Lower critical demixing of a polyketone in hexafluoroisopropanol

A. Wakker
*Koninklijke/Shell Laboratorium, Amsterdam (Shell Research B.V.), Badhuisweg 3,
1031 CM Amsterdam, The Netherlands*
(Received 23 January 1990; accepted 26 February 1990)

A static light scattering study has shown that the phase behaviour of a polyketone dissolved in hexafluoroisopropanol is governed by specific molecular interactions between the polymer and the solvent. Miscibility decreases with increasing temperature, leading to phase separation into two liquid phases (lower critical demixing) above 453 K. It is shown that phase separation is mainly driven by entropy effects associated with the formation of directional specific interactions.

(Keywords: static light scattering; specific interactions; thermodynamics; phase separation; polyketone)

INTRODUCTION

Ever since the phenomenon of lower critical demixing (phase separation upon heating) was observed in polymer solutions and melts, it has been a driving force for modifying the Flory–Huggins (F–H) expression for the free energy of mixing, which cannot predict this type of phase behaviour in its original formulation[1]. The F–H expression for the free energy of mixing expression consists of two competing terms: a mean field type combinatorial entropy of mixing term $-T\Delta S_{\mathrm{mix}}$, which is favourable for mixing because ΔS_{mix} is positive, and an unfavourable, dispersive interaction term ΔH_{mix}, which is always positive in this theory and which can be modelled by means of the well known binary interaction parameter χ. The entropy of mixing term will always win the competition between the two terms at high temperatures, so that miscibility will increase with increasing temperature. Consequently, lower critical demixing cannot be described by this theory.

By regarding the interaction parameter χ as a free energy parameter rather than as an energy parameter, thus introducing an enthalpic part χ_h and an entropic part χ_s, one can modify the model in order to predict phase separation upon heating as well. It has been shown that lower critical demixing can be caused either by the compressible nature of polymer solutions and melts[2], or by the formation of specific interactions between unlike molecules[3], or, obviously, by a combination of both[4].

From an experimental point of view, the measurement of polymer–polymer interactions may certainly help to provide more insight into the physics behind the contribution of various interactions to the free energy of mixing. For a straightforward determination of interaction parameters in polymer systems, the small angle neutron scattering technique (SANS)[5–7], as well as the static light scattering technique[8–10], are particularly suited. The SANS technique has perhaps the disadvantage that deuteration has a (small) influence on the phase diagram, while the difficulty with static light scattering is that it requires a dust-free sample preparation procedure.

In general, we define polyketones as copolymers of carbon monoxide and one or more olefinically unsaturated compounds. In the present study, we use a special type of polyketone, namely a linear, alternating CO/ethane copolymer of repeating formula $-CH_2CH_2C(=O)-$. For convenience, we will refer to this polymer as polyketone.

Hexafluoroisopropanol (HFIPA), $(CF_3)HCOH(CF_3)$, happens to be one of the few solvents that can dissolve this crystalline polymer at room temperature. In this paper, the temperature dependence of the interaction parameter χ of a dilute solution of polyketone dissolved in HFIPA will be discussed. χ parameter values have been obtained from the osmotic second virial coefficients, determined from standard static-light-scattering analysis[8–10]. The observed temperature dependence of the χ parameter indicated that the mixture would phase separate upon heating well above the boiling point of HFIPA. Therefore, a separate cloud point experiment in a sealed off tube was carried out in order to determine the lower critical demixing temperature of this mixture.

The temperature range in which the χ parameter was measured by means of static light scattering together with the cloud point experiment allows a fit of the experimental data to theoretical predictions. It will be investigated whether the data can be described in terms of the compressible nature of this system or by certain effects associated with the formation of specific interactions in this polar mixture.

RESULTS

The static light scattering experiments were performed with an automatic goniometer together with accompanying hardware and optics (from ALV Laservertriebsges, mbH), which can be accurately aligned for static measurements using a procedure adapted from Bantle *et al.*[11]. The laser used was an argon ion laser operating at a wavelength of 514.5 nm at a power of 200 mW, which allows very rapid measurement. Spurious fluorescence was suppressed by using an appropriate filter. Refractive index increments were measured using a differential

0032-3861/91/020279-05

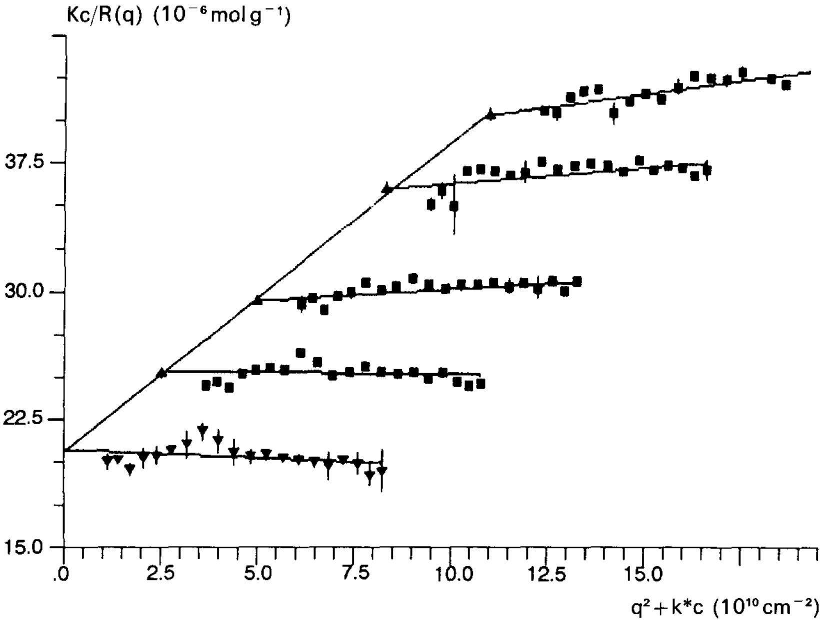

Figure 1 Zimm plot of polyketone in HFIPA at 296 K

refractometer. A typical Zimm plot of polyketone in HFIPA is shown in *Figure 1*. The molecular weight of the polymer sample used here ($M_w = 49\,000$) was too low to determine a radius of gyration. Values of the osmotic second virial coefficient A_2, which contains all information on the contributions of binary interactions to the free energy of mixing, could be determined from an extrapolation to $q = 0$ for temperatures between 283 and 323 K (the boiling point of HFIPA is 332 K)[8–10].

By using the following expression for the interaction parameter χ, which can be derived from the Flory–Huggins theory[12]:

$$\chi = 1/2 - A_2(V_m/V_{pol}^2) \qquad (1)$$

the χ parameter can be determined from the measured A_2 values. V_{pol} is the specific volume of the polymer and V_m is the molar volume of the solvent (*Table 1*). Results are shown in *Figure 2*. The binary interaction parameter χ is negative at ambient temperature, which means that the enthalpy of mixing term ΔH_{mix} is favourable for mixing in this system, i.e. heat is released upon mixing. This is indicative of the existence of specific molecular interactions, most likely between the carbonyl group in the polymer chain and the hydroxyl group in HFIPA.

The χ parameter was observed to increase with increasing temperature and to become positive, and thus, unfavourable for mixing, at temperatures higher than approximately 340 K. We expected that the mixture would phase separate when, by further heating, χ would become as high as the critical value for polymer solutions $\chi_c = 0.5$[2]. Following up this idea, we prepared a 1% high-molecular-weight ($M_w \approx 10^6$) solution, which was then sealed off in a glass tube suited for high pressures. Phase separation into two liquid phases was observed at 453 K. Because the volumes of the two separated liquid phases appeared to be approximately equal, we concluded that the solution was close to the critical concentration. This means that the observed lower critical demixing temperature (453 K) corresponds to a χ parameter value of 0.5, which is shown in *Figure 3*. By

Table 1 Physical properties of polyketone and HFIPA

	Polyketone	HFIPA
V_{pol} (cm^3 g^{-1})	0.81	
V_m (cm^3 mol^{-1})		105
α (10^{-4} K^{-1})	6.3	15.2
δ (J/(cm^3))$^{1/2}$)	24.2	18.2

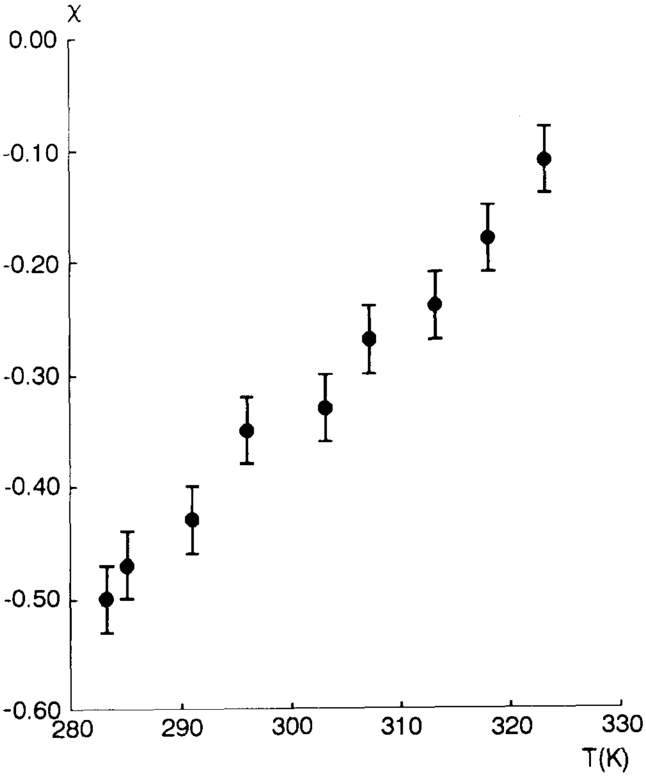

Figure 2 Interaction parameter χ of polyketone in HFIPA as a function of temperature

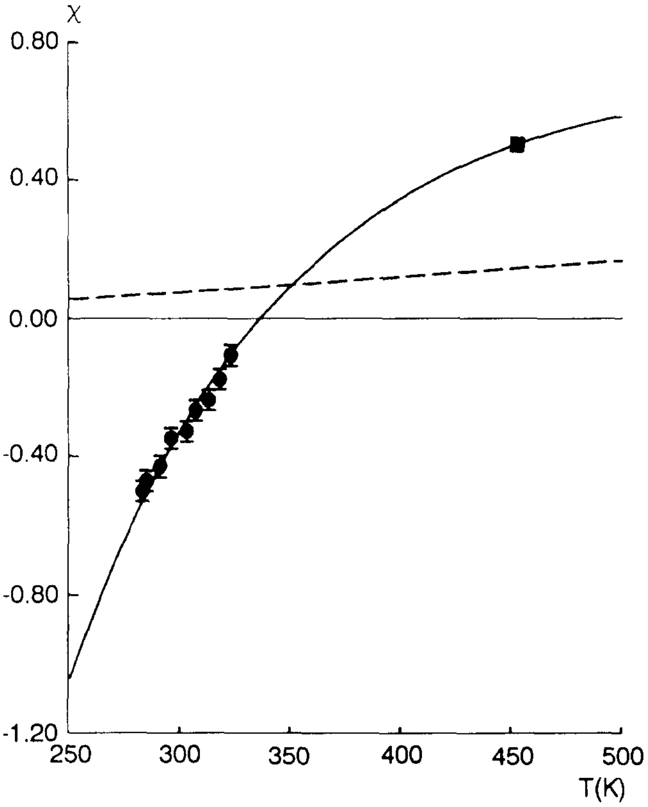

Figure 3 Test of thermodynamic models against the experimental data: ●, light scattering data; ■, lower critical demixing temperature (cloud point observation); – – – –, free volume effects (equation 2); ———, specific interactions (equation 6)

means of a model vapour pressure calculation, we could estimate the vapour pressure of HFIPA at 453 K to be 25 bar.

DISCUSSION

We now come to the interesting question whether the observed trends in the χ parameter can be understood in terms of certain interactions that govern the phase behaviour of this system.

For non-polar systems, where we are dealing with dispersive interactions exclusively, lower critical demixing can only be caused by the compressible nature of polymer solutions (and also, although to a lesser extent, of polymer blends). The reason for this has been discussed by, amongst others, Sanchez[2], who has shown that the compressible part of the free energy of mixing is always unfavourable for mixing. Because the magnitude of this effect increases with increasing temperature, it will lead to lower critical demixing.

Although it can be expected that the phase behaviour of polyketone in HFIPA will largely be determined by polar interactions, compressibility effects cannot be ruled out *a priori*. However, from theoretical calculations[13,14], as well as experimental data on cloud point curves and spinodals of polymer solutions[15,16], it is found that the effect of pressure on the phase diagram of polymer solutions is in the order of 0.1 K/bar. In our case, it can thus be expected that the 25 bar vapour pressure may affect the observed lower critical demixing point by only about three degrees. Thus, the effect of pressure on the phase diagram is quite small and lower critical demixing can certainly not be explained by it.

Besides the bare pressure effect, the free volume difference between polymer and solvent also contributes to the compressible part of the free energy of mixing[2,13,14]. The order of magnitude of the free volume effects can be quite easily calculated using a model in which the free volume difference is expressed in terms of the difference between the thermal expansion coefficients α of polymer and solvent[14]. The magnitude χ_{free} of free volume effects on the interaction parameter can be expressed as[14]:

$$\chi_{\text{free}} = \frac{(V_r)_1^{1/3}}{2(4/3 - (V_r)_1^{1/3})}\tau^2 \qquad (2)$$

where $(V_r)_1$ is the reduced volume of the solvent defined by

$$(V_r)_1^{1/3} = 1 + [\alpha_1 T/3(1 + \alpha_1 T)] \qquad (3)$$

The free volume difference τ is given by

$$\tau = 1 - (T_r)_2/(T_r)_1 \qquad (4)$$

where $(T_r)_2$ and $(T_r)_1$ are reduced temperatures of polymer and solvent, respectively, which are related to the reduced volumes by the equation of state:

$$T_r = (V_r^{1/3} - 1)/V_r^{4/3} \qquad (5)$$

Using experimental values of the thermal expansion coefficients of polyketone and HFIPA (*Table 1*), χ_{free} could be calculated as a function of temperature. The result is shown in *Figure 3* (dashed line). χ_{free} increases from 0.06 at 250 K to 0.16 at 500 K. In comparison with the experimental data, it is a slowly increasing background term which cannot describe the observed trend in the χ parameter.

Obviously, both pressure and free volume effects play only a minor role in the phase behaviour of this system. The main cause of the lower critical demixing in this particular mixture must be sought instead in the losses of degrees of freedom due to the formation of specific interactions in polar systems. Although a specific interaction may be favoured enthalpically, it is entropically unfavourable because degrees of freedom are 'frozen in' in one specific interaction channel. This leads to an additional, positive entropy term $-T\Delta S_{\text{spec}}$ in the free energy of mixing expression. Compared to the enthalpy loss on forming a specific interaction (negative heat of mixing effect), this unfavourable entropy loss will become more prominent with increasing temperature and will finally lead to demixing[3,4,17–19].

The effect of entropy loss in the formation of specific interactions has been taken into account in an elegant and simple model proposed by Ten Brinke and Karasz[19]. The essence of this model can perhaps most easily be summarized as follows. Two different monomers A and B can either form a specific interaction with an energy $U_1 < 0$, or form a repulsive interaction with energy $U_2 > 0$. It is assumed that a specific interaction is formed only when the monomers are in the same state in configuration space (for instance, a certain orientation). If there are q different states available for each monomer, then a specific interaction can only be formed in q ways, whereas a repulsive interaction can be formed in $q(q-1)$ ways. The entropy loss due to the formation of a specific interaction (assuming that q is large) is thus proportional to $\ln(q)$. The more degrees of freedom a monomer has, the higher the price that has to be paid for forming a specific interaction. Within the framework of the original Flory–Huggins formulation, taking into account the above mentioned effects, one can show that the expression for the interaction parameter χ now becomes[19]:

$$\chi = \chi(z, q, U_1, U_2) = z[(1/RT)U_2 + \ln(1-\lambda) + \ln((q+1)/q)] \quad (6)$$

where z is a lattice coordination number and λ is the fraction of directional specific interactions, given by

$$\lambda = [1 + q\exp((U_1 - U_2)/RT)]^{-1} \quad (7)$$

The repulsive interaction U_2 can be modelled by using the solubility parameter concept for dispersive forces[20]:

$$U_2 = V_m(\Delta\delta)^2 \quad (8)$$

where $\Delta\delta$ is the solubility parameter difference between polymer and solvent. In our case, the solubility parameters of polyketone and HFIPA can be calculated using Small's group contribution scheme[21]. The values are listed in *Table 1*. From the rather large solubility parameter difference $\Delta\delta = 6.0$ $(\mathrm{J/cm^3})^{1/2}$, a value for the repulsive interaction parameter $U_2 = 3.78$ kJ mol^{-1} could be obtained. By using this value as an input parameter, and ignoring the small compressibility effects, equation (6) was fitted to the datapoints, and the result is shown in *Figure 3* (solid line).

From the fit, the following values for the three remaining parameters have been found. The enthalpy of formation of the specific interaction amounts to $U_1 = -3.85$ kJ/mol. The value for the degrees of freedom parameter $q = 3.94$, and the lattice coordination number $z = 3.1$.

Although we believe that, within the approximations involved in lattice theory, the parameter values must be regarded as mainly phenomenological, they do have rather realistic values. An interaction enthalpy of -3.85 kJ mol^{-1} is indicative of a moderately polar interaction[22]. Also, the value of the q parameter is quite low compared to values found in low-molecular-weight systems[22]. Ten Brinke and Karasz[19] already expected that q should be quite low for polymer systems, because monomers in a polymer chain already have few degrees of freedom and therefore, the entropy loss on forming a specific interaction should remain small. To the best of our knowledge, this is the first experimental observation of this effect. Although the specific value found for the lattice coordination number is not unrealistic, it cannot be expected that this value directly reflects the real coordination of HFIPA molecules around the polyketone chain, on account of the semi-empirical character of the model used.

Finally, it is interesting to separate the interaction parameter χ into the sum of an enthalpic component χ_h and an entropic component χ_s by using the thermodynamic identities

$$\chi_h = -T\partial\chi/\partial T \qquad \chi_s = \partial(T\chi)/\partial T \quad (9)$$

The explicit expressions are given by Ten Brinke and Karasz[19], and the results are shown in *Figure 4*.

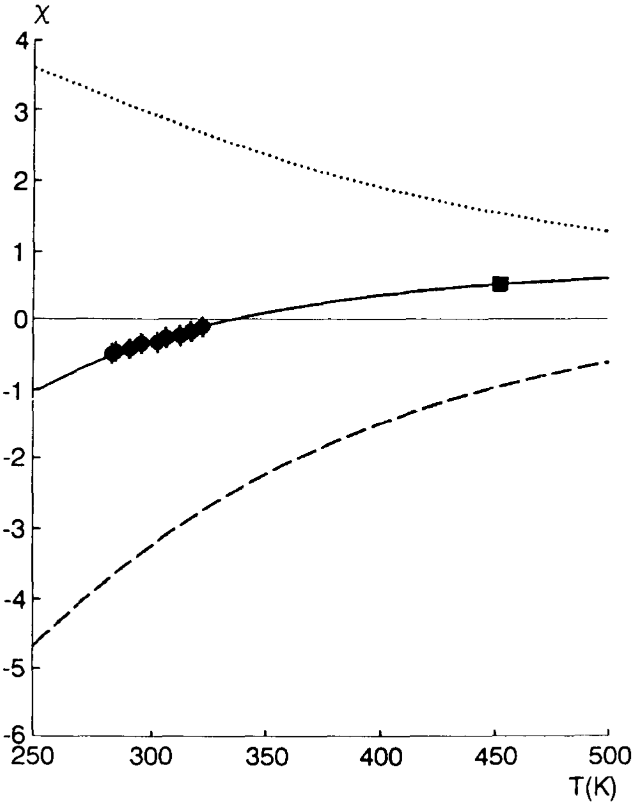

Figure 4 Separation of the χ parameter into enthalpic (- - - -, χ_h) and entropic (·····, χ_s) contributions

There is a competition between a large negative enthalpic term, which is favourable for mixing and which represents the enthalpic effect of forming specific interactions, and a large unfavourable entropic term, which represents the entropy loss on forming specific interactions. The sum of these terms results in a net χ parameter which is relatively small. Lower critical demixing is caused by the fact that the unfavourable entropy loss due to the formation of directional specific interactions becomes relatively more important with increasing temperature.

CONCLUSIONS

By means of static light scattering experiments over a certain temperature range, together with a cloud point observation, we have been able to determine the temperature dependence of the interaction parameter χ in a solution of polyketone in HFIPA. It is shown that the results can only be described by means of a thermodynamic model in which the formation of specific interactions is taken into account. In particular, it is shown that the observed lower critical demixing behaviour is driven by the entropy loss due to the formation of specific interactions. The number of ways in which a directional specific interaction can be formed (represented by the degrees of freedom parameter q) is quite low compared to the values found in low molecular weight systems. This is probably an intrinsic property of polymer systems. Compressibility effects only play a minor role in the phase behaviour of this system.

ACKNOWLEDGEMENTS

The author would like to thank M. A. van Dijk and R. Reijnhart for helpful discussions, V. Hommels for preparing dust-free samples, and M. G. W. M. Seelen for measuring refractive index increments.

REFERENCES

1 Flory, P. J. 'Principles of Polymer Chemistry', Cornell, London, 1953

2 Sanchez, I. C. in 'Polymer Compatibility and Incompatibility: Principles and Practices', (Ed. K. Solc), Harwood, New York, 1982; MMI Symp. Ser., Vol. 3

3 Walsh, D. J. and Rostami, S. *Advances in Polymer Science* 1985, **70**, 121

4 Sanchez, I. C. and Balazs, A. C. *Macromolecules* 1989, **22**, 2325

5 Lapp, A., Picot, C. and Benoit, H. *Macromolecules* 1985, **18**, 2437

6 Tomlins, P. E. and Higgins, J. S. *Macromolecules* 1988, **21**, 425

7 Han, C. C., Bauer, B. J., Clark, J. C., Muroga, Y., Matsushita, Y., Okada, M., Tran-cong, Q., Chang, T. and Sanchez, I. C. *Polymer* 1988, **29**, 2002

8 Su, A. C. and Fried, J. R. *Macromolecules* 1986, **19**, 1417

9 Park, I. H., Wang, Q. W. and Chu, B. *Macromolecules* 1987, **20**, 1965

10 Chu, B., Park, I. H., Wang, Q. W. and Wu, C. *Macromolecules* 1987, **20**, 2833

11 Bantle, S., Schmidt, M. and Burchard, W. *Macromolecules* 1982, **15**, 1604

12 Fukuda, T., Nagata, M. and Inagaki, H. *Macromolecules* 1984, **17**, 548

13 McMaster, L. P. *Macromolecules* 1973, **6**, 761

14 Patterson, D. and Robard, A. *Macromolecules* 1978, **11**, 691

15 De Loos, Th. W., *Ph.D. Thesis*, Technical University Delft, 1981

16 Kiepen, F. and Burchard, W. *Macromolecules* 1988, **21**, 1784

17 Howe, S. E. and Coleman, M. M. *Macromolecules* 1986, **19**, 72

18 Sham, C. K. and Walsh, D. J. *Polymer* 1987, **28**, 804

19 Ten Brinke, G. and Karasz, F. E. *Macromolecules* 1984, **17**, 815

20 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979

21 Small, P. A. *J. Appl. Chem.* 1953, **3**, 71

22 Goldstein, R. E. and Walker, J. S. *J. Chem. Phys.* 1983, **78**, 1492