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# Phase behaviour of poly(*N*-vinyl caprolactam) in water

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## Abstract

The solution behaviour of the system poly(*N*-vinyl caprolactam)/water has been studied. Experiments and theoretical calculations indicate a typical Flory–Huggins (Type I) demixing behaviour with a lower critical solution temperature (LCST). The critical concentration and LCST shift to lower values with increasing molar mass of the polymer. The phenomenological description of such a system predicts a continuous temperature controlled swelling behaviour of the corresponding network. A comparison with literature data confirms this prediction.

A calorimetric study of the crystallisation and melting behaviour of water and the concentration dependence of the glass transition temperature, gives no evidence for the formation of a polymer/solvent complex. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Poly(*N*-vinyl caprolactam); Phase behaviour; LCST

## 1. Introduction

Many water soluble polymers demix from their solutions in water upon heating. Different types of such "lower critical solution temperature" behaviour (LCST behaviour) have been discussed recently [1–3]. A general phenomenological analysis of the critical miscibility behaviour distinguished three types of limiting critical behaviour. Type I represents the "classical" Flory–Huggins (FH) miscibility behaviour: by increasing the chain length of the polymer, the position of the critical point shifts towards lower polymer concentration. In the limit of infinite chain length, the critical point is characterised by a limiting critical concentration, $\phi_L = 0$, at the $\Theta$-temperature. On the other hand, Type II shows a single off-zero limiting critical concentration, $\phi_L \neq 0$, at non-$\Theta$-conditions. Furthermore, the critical point of consolute state is almost independent on the polymer chain length. Finally, Type III is characterised by one zero limiting critical concentration and two off-zero limiting critical concentrations. The first critical point, located at low polymer concentration, behaves in the classical Flory–Huggins way and shifts to zero concentration and to the $\Theta$-temperature at infinite chain length. The chain length does almost not influence the other critical points, at high polymer concentration. These three types of behaviour can be modelled by the introduction of a strong, concentration dependent polymer–solvent interaction function in the expression of the FH theory [1–3].

Evidence for such strong interactions with water were found for the system poly(vinyl methylether) (PVME)/water for which the formation of a molecular complex was demonstrated [4]. Such experimental evidence is based on the study of the crystallisation and melting behaviour of the water and the concentration dependence of the glass transition. This complex formation reduces the amount of water that can crystallise because part of it remains trapped in the complex. This approach however has to be used with much care as interference of the crystallisation of water with the vitrification of the solution can also take place. The major condition is that the glass transition of the polymer is below the crystallisation temperature of water so that the absence of the crystallisation of water can only be ascribed to the complex formation. When this condition is not fulfilled, the reduced crystallisability of water cannot be used as a solid argument for complex formation.

It was further shown that the swelling behaviour of the corresponding cross-linked polymers can be directly related to the type of demixing [3]. The classical Type I demixing results in a temperature induced continuous network

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Table 1
Reaction conditions for the solution polymerization of N-vinylcaprolactam with 2,2′-azobisisobutyronitrile (AIBN)

| | Mass of monomer (g) | Volume of solvent (ml) | Mass of AIBN (mg) | $T$ (°C) | Time (h) | $M_v$ |
|---|---|---|---|---|---|---|
| Sample 1 | 15 | 130 | 100 | 70 | 6 | 9000 |
| Sample 2 | 15 | 130 | 10 | 70 | 6 | 20000 |
| Sample 3 | 30 | 100 | 100 | 60 | 12 | 275000 |

swelling–deswelling. The more unusual Type II and Type III miscibility leads to discontinuous swelling with temperature, a phenomenon that has attracted much attention in literature [5–8].

This general phenomenological analysis has also been confirmed to some extend by experimental evidence. The demixing behaviour of aqueous solutions of linear poly(*N*-isopropyl acrylamide) (NIPA) can be classified as Type II demixing [9], whereas the behaviour of linear PVME in water corresponds to Type III behaviour [2,3]. In agreement with the phenomenological analysis it was found that the temperature-induced swelling/deswelling of NIPA- and PVME-networks in water is discontinuous.

Experimental evidence for a Type I demixing behaviour has not yet been found to our knowledge. Recent literature data on the system poly(vinyl caprolactam) (PVCL)/water [11,25] suggest that this system could be a good candidate for such a behaviour. The LCST behaviour shows one minimum in the demixing curve, situated close to the pure solvent axis in the temperature–concentration diagram.

## 2. Experimental

### 2.1. Materials and techniques

#### 2.1.1. Synthesis of linear poly(N-vinyl caprolactam)

*N*-vinyl caprolactam (VCL: Aldrich 98%) was purified by distillation at 128°C at a pressure of 21 mm and stored at 4°C. The melting point of VCL is 35–38°C under atmospheric pressure. 2-propanol was distilled, then refluxed over CaO before use. Benzene was distilled and subsequently refluxed over Na/benzophenone until a deep blue color was achieved. AIBN (Across 98%) was used without further purification.

In order to obtain three poly(*N*-vinyl caprolactam) (PVCL) samples with different molar masses, VCL was polymerised in 2-propanol (PVCL1 and PVCL2) or in benzene (PVCL3), both using 2,2′-azobisisobutyronitrile (AIBN) as radical initiator. The synthesis was performed under nitrogen atmosphere. The use of 2-propanol leads to transfer reactions, which cause lower molar masses [10,11]. The reaction conditions are summarised in Table 1.

After the reaction, the solution was cooled to room temperature and PVCL was precipitated in diethyl ether (1:10). The polymer was dissolved in a mixture of acetone and water (3:7) and precipitated again by heating the solution to 80°C. This purification was repeated twice, then the precipitate was dissolved in water and freeze-dried.

#### 2.1.2. Molar mass determination

The viscosity average molar masses ($M_v$), shown in Table 1, are determined from the intrinsic viscosity employing the Mark–Houwink relation $[\eta] = KM^a$ with $K = 0.0105$ mL/g and $a = 0.69$ [11].

The intrinsic viscosity of the three samples was measured with an Ubbelöhde-Type viscosity meter at 25°C using water as solvent.

#### 2.1.3. Calorimetry

A Perkin Elmer DSC 7 is used. The scanning rate was 3°C/min unless otherwise stated in the text. Samples of ca. 20 mg for DSC7 measurements were prepared by adding the appropriate amounts of dry polymer and water in the sample holder. After sealing the sample holders, the samples were left to homogenise at room temperature for several days. Concentrations are expressed in mass fractions of the polymer, $w_2$.

#### 2.1.4. Optical measurements

Glass tubes were filled with polymer solutions of different concentration and placed in a water bath. Turbidimetric experiments were performed between 20°C and 80°C at a scanning rate of 2°C/min. For this purpose, light is passed trough the glass tube containing the solution by using glass fibres immersed in the water bath and connected on one side to the light source and on the other hand to the detector. The intensity of the light that comes trough the solution is registered as a function of temperature.

### 2.2. Theoretical considerations

#### 2.2.1. Non-cross-linked systems

The critical point, or consolute state, of a polymer solution is generally situated at relatively low polymer concentration. The position of this critical point in the temperature–concentration phase diagram depends, among other factors, on the molar mass of the polymer. An increase in molar mass shifts this point to lower concentrations. The limiting situation for infinite molar mass corresponds to $w_2 = 0$ ($\phi_L = 0$) and the $\Theta$-temperature. Several polymer/water systems with LCST behaviour do not follow this classic FH scheme and off–zero critical conditions have been reported [1–3]. A recent phenomenological analysis distinguishes between three Types of limiting critical behaviour that can be described by the expression for the Gibbs free energy of mixing, developed by Flory [12–14], Huggins [15,16] and Staverman [17–19] if a strong

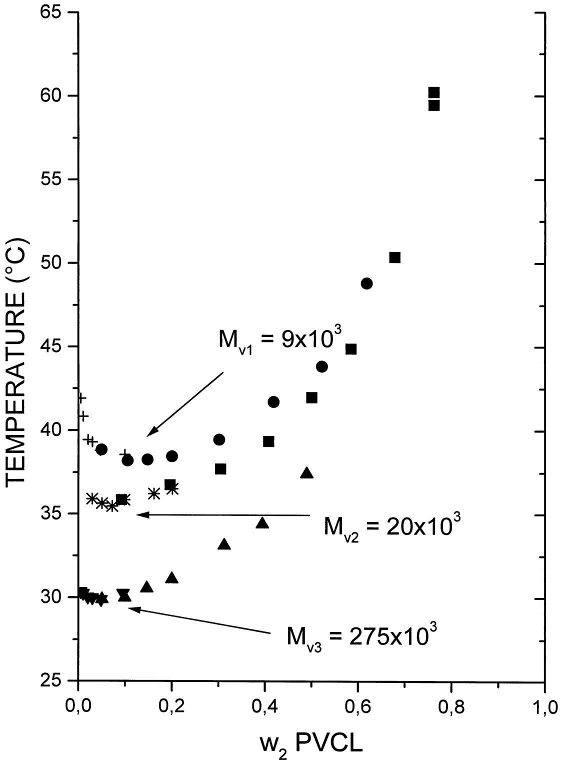

Fig. 1. Demixing of PVCL in water for three samples with different chain length. PVCL1: $M_v = 9$ kg/mol, cloud point temperatures $T_{cl}$ (+), demixing temperature $T_{dem}$, (●); PVCL2: $M_v = 20$ kg/mol, cloud point temperatures $T_{cl}$ ( ∗ ), demixing temperature $T_{dem}$, (■); PVCL3: $M_v =$ 275 kg/mol, cloud point temperatures $T_{cl}$ (▼), demixing temperature $T_{dem}$, (▲).

concentration dependent interaction function $g$ is used:

$$\Delta G/NkT = (\phi_1/m_1)\ln \phi_1 + \sum(\phi_{2i}/m_{2i})\ln \phi_{2i} + \phi_1\phi_2 g(T, \phi_2) \qquad (1)$$

where $\phi_1$ and $\phi_{2i}$ are the volume fractions of solvent and species $i$ in the polymer, respectively; $\phi_2 = \Sigma\phi_{2i}$. The total volume is built up of $N$ identical basic volume units (BVU), and $m_1$ and $m_{2i}$ represent the number of BVUs occupied by solvent molecules and a macromolecule $i$, respectively. The interaction function $g$ is represented by a second order polynomial in $\phi_2$:

$$g = g_0 + g_1\phi_2 + g_2\phi_2^2 \qquad (2)$$

The coefficients $g_i$ may depend on temperature $T$, for instance by $g_i = g_{is} + g_{ih1}/T + g_{ih2}T$. The values of $g_1$ and $g_2$ at the consolute point determine the type of phase behaviour [2]. As discussed in the literature [24], Type I phase behaviour is found if $g_1$ and $g_2$ obey the following inequalities:

$$g_0 \geq (1/2) + g_1 \text{ and } g_2 \geq g_1 - (1/6) \qquad (3)$$

### 2.2.2. Cross-linked systems

Cross-linking has two important general consequences: (i) the molar mass of the polymer becomes infinite and (ii) the system cannot reach a state of infinite dilution but is only able to swell. In the presence of a solvent, equilibrium is established between the osmotic swelling pressure and the elastic force generated by the swelling process. An elastic term has therefore to be added to the expression of the Gibbs free energy of mixing:

$$\Delta G/NkT = \{(\phi_1/m_1)\ln \phi_1 + g\phi_1\phi_2\} + \Delta G_{\text{elastic}} \qquad (4)$$

Networks prepared from systems with Type I miscibility behaviour show continuous swelling–deswelling behaviour with a change in temperature. In the temperature region where less interactions between the solvent and the polymer occur, the network will gradually contract. No direct intersection between the swelling curve and the demixing curve will occur. Discontinuous swelling-deswelling is observed with networks based on linear systems that show Type II and Type III (LCST) behaviour. The discontinuous swelling response results from the interference of the swelling of the network and the miscibility gap. At the temperature of interference, a three phase equilibrium is established, and as a consequence of the Gibbs' phase rule this results in an invariant situation that leads to a concentration jump in the network at that temperature [1,3].

## 2.3. Experimental observations

### 2.3.1. Demixing behaviour in the system PVCL/water

The demixing behaviour of aqueous PVCL solutions was investigated for three PVCL samples with different chain length. The concentration dependence of the LCST demixing is measured in two different ways. Turbidimetric observation allows the determination of the cloud point. The temperature at which the first change in the intensity of the scattered light is observed is taken as the cloud point temperature ($T_{cl}$).

Furthermore, the endothermic nature of the LCST demixing is revealed in a calorimetric experiment. The temperature at the onset of this signal is taken as the demixing temperature ($T_{dem}$). Samples with different polymer content were heated from 20°C to 80°C. The concentration dependence of $T_{cl}$ and $T_{dem}$ is represented in Fig. 1 and a good agreement is found between the transition temperatures obtained by the two different experimental methods. The minimum of the demixing curve shifts towards lower temperature and lower polymer concentration by increasing the chain length of the polymer.

In Fig. 2 the computed phase behaviour, based on Eqs. (1) and (2), is presented. In Eq. (2), all $g_i$ were assumed to be temperature-dependent according to $g_i = g_{is} + g_{ih2} \times T$ (with $g_{ih1} = 0$). The cloud point data of the system PVCL2/$H_2O$ were used to obtain values for the six interaction constants in the model. The polydispersity of the polymer samples was ignored, i.e. the experimental data were treated as coexisting data.

Quite generally, the coexistence in a binary system is

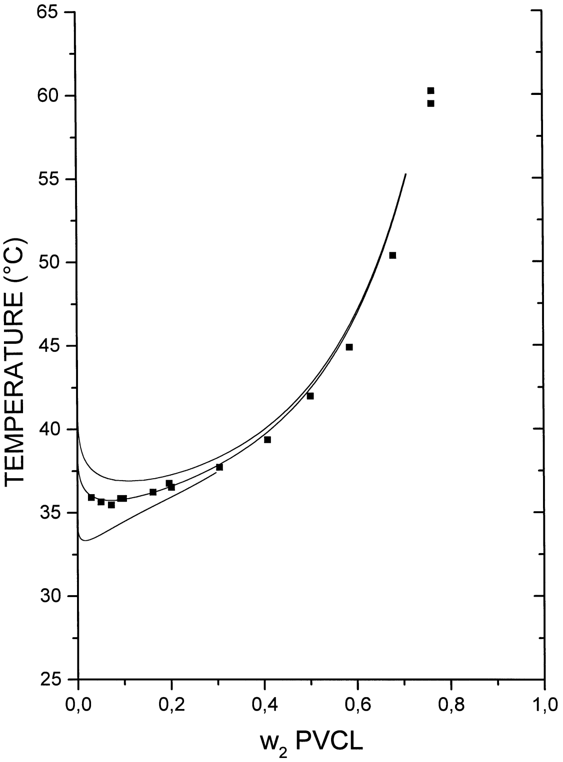

Fig. 2. Calculated Type I demixing behaviour. —: calculated curves with molar masses equal to samples PVCL1, PVCL2 and PVCL3. ■ : experimental data of PVCL2. Parameter values are collected in Table 2.

given by

$$\Delta\mu_1'(\phi_2', \phi_2'') = \Delta\mu_1''(\phi_2', \phi_2'')$$

and

$$\Delta\mu_2'(\phi_2{}', \phi_2{}'') = \Delta\mu_2{}''(\phi_2', \phi_2'')$$

with $\Delta\mu_i'(\phi_2', \phi_2'')$ being the excess chemical potential of component $i$ and $\phi_2'$ and $\phi_2''$ being the concentrations in the coexisting phases, denoted by the single and double prime, respectively.

Expressions for the excess chemical potentials of both components are easily derived from Eqs. (1) and (2). Clearly, the model parameters ($g_{0s}$, $g_{0h2}$, $g_{1s}$, $g_{1h2}$, $g_{2s}$, $g_{2h2}$) are also present in these expressions. Values for the six parameters in the model can be obtained by adjusting them such that the best fit is obtained with the experimental coexistence data. This is a non-linear least square problem which is solved using a multi-parameter estimation computer program [20].

Table 2
Calculated interaction coefficients in Eq. (2)

| Coefficient | Value [unit] |
|---|---|
| $g_{0s}$ | $-2.2213$ |
| $g_{0h2}$ | $9.5 \times 10^{-3}$ [K$^{-1}$] |
| $g_{1s}$ | $-1.5953$ |
| $g_{1h2}$ | $5.8113 \times 10^{-3}$ [K$^{-1}$] |
| $g_{2s}$ | $1.2772$ |
| $g_{2h2}$ | $-3.9393 \times 10^{-3}$ [K$^{-1}$] |

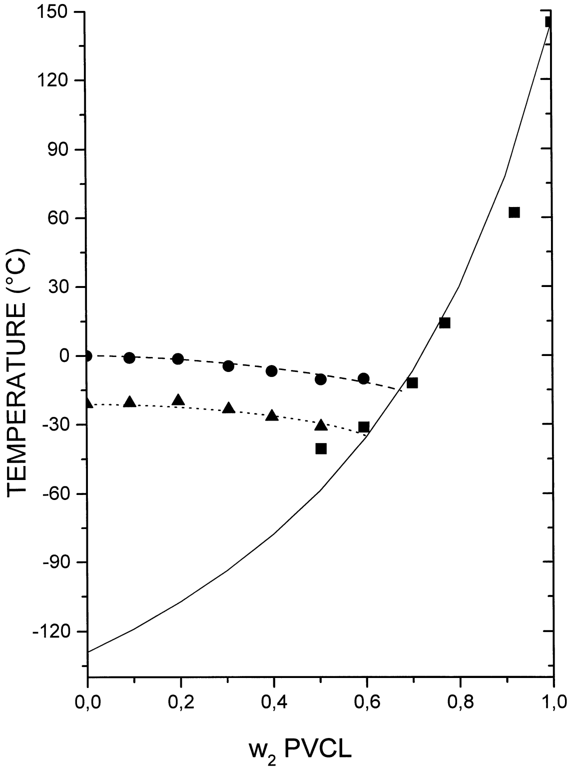

Fig. 3. Concentration dependence of the melting temperature (●) and the crystallisation temperature (▲) of water obtained by dynamic measurements, and glass transition temperature (■) in the system PVCL/water. The Fox equation is given by the solid curve. The dashed curve and the dotted curve were drawn as a guide to the eye.

With this procedure, the values shown in Table 2 were obtained for the interaction constants.

The results of the fitting procedure are shown in Fig. 2. Clearly, the fit between the experimental data and Eqs. 1 and 2 is excellent. However, the predicted phase behaviour for the systems PVCL1/H$_2$O and PVCL3/H$_2$O is not quantitative. The predicted change with molar mass is not as strong as what was found with the experimental data. Allowing for additional interaction constants, e.g. an additional reciprocal temperature dependence, does not result in a substantial improvement of the theoretical fit. We therefore restrict our theoretical considerations to the presented results. Inserting the values of the interaction constants and the predicted critical temperatures in Eq. (3) proves that the phase behaviour of the system PVCL/H$_2$O corresponds indeed to a Type I.

### 2.4. Crystallisation and melting behaviour of water in the system PVCL/water

The crystallisation and melting behaviour of water in an aqueous polymer system can be used to study the

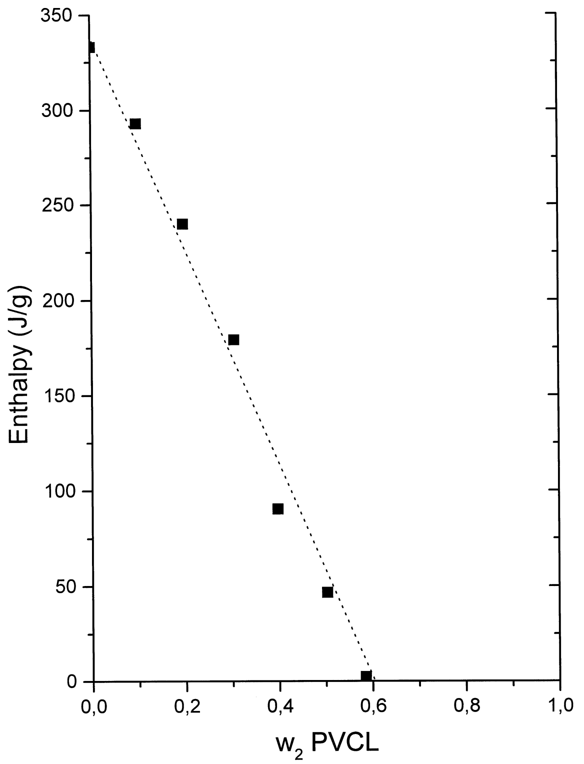

Fig. 4. Heat of melting of water ($\Delta H_{exp}$) per gram solution of PVCL/water samples as a function of polymer concentration: ■ : experimental data, - - - - : curve to show the tendency of $\Delta H_{exp}$ to go to zero at $w_2 = 0.6$.

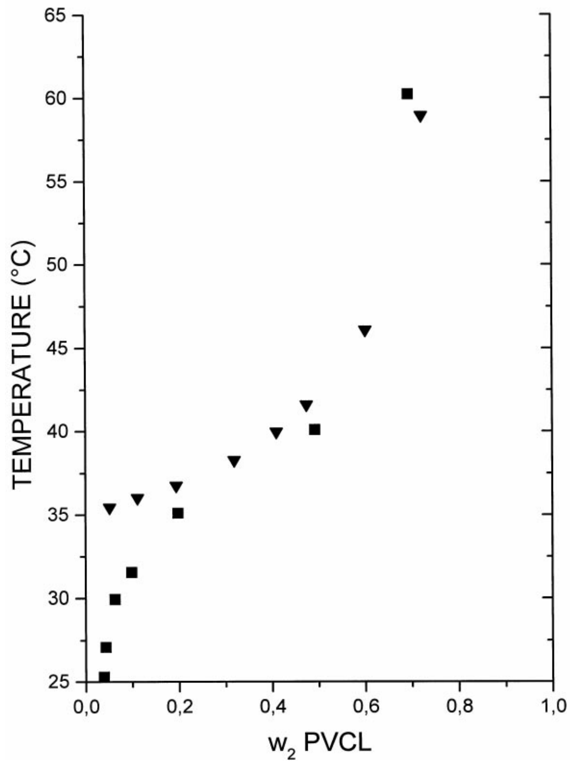

Fig. 5. Demixing curve of PVCL2/water system: DSC7 3°C/min (▼); swelling curve of chemically cross-linked PVCL in water (■, swelling data after reference [23]).

intermolecular interactions between water and the repeating units of the polymer chain [4]. A strong binding of water molecules to these chain units, resulting in the formation of a molecular complex, will prevent the crystallisation of a fraction of the water, present in the solution. In order to detect such complex formation, calorimetric experiments were performed on PVCL2 solutions with varying concentration.

The samples were cooled in the DSC from 20°C to −80°C at a scanning rate of 10°C/min. Subsequently, the samples were heated at the same scanning rate from −80°C to 20°C. From these experiments, several results can be derived. From the dynamic cooling run, the temperature at the onset of the crystallisation of water ($T_c$) as a function of the concentration is obtained and presented in Fig. 3. From the subsequent heating run, the melting temperature as well as the experimental heat of melting ($\Delta H_{exp}$) of water can be determined. The concentration dependence of the melting point of water is represented in Fig. 3 by the solid circles. The concentration dependence of $\Delta H_{exp}$ is represented in Fig. 4. Clearly, a linear decrease is observed and $\Delta H_{exp}$ tends to zero at a concentration of ca. $w_2 = 0.6$. This is shown in the figure by a dotted line.

### 2.5. The Glass transition temperatures of the PVCL solutions

The glass transition temperature, $T_g$, was measured as a function of polymer concentration. In the concentration range $0.6 < w_2 < 1$, the experimental data are accurately described by the Fox-equation [21]:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \qquad (5)$$

The solid curve in Fig. 3 represents the concentration dependence of the glass transition of the solutions ($T_g$). This curve is obtained using Eq. (5) and setting $T_{gPVCL} = 145°C$ ($T_{g1}$), determined experimentally, and $T_{gH_2O} = -133°C$ ($T_{g2}$) [22]. The $T_g$–$w_2$ relation intersects with the dashed curve, representing the liquidus of water, at $w_2 = 0.67$. The dotted curve, which represents the crystallisation, intersects with the $T_g$–$w_2$ relation at $w_2 = 0.6$.

## 3. Discussion

From the reported data, several conclusions can be drawn.

1. The calculations show that the system PVCL/water corresponds to a Type I miscibility behaviour. The LCST demixing curve shows a minimum that, if taken as the critical point, shifts to lower polymer concentrations with increasing polymer chain length.

The relation between the Type I behaviour and the swelling behaviour of the corresponding chemical networks is confirmed by the literature data depicted in Fig. 5 [23]. In this figure, the demixing behaviour PVCL2 is plotted together with the swelling data of a PVCL network, reported in the literature [23]. The continuous swelling behaviour coincides very well with the LCST demixing data. Further analysis is not feasible as detailed information on the network is missing. Measurements on the cross-linked PVCL are being performed in our workgroup.

2. The study of the melting behaviour of water leads to the conclusion that the formation of a stable complex between water and the chain repeating units could not be demonstrated. Such a complex would prevent the crystallisation of certain amounts of water. If any complex formation takes place, then such a complex is not stable enough to oppose crystallisation of bound water. Crystallisation of water vanishes at $w_2 = 0.6$ where $\Delta H_{\mathrm{exp}}$ becomes zero as a consequence of the interference of the crystallisation process with the vitrification of the solution (Fig. 4). This intersection of the crystallisation line with the $T_g$–$w_2$ relationship is illustrated in Fig. 3. During the crystallisation of water a separation between ice crystals and a more concentrated solutions takes place. This process of phase separation is stopped when the solution reaches a concentration that leads to vitrification. This limit for the crystallisation of water, has to be taken as the point of interference between the crystallisation temperature of water and vitrification point because of the dynamic character of the measurement that leads to a certain degree of undercooling.

## 4. Conclusions

1. The LCST demixing behaviour of the system PVCL/water a type I behaviour.
2. No conclusion can be drawn concerning complex formation between PVCL and water on the basis of the limitation in the crystallisation of water.

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## References

[1] Moerkerke R, Koningsveld R, Berghmans H, Dušek K, Šolc K. Macromolecules 1995;28:1103.
[2] Schäfer-Soenen H, Moerkerke R, Berghmans H, Koningsveld R, Dušek K, Šolc K. Macromolecules 1997;30:410.
[3] Moerkerke R, Meeussen F, Berghmans H, Koningsveld R, Mondelaers W, Schacht E, Dušek K, Šolc K. Macromolecules 1998;31:2223.
[4] Meeussen F, Bauwens Y, Moerkerke R, Nies E, Berghmans H. Polymer 1999, in press.
[5] Tanaka T. Phys Rev Lett 1978;87:1392.
[6] Ilavsky M. Macromolecules 1982;15:782.
[7] Hirasa O, Suzuki M. Adv Polym Sci 1993;110:241.
[8] Dušek K, editor, Responsive gels. Volume phase transition, Adv Polym Sci, 1993, vols. 109, 110.
[9] Afroze F, Nies E, Berghmans H. to be published.
[10] Eisele M, Burchard W. Makromol Chem 1990;191:169.
[11] Kirsh YuE, Yanul' NA, Kalninsh KK. Eur Polym J 1999;35:305.
[12] Flory PJ. J Chem Phys 1941;9:660.
[13] Flory PJ. J Chem Phys, 1942;10:51; 1944;12:425.
[14] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1953.
[15] Huggins ML. J Chem Phys 1941;9:440.
[16] Huggins ML. Ann NY Acad Sci 1942;43:1.
[17] Staverman AJ. Rec Trav Chim 1937;56:885.
[18] Staverman AJ. Rec Trav Chim 1941;60:640.
[19] Staverman AJ, Van Santen JH. Rec Trav Chim 1941;60:76.
[20] Hillegers LTME. The estimation of parameters in functional relationship models, PhD thesis, Eindhoven, 1986.
[21] Fox TG. Bull Am Phys Soc 1956;1:123.
[22] Brüggeler P, Mayer E. Nature 1980;288:569.
[23] Makhaeva EE, Thanh L, Starodoubtsev TM, Khokhlov SG. Macromolecules 1996;197:1973.
[24] Šolc K, Dušek K, Koningsveld R, Berghmans H. Coll Cz Chem Comm 1995;60:1661.
[25] Tager AA, Safronov AP, Sharina SV, Galaev IYu. Colloid Polymer Sci 1993;271:868–72.