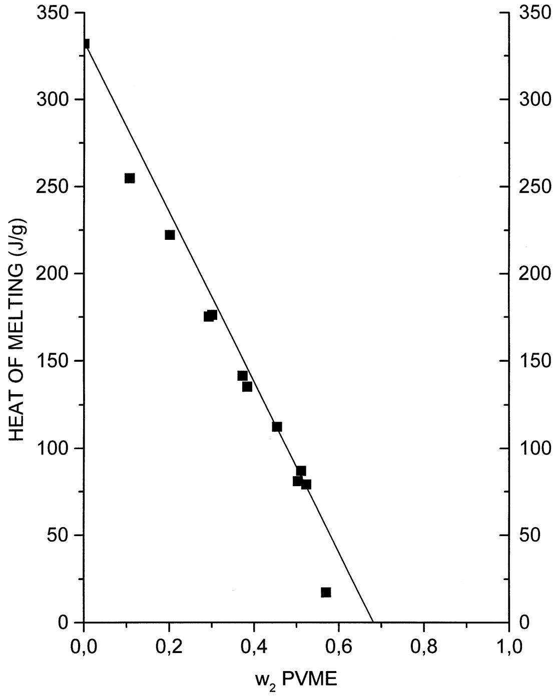


Fig. 8. Heat of melting of water per gram solution of cross-linked-PVME/water (solid line: calculated, squares: measured).

was calculated using Eq. (1) in which 0.61 was replaced by 0.68.

3.4. Concentration dependence of the glass transition

3.4.1. PVME solutions

Two different concentration domains have also to be considered. A $w_2 \geq 0.61$, T_g can be measured in a dynamic experiment in the DSC. Samples cooled at −10°C/min show almost the same behaviour as those quenched in liquid nitrogen. In the low concentration range ($w_2 < 0.61$), the samples have to be quenched in liquid nitrogen before they are heated in the DSC in order to prevent the crystallisation of water. However, the fast crystallisation of water limits the observation of a glass transition to $w_2 \leq 0.35$. The quenched samples were heated from −100 to 20°C.

The concentration dependence of T_g, represented in Fig. 5, can be subdivided in two domains. One is situated below and the other above $w_2 = 0.61$. They do not follow the concentration dependence calculated using the Fox equation [12], which is based on complete additivity of properties.

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \tag{2}$$

In this equation, T_g is the transition temperature of the solution. T_{g1} that of PVME (−19°C,) and T_{g2} that of water (−133°C [13]) when the concentration dependence is calculated over the whole concentration range. To obtain the calculated curve in the low concentration range, the T_g of the solution with $w_2 = 0.61$ ($T_{g1} = -58$°C,) and the one of water ($T_{g2} = -133$°C) were used. These calculated relationships are represented in Fig. 5.

In the high concentration range, the experimental data do not follow this calculated curve: the experimental values lie above the calculated one especially when $w_2 = 0.61$ is approached. A similar deviation is observed in the lower concentration range.

3.4.2. PVME gels

The chemically cross-linked samples show the same concentration dependence with two minor differences. The T_g of the cross-linked, dry sample is higher than that of the linear sample. The concentration limit that separates the two domains is situated at $w_2 = 0.68$ instead of $w_2 = 0.61$.

4. Discussion

From the reported data several conclusions can be drawn.

(I) A molecular complex is formed between the PVME chain repeating units and water.

1. Water can be strongly bound to the polymer chain. The absence of crystallisation of water at $w_2 \geq 0.61$ in the solutions must be ascribed to the formation of a molecular complex between water and PVME. The limit of 0.61 indicates that this complex is composed of maximum two water molecules per chain repeating unit. The same complex is found in the networks. The higher polymer concentration limit (0.68 instead of 0.61) is ascribed to the steric hindrance exerted by the cross-linking points, which are not able to bind these two water molecules. This molecular complex is stable at least up to a temperature close to the melting point of water. This can be concluded from annealing experiments performed with solutions with $w_2 \leq 0.61$. The amount of water that crystallises under these circumstances will never exceed the amount reported in Figs. 7 and 8. This means that the crystallising water always expels the molecular complex with $w_2 = 0.61$.
2. The molecular complex with two water molecules per chain repeating unit has a T_g of −58°C. Molecular complexes with less than two water molecules per chain repeating unit show a higher T_g and this glass transition temperature increases when the average number of bound water molecules per chain repeating unit is decreased. Such complexes are obtained from solutions with $w_2 > 0.61$. A value of $T_g = -19$°C is found for the completely dry sample. The T_g of cross-linked PVME and the T_g of the corresponding molecular complex is slightly higher. The deviation of the experimental T_g values from the calculated relationship in the high concentration range has to be ascribed to this molecular complex formation.
3. Two possibilities can be proposed for the complex in the composition range $0.61 < w_2 < 1.00$.

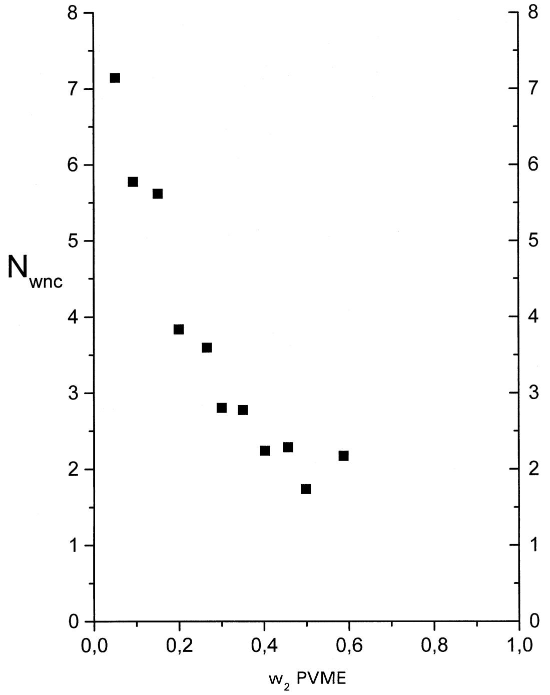
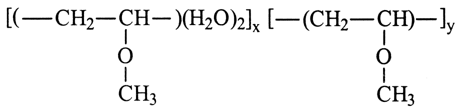


Fig. 9. Number of non-crystallisable water molecules (N_{wnc}) per PVME chain repeating unit as a function of w_2 (linear PVME).

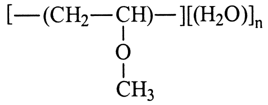
(i) Introduction of water leads always to the binding of two water molecules to one repeating unit while the remaining chain units have no bound water. This results in a statistical copolymer composed of hydrated and non-hydrated repeating units.



$$[(-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{O}\\ |\\ \mathrm{CH_3}}}{\mathrm{CH}}-)(\mathrm{H_2O})_2]_x\;[-(\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{O}\\ |\\ \mathrm{CH_3}}}{\mathrm{CH}})-]_y$$

y, x: fractions of repeating units; $y = 1$, $x = 0$ for $w_2 = 1.00$; and $y = 0$, $x = 1$ for $w_2 = 0.61$.

(ii) The water molecules are attached statistically to the polymer chain repeating units.



$$[-(\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{O}\\ |\\ \mathrm{CH_3}}}{\mathrm{CH}})-][(\mathrm{H_2O})]_n$$

n = average value; $n = 0$ for $w_2 = 1.00$; and $n = 2$ for $w_2 = 0.61$.

(II) A second conclusion is that water in excess to the amount trapped in the complex is also able to remain attached to this complex. This is especially the case for the linear system. From the experimental data of Fig. 7, the number of additional water molecules per chain repeating unit that do not crystallise can be calculated.

The fraction of non-crystallisable water of the total amount of water (w_{wn}) is

$$w_{wn} = (1 - (\Delta H_{we}/\Delta H_w^0)) \tag{3}$$

with

$$\Delta H_{we} = \Delta H_{exp}/(1 - w_2) \tag{4}$$

ΔH_w^0 is the heat of melting of pure water.

The fraction of non-crystallisable water of the solution as a whole is (w_{tn})

$$w_{tn} = w_{wn} w_1 \tag{5}$$

The number of non-crystallisable water molecules per chain repeat (N_{wnc}) unit is

$$N_{wnc} = (58 w_{tn})/(18 w_2) \tag{6}$$

The results are represented in Fig. 9. It is clear that the number of non-crystallisable water molecules per chain repeating unit strongly increases with the overall water content. The agreement with the calculated values is the best in the high concentration range, close to $w_2 = 0.61$ and becomes more pronounced at lower polymer content. One can therefore conclude that there exists an association equilibrium between the molecular complex and water. This equilibrium shifts to the side of the hydrated system with increasing water content.

This problem is less pronounced in the cross-linked system as can be seen in Fig. 10. Such a behaviour of solvent/network systems can be expected from theoretical considerations reported in the literature [14]. The network collapse will squeeze out the free water and most of the hydration water from the network. This hydration process

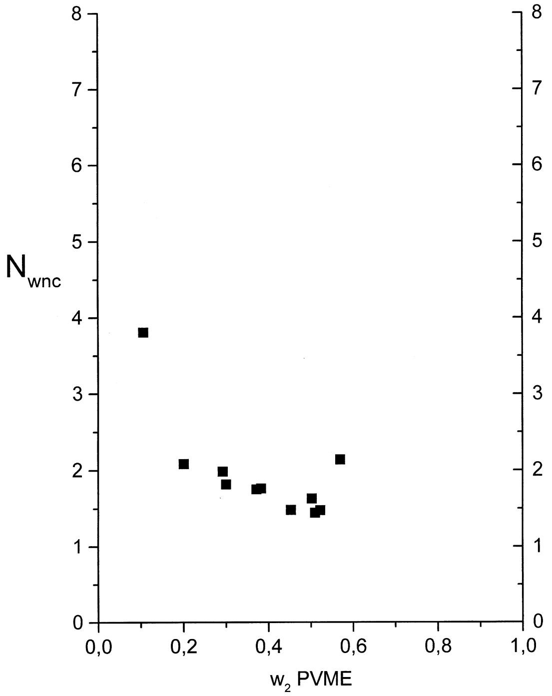


Fig. 10. Number of non-crystallisable water molecules (N_{wnc}) per PVME chain repeating unit as a function of w_2 (cross-linked-PVME).

can lead to a too high T_g value in this concentration range in comparison with the calculated values.

5. Conclusions

A molecular complex can be formed between water and PVME with maximum two water molecules strongly bound to the chain repeating unit. From our experimental observations, it can be concluded that such a complex is stable up to at least a temperature very close to the melting point of water. The data reported earlier in the literature suggest that the complex will even exist at room temperature. This problem is investigated further. Such a complex formation leads to a specific T_g–w_2 relation with -58°C as the T_g of the complex with two water molecules per repeating unit.

Addition of water in excess to the composition of the complex leads to a hydration of this molecular complex. The corresponding degree of hydration becomes more important with increasing water content.

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