

# On the excess volume in polymer blends

Hans-Werner Kammer

Department of Chemistry, Dresden University of Technology, Mommsenstrasse 13,  
DDR-8027 Dresden, Germany

(Received 11 December 1989; accepted 26 February 1990)

A refined version of an equation-of-state theory developed earlier to explain the simultaneous occurrence of upper and lower critical solution temperatures (*UCST* and *LCST*) in miscible polymer blends has been extended to discuss the volume of mixing. The theory explains the recently observed positive excess volumes in miscible polymer blends. A characteristic of the theory is the so-called size effect resulting from the differences in the sizes of the segments and represented by the parameter  $\rho$ . When the size effect is negligible, only negative excess volumes occur. With increasing parameter  $\rho$ , however, the excess volume may change for miscible polymers to positive values. As a rule, positive volumes of mixing may be expected when the gap between *UCST* and *LCST* is small.

(Keywords: excess volume; polymer blends; thermodynamics; miscibility; upper and lower critical solution temperatures)

## INTRODUCTION

Generally, as in the case of low-molecular-weight mixtures, mixing of polymers is accompanied by volume changes. For mixtures of low-molecular-weight compounds, one observes both positive and negative volume changes. Owing to the intimate contact between the different molecules in miscible polymer blends, one expects, in the first instance, for miscible polymers, a negative excess volume. This has been confirmed experimentally for blends of poly(ether sulphones) and poly(ethylene oxide) and blends of poly(ethylene-co-vinyl acetate) and chlorinated polyethylenes<sup>1,2</sup>. Similar results were reported for the binary systems poly(propylene oxide)/polystyrene<sup>3</sup> and for poly(vinyl nitrate)/poly(vinyl acetate)<sup>4</sup>. Nevertheless, our knowledge of volume changes during mixing of polymers is scant.

Recently, Wendorff *et al.*<sup>5,6</sup> have reported very precise and reliable results on excess volumes for poly(vinylidene fluoride) (PVDF) blended either with poly(methyl methacrylate) (PMMA) or poly(ethyl acrylate). Surprisingly, for these miscible systems, the excess volumes are positive, in contradiction to generally accepted expectations.

In some miscible polymer blends the simultaneous occurrence of upper (*UCST*) as well as lower critical solution temperatures (*LCST*) can be observed. This behaviour can be readily explained in terms of a refined version of an equation-of-state theory<sup>7</sup>. (This paper will be referred to as I in the following.) The essence of this theory is a generalized interaction parameter, which is ruled by three contributions: (i) the segmental interaction represented by the parameter  $X_{AB}$ ; (ii) the free-volume effect arising from the different free volumes of the components and represented by the parameter  $\Gamma$ ; and (iii) the size effect resulting from the differences in the sizes of the segments and represented by the parameter  $\rho$ . The gap between *LCST* and *UCST* depends highly on the parameter  $\rho$ . With increasing size effect, the *UCST* and *LCST* approach and, finally, merge into an hour-glass-shaped binodal.

When one calculates, in the context of this theory, the excess volume to the same approximation as the Gibbs free energy of mixing in paper I, it is found that the volume of mixing also depends sensitively on the parameter  $\rho$ . When the size effect is negligible in miscible polymers, then the excess volume of mixing,  $\Delta V^E$ , is indeed negative. With increasing  $\rho$ , however, the sign of  $\Delta V^E$  may change for miscible systems. This will be discussed in more detail in the following. As will be shown below, even small values of  $\rho$  may have large effects on the sign and the value of  $\Delta V^E$ .

## THEORY

### Excess volume

The excess volume  $\Delta V^E$  of a binary system is given by:

$$\Delta V^E = \phi_A(V_A - V_{AA}) + \phi_B(V_B - V_{BB}) \quad (1)$$

where  $\phi_i$  is the volume fraction of component  $i$  and the quantities  $V_i$  and  $V_{ii}$  represent the partial specific volume and the specific volume of constituent  $i$ , respectively. In the context of the theory presented in I, the basic quantities characterizing the thermodynamic state of a system are the reduced quantities  $\tilde{Y}$  defined by:

$$\tilde{Y} \equiv Y/Y^* \quad (2)$$

where  $Y$  is a thermodynamic quantity and  $Y^*$  an accompanying reference parameter. If the interaction energy of a pair of segments belonging to  $r$ -mers is expressed by a general function with two scale factors,  $\varepsilon^*$  and  $r^*$ , which represent the coordinates of the minimum of the potential function and are characteristic of the molecular species, then the reference parameters can be represented by the same scale factors. For the reference volume  $V^*$  it follows that:

$$V^* = r^{*3} \quad (3)$$

Using equation (3) in equation (1), one obtains with  $\langle \tilde{V} \rangle \equiv V/\langle r^* \rangle^3$ :

$$V_i - V_{ii} = \langle r_i^* \rangle^3 \langle \tilde{V}_i \rangle - \langle r_{ii}^* \rangle^3 \langle \tilde{V}_{ii} \rangle \quad i = A, B \quad (4)$$

where the quantities  $\langle r^* \rangle$  are average composition-dependent quantities defined in I. We may expand the quantity  $\langle \tilde{V}_i \rangle$  in powers of  $1/\langle \tilde{T}_{AA} \rangle$  around  $\langle \tilde{V}_{AA} \rangle$  at  $\tilde{P} = 0$ . It follows that:

$$\begin{aligned} \langle \tilde{V}_i \rangle \langle \tilde{T}_i \rangle &= \langle \tilde{V}_{AA} \rangle + \left( \frac{\partial \langle \tilde{V}_i \rangle}{\partial (1/\langle \tilde{T} \rangle)} \right)_{AA} \frac{1}{\langle \tilde{T}_{AA} \rangle} \\ &\times \left( \frac{\langle \tilde{T}_{AA} \rangle}{\langle \tilde{T}_i \rangle} - 1 \right) + \frac{1}{2} \left( \frac{\partial^2 \langle \tilde{V}_i \rangle}{\partial (1/\langle \tilde{T} \rangle)^2} \right)_{AA} \\ &\times \frac{1}{\langle \tilde{T}_{AA} \rangle^2} \left( \frac{\langle \tilde{T}_{AA} \rangle}{\langle \tilde{T}_i \rangle} - 1 \right)^2 \quad i = A, B \end{aligned} \quad (5)$$

An analogous expression exists when  $\langle \tilde{V}_{BB} \rangle$  is expanded in the same way. The reduced quantity  $\langle \tilde{T} \rangle$  is defined according to equation (2) as  $\langle \tilde{T} \rangle \equiv T/\langle \tilde{T}^* \rangle$  where:

$$\langle \tilde{T}^* \rangle \sim \langle \varepsilon^* \rangle \quad (6)$$

Inserting equation (6) into equation (5) one arrives at:

$$\begin{aligned} \langle \tilde{V}_i \rangle \langle \tilde{T}_i \rangle &= \langle \tilde{V}_{AA} \rangle - \left( \frac{\partial \langle \tilde{V}_i \rangle}{\partial \langle \tilde{T} \rangle} \right)_{AA} \langle \tilde{T}_{AA} \rangle \left( \frac{\langle \varepsilon_i^* \rangle}{\langle \varepsilon_{AA}^* \rangle} - 1 \right) \\ &+ \frac{1}{2} \left( \frac{\partial^2 \langle \tilde{V}_i \rangle}{\partial \langle \tilde{T} \rangle^2} \right)_{AA} \langle \tilde{T}_{AA} \rangle^2 \left( \frac{\langle \varepsilon_i^* \rangle}{\langle \varepsilon_{AA}^* \rangle} - 1 \right)^2 \end{aligned} \quad i = A, B \quad (7)$$

As can be seen easily from equations (4) and (7), the excess volume (1) is governed by the ratios  $\langle r_i^* \rangle^3/\langle r_{AA}^* \rangle^3$ ,  $\langle r_{BB}^* \rangle^3/\langle r_{AA}^* \rangle^3$ ,  $\langle \varepsilon_i^* \rangle/\langle \varepsilon_{AA}^* \rangle$  and  $\langle \varepsilon_{BB}^* \rangle/\langle \varepsilon_{AA}^* \rangle$  ( $i = A, B$ ). In I, it has been shown that these ratios can be represented by the three parameters  $X_{AB}$ ,  $\Gamma$  and  $\rho$  mentioned above. Second-order contributions to  $\rho$  were only taken into account for the ratios  $\langle \varepsilon_i^* \rangle/\langle \varepsilon_{AA}^* \rangle$ . This is adequate when one calculates the Gibbs free energy of mixing. Here, however, one has also to pay attention to second-order terms of the ratios  $\langle r_i^* \rangle/\langle r_{AA}^* \rangle$ , because the quantity  $(\langle \tilde{V}_i \rangle - \langle \tilde{V}_{ii} \rangle)$  enters into the Gibbs free energy of mixing only in the second order, whereas the excess volume depends linearly on this quantity. As an extension to equation (8) of I one gets:

$$\frac{\langle r_A^* \rangle}{\langle r_{AA}^* \rangle} = \left( \frac{\phi_A + \phi_B (\langle \varepsilon_{AB}^* \rangle / \langle \varepsilon_{AA}^* \rangle) (\langle r_{AB}^* \rangle / \langle r_{AA}^* \rangle)^{12}}{\phi_A + \phi_B (\langle \varepsilon_{AB}^* \rangle / \langle \varepsilon_{AA}^* \rangle) (\langle r_{AB}^* \rangle / \langle r_{AA}^* \rangle)^6} \right)^{1/6} \quad (8)$$

If one neglects the second-order terms in  $X_{AB}\rho$ ,  $X_{AB}\Gamma$  and  $X_{AB}^2$ , as in I, and uses the definitions:

$$\begin{aligned} \Gamma &\equiv \frac{\langle \varepsilon_{BB}^* \rangle}{\langle \varepsilon_{AA}^* \rangle} - 1 & \rho &\equiv \frac{\langle r_{BB}^* \rangle}{\langle r_{AA}^* \rangle} - 1 \\ X_{AB} &\equiv \frac{1}{2} \left( 1 + \frac{\langle \varepsilon_{BB}^* \rangle}{\langle \varepsilon_{AA}^* \rangle} \right) - \frac{\langle \varepsilon_{AB}^* \rangle}{\langle \varepsilon_{AA}^* \rangle} \\ R_{AB} &\equiv \frac{1}{2} \left( 1 + \frac{\langle r_{BB}^* \rangle}{\langle r_{AA}^* \rangle} \right) - \frac{\langle r_{AB}^* \rangle}{\langle r_{AA}^* \rangle} = 0 \end{aligned} \quad (9)$$

equation (8) can be written as:

$$\frac{\langle r_A^* \rangle}{\langle r_{AA}^* \rangle} = \left( \frac{\phi_A + \phi_B (1 + \Gamma/2) (1 + \rho/2)^{12}}{\phi_A + \phi_B (1 + \Gamma/2) (1 + \rho/2)^6} \right)^{1/6} \quad (10)$$

Therefore, one arrives at:

$$\left( \frac{\langle r_A^* \rangle}{\langle r_{AA}^* \rangle} \right)^3 = 1 + \frac{3}{2} \phi_B \rho \left[ 1 + \frac{\Gamma}{2} \phi_A + \frac{\rho}{2} \left( 1 + \frac{15}{2} \phi_A \right) \right] \quad (11)$$

and analogously it follows that:

$$\begin{aligned} \left( \frac{\langle r_B^* \rangle}{\langle r_{AA}^* \rangle} \right)^3 &= 1 + 3\rho - \frac{3}{2} \phi_A \rho \\ &\times \left[ 1 - \frac{\Gamma}{2} \phi_B - \frac{17}{4} \phi_B \rho - \frac{2\rho}{\phi_A} \left( 1 - \frac{\phi_A}{2} \right)^2 \right] \\ \left( \frac{\langle r_{BB}^* \rangle}{\langle r_{AA}^* \rangle} \right)^3 &= 1 + 3\rho + 3\rho^2 \end{aligned} \quad (12)$$

The remaining ratios are taken from I (equations (14) and (16)):

$$\begin{aligned} \frac{\langle \varepsilon_A^* \rangle}{\langle \varepsilon_{AA}^* \rangle} &= 1 + \frac{\phi_B}{2} \Gamma - \phi_B X_{AB} - 9\rho^2 \phi_A \phi_B \\ \frac{\langle \varepsilon_B^* \rangle}{\langle \varepsilon_{AA}^* \rangle} &= 1 + \left( \phi_B + \frac{\phi_A}{2} \right) \Gamma - X_{AB} \phi_A - 9\rho^2 \phi_A \phi_B \end{aligned} \quad (13)$$

$\langle \varepsilon_{BB}^* \rangle/\langle \varepsilon_{AA}^* \rangle$  is given simply by equation (9). To simplify the notation we put, in equation (7),  $\langle \tilde{V}_{AA} \rangle \equiv \tilde{V}_A$  and  $\langle \tilde{T}_{AA} \rangle \equiv \tilde{T}_A$ . Applying Flory's equation-of-state theory at  $\tilde{P} = 0^8$ :

$$\tilde{T} = \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^{4/3}} \quad (14)$$

one obtains:

$$\begin{aligned} \left( \tilde{T} \frac{\partial \tilde{V}}{\partial \tilde{T}} \right)_A &= \frac{\tilde{V}_A (\tilde{V}_A^{1/3} - 1)}{\frac{4}{3} - \tilde{V}_A^{1/3}} \\ \left( \tilde{T}^2 \frac{\partial^2 \tilde{V}}{\partial \tilde{T}^2} \right)_A &= \frac{\tilde{V}_A^{2/3} (\tilde{V}_A^{1/3} - 1)^2}{2(\frac{14}{9} - \tilde{V}_A^{1/3})} \end{aligned} \quad (15)$$

Finally, inserting all the expressions (11)–(13) and (15) into equations (7) and (4), respectively, one gets for the excess volume (1) after simple manipulations:

$$\begin{aligned} \frac{\Delta \tilde{V}^E}{\phi_A \phi_B \tilde{V}_A} &= \frac{3}{4} \rho \left( \Gamma + \frac{11}{9} \rho \right) + \frac{\tilde{V}_A^{1/3} - 1}{\frac{4}{3} - \tilde{V}_A^{1/3}} (2X_{AB} + 9\rho^2 + \frac{9}{4} \rho \Gamma) \\ &+ \frac{(\tilde{V}_A^{1/3} - 1)^2}{\tilde{V}_A^{1/3} (\frac{14}{9} - \tilde{V}_A^{1/3})} \frac{3}{16} \Gamma^2 \end{aligned} \quad (16)$$

The reduced volume  $\tilde{V}^{1/3}$  varies in the range 1–4/3 when the temperature increases from  $T = 0$  K to infinity. As may be concluded from equation (16), at low temperatures the relative excess volume approaches a constant value. With increasing temperature, the second term of equation (16) becomes more and more dominant.

#### Gap between UCST and LCST

In the limit in which the degree of polymerization tends to infinity, the Gibbs free energy of mixing for a binary polymer mixture is given by:

$$\Delta G^M/RT = \phi_A \phi_B X \quad (17)$$

The free energy parameter  $X$  was calculated in I:

$$X = \frac{\tilde{V}_A^{1/3}}{\tilde{V}_A^{1/3} - 1} \left( X_{AB}^T + \frac{\frac{4}{3} - \tilde{V}_A^{1/3}}{\tilde{V}_A^{1/3} - 1} \frac{9}{16} \rho^2 \right) + \frac{\tilde{V}_A^{1/3}}{\frac{4}{3} - \tilde{V}_A^{1/3}} \frac{7}{16} \Gamma^2 \quad (18)$$

where

$$X_{AB}^T = X_{AB} + \frac{9}{2} \rho^2 - \frac{3}{8} \Gamma \rho \quad (18a)$$

The locations of the *UCST* and *LCST* result from  $X = 0$ , when the degree of polymerization tends to infinity. From equation (18) it follows to a good approximation that:

$$\text{UCST: } \tilde{V}_A^{1/3} = 1 + \frac{\frac{3}{16}\rho^2}{\frac{9}{16}\rho^2 - X_{AB}^T} \quad (19)$$

$$\text{LCST: } \tilde{V}_A^{1/3} = \frac{4}{3} - \frac{\frac{7}{48}\Gamma^2}{\frac{7}{16}\Gamma^2 - X_{AB}^T} \quad (20)$$

In this approximation the positions of the *UCST* and *LCST* are governed by the positions of the parameters  $\rho$  and  $\Gamma$ , respectively, which means that the *UCST* is caused by the enthalpic contribution associated with the hard-core repulsion at low temperatures or the size effect, whereas the *LCST* behaviour is an entropy-driven process related to the free-volume effect.

## DISCUSSION

As can be seen from equations (17) and (18), for miscible polymers, the interaction parameter has to be negative. When the size effect is negligible for a miscible pair of polymers, i.e.  $\rho = 0$  and  $X_{AB} < 0$ , then equation (16) shows that the excess volume of mixing,  $\Delta V^E$ , is negative. However, with increasing  $\rho$  the sign of  $\Delta V^E$  will change whereas  $\Delta G^M$  keeps the same sign, i.e. the blend remains miscible. This is demonstrated in Figure 1. As shown in I, the system is miscible for the parameters used and over the whole range of the parameter  $\rho$  depicted in Figure 1. The volume of mixing, however, changes sign.

Positive volumes of mixing were observed in blends of PMMA and PVDF, as mentioned above<sup>5,6</sup>. The phase diagram of the system<sup>9</sup> is shown in Figure 2. The system displays simultaneously *LCST* and *UCST*, which means that the size effect has to be taken into consideration. The *LCST* and *UCST* are reported to be at about 325 and 140°C, respectively, for 50/50 blends<sup>9</sup>. These data can be used to estimate, from equations (19) and (20), the parameters  $X_{AB}$  and  $\rho$ . As the reference substance A we choose the polymer PMMA. To apply the equations (19) and (20) one needs the reference temperatures  $T^*$  for the polymers. The reduced volume is related to the thermal expansion coefficient  $\alpha$ :

$$\tilde{V}^{1/3} - 1 = \frac{\alpha T}{3(1 + \alpha T)} \quad (21)$$

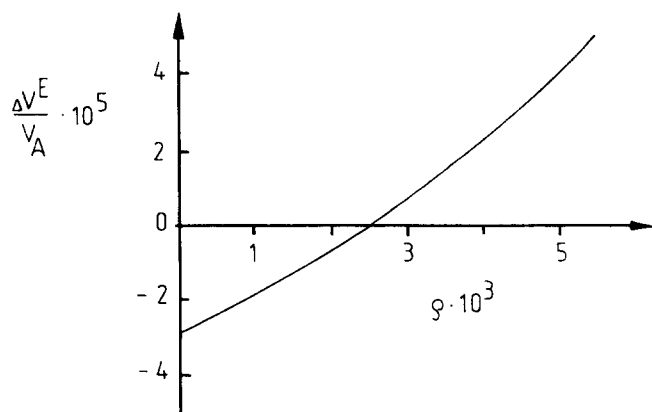


Figure 1 Variation of the volume of mixing as a function of the parameter  $\rho$  according to equation (16). The parameters used are:  $X_{AB} = -1.8 \times 10^{-4}$ ,  $\Gamma^2 = 6 \times 10^{-4}$ ,  $\phi_A = 0.5$ ,  $\tilde{V}_A^{1/3} = 1.082$

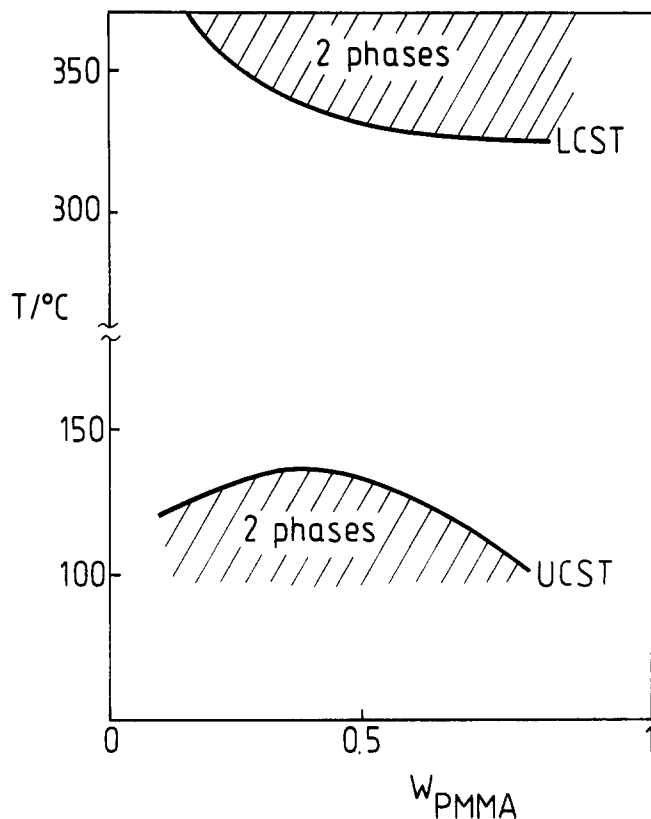


Figure 2 Phase diagram<sup>9</sup> of the blend PMMA/PVDF

Table 1

Polymer	$\alpha$ ( $10^{-4} \text{ K}^{-1}$ ) in range 150–200°C	$T^*$ (K)
PMMA	6.3 <sup>10</sup>	8100
PVDF	7.6 <sup>11</sup>	7320

Table 2 PMMA/PVDF

	$\theta$ (°C)	$\tilde{V}_A^{1/3}$
UCST	140	1.0658
LCST	325	1.1135

The parameter  $T^*$  can then be calculated from the equation of state (14). Employing the thermal expansion coefficients listed in Table 1, which are valid in the range from approximately 150 to 200°C, one obtains the indicated reference temperatures.

Table 2 shows the *UCST* and *LCST* and the corresponding reduced volumes according to equation (14). Knowing the reference temperatures  $T^*$ , the quantity  $\Gamma$  immediately follows from equation (9):

$$\Gamma = T_B^*/T_A^* - 1 = -0.096 \quad \Gamma^2 = 9.3 \times 10^{-3} \quad (22)$$

Now, all data are known and the upper limits of the quantities  $X_{AB}$  and  $\rho$  can be extracted from equations (19) and (20):

$$\begin{aligned} X_{AB} &= -5.2 \times 10^{-3} \\ \rho &= -0.030 \end{aligned} \quad \rho^2 = 9.2 \times 10^{-4} \quad (23)$$

where  $X_{AB}$  agrees well with the result  $X_{AB} = -0.007$  reported elsewhere<sup>12</sup>.

Employing the values of the parameters as presented in equations (22) and (23), one can easily calculate the excess volume according to equation (16) for a 50/50 blend of PMMA and PVDF at 456 K (equivalent to  $\bar{V}_A^{1/3} = 1.07525$ ):

$$\Delta V^E/V_A = 1.1 \times 10^{-3} \quad (24)$$

This is in excellent agreement with the experimental result  $2 \times 10^{-3}$ .

Thus, the general conclusion drawn from equation (16) is that negative and positive volumes of mixing may occur in miscible polymer blends. Obviously, when the size effect is negligible, only negative excess volumes can be observed. With increasing values of the parameter  $\rho$ , however, the sign of the volume of mixing may change and positive excess volumes are detected. As a rule, as shown by the theory presented in I and in this paper, positive volumes of mixing are likely when the gap between the *LCST* and *UCST* is sufficiently small. In other words, an increasingly positive volume of mixing is unfavourable for miscibility of polymers and leads ultimately to phase instability.

In conclusion, the theory discussed here explains the unexpected volume behaviour of miscible blends.

## REFERENCES

- 1 Walsh, D. J. and Rostami, S. *Macromolecules* 1984, **17**, 315
- 2 Walsh, D. J. and Rostami, S. *Macromolecules* 1985, **18**, 216
- 3 Zoller, P. and Hoehn, H. H. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 1385
- 4 Akiyama, S. *Bull. Chem. Soc. Jap.* 1972, **45**, 1389
- 5 Li, Y., Wolf, M. and Wendorff, J. H. *Polym. Commun.* 1987, **28**, 265
- 6 Wolf, M. and Wendorff, J. H. *Polymer* 1989, **30**, 1524
- 7 Kammer, H. W., Inoue, T. and Ougizawa, T. *Polymer* 1989, **30**, 888
- 8 Flory, J. P. *Disc. Faraday Soc.* 1970, **49**, 7
- 9 Saito, H., Fujita, Y. and Inoue, T. *Polym. J. (Tokyo)* 1987, **19**, 405
- 10 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', Interscience, New York, 1966
- 11 ten Brinke, G., Eshuis, A., Roerdink, E. and Challa, G. *Macromolecules* 1981, **14**, 867
- 12 Riedl, B. and Prud'homme, R. E. *J. Polym. Sci. (B) Polym. Phys.* 1988, **26**, 1769