Polymer Vol. 37 No. 12, pp. 2367–2371, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00+0.00

On the melting behaviour of polymer single crystals in a mixture with a compatible oligomer:
2. Polyethylene/paraffin

J. Martínez-Salazar*, A. Alizadeh, J. J. Jiménez and J. Plans
Instituto de Estructura de la Materia, CSIC, Serrano, 119, 28006 Madrid, Spain
(Received 18 April 1995)

A study of the melting behaviour of polyethylene single crystals in a paraffin medium is presented. The diluent effect of the paraffin upon the polyethylene crystals is monitored by changes in the melting curves. The experimental depression values of the melting temperatures fit very well with those predicted by the combinatorial term of the Flory–Huggins equation. Kinetic effects associated with the melting process are also discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymer compatibility; melting point depression; polyethylene/paraffin mixtures)

INTRODUCTION

It is now widely accepted that the melting point temperature depression (m.p.d.) of a polymer crystal in a mixture with a compatible polymer can be derived by setting the free energy of melting of the crystals equal to the partial free energy of this component in the mixture[1]. The expression for the latter free energy is based on the classical lattice model theory of Flory, Huggins and Scott[2,3] for polymer/solvent mixtures. However, the obtained equation for the m.p.d. is, strictly speaking, valid only as long as: (i) the crystals are grown under equilibrium conditions (infinitely thick crystals); (ii) the crystals melt under equilibrium conditions; and (iii) the presence of the second component does not induce any change in the structure of the crystals[4]. Unfortunately, most of the available data on polymer crystallization and melting are to be obtained under non-equilibrium conditions. To satisfy requirements (i) and (ii) the equilibrium melting temperature, T_m^0, is usually approximated through extrapolation of T_m *versus* T_c (Hoffman–Weeks plots)[5]. This procedure introduces an uncertainty in the equilibrium value, T_m^0, since it is usually taken far from the actual experimental range[5]. As to requirement (iii), changes in the melting temperature of the crystals, originating from crystallization, are commonly observed[6–8]. Indeed, structural parameters such as lamellar thickness[6], crystal interphase[7] and spherulitic growth rates[8] are substantially modified by the second component. An explicit separation of both effects would imply an extensive and systematic study on crystallization and melting of the crystalline polymer for various mixture concentrations. The use of single crystals of polymer dispersed in the matrix of the second component is a simple and effective method of studying the m.p.d.–composition relation over a wide range of concentrations[9–11].

Our previous results on the poly(vinylidene fluoride)/poly(methyl methacrylate) (PVDF/PMMA)[11] system have shown that the m.p.d. method could describe the extent of compatibility between the two polymers on the basis of a pure enthalpic interaction.

The compatibility between linear polyethylene (LPE) and branched polyethylene (BPE) has also been studied by means of embedding identical crystals of LPE in a medium of BPE[9,10]. In such a system a limiting value for the degree of molecular branching compatible with linear segments was experimentally determined. However, due to the presence of the branches it was difficult to distinguish between the two expected contributions to the interaction: the slightly positive enthalpic term, unfavourable to mixing (increasing with branching) and the entropic contribution, favourable to mixing, caused by the free volume excess of branches.

The purpose of the present work is to apply the above method to a better defined system where purely entropic interactions are expected. Thus, we have analysed the melting behaviour of single crystals of PE fractions in a mixture with two n-alkanes. The mixture of two chemically identical species with two different molecular lengths has been mainly studied and special attention has been paid to the determination of the interaction parameter from the melting point measurements[12–16]. In spite of the large discrepancies of the interaction parameters reported by different authors, it now seems to be well established that the mixing of two chemically identical species should be athermal[17]. The differences reported in the values can be attributed to the method of sample preparation. For instance, the use of high molecular weight samples crystallized at temperatures

---

* To whom correspondence should be addressed

close to equilibrium[13,15] or the use of low molecular weight species that form extended chain crystals[16] lead to different results. The experimental method developed in the present work enables us to use samples with higher molecular weights than those reported previously, at the same time keeping the structural parameters unchanged.

MELTING POINT EQUATION

In the following the index 2 refers to the semicrystalline polymer which melts in the presence of the low molecular weight component 1. The partial free energy difference per mole of polymer 2 between a crystal of infinite thickness and the supercooled liquid is given by the standard approximation:

$$\Delta G_{\mathrm{melt}} = \Delta H - T\Delta S = \Delta H\left(1 - \frac{T_{\mathrm{m}}}{T_{\mathrm{m}}^{0}}\right) \tag{1}$$

where ΔH and ΔS are the enthalpy and entropy of fusion per repeating unit, respectively. In the last equation ΔH and ΔS are assumed to be temperature independent and the ratio $\Delta H/\Delta S$ equal to the equilibrium melting temperature, T_{m}^{0}. The Flory–Huggins–Scott lattice model theory for the free energy of mixing is used to evaluate the difference in the free energy per mole of polymer 2 between the pure melt and the mixture:

$$\Delta G_{\mathrm{mix}} = RT\frac{V_2}{V_1}\left[\frac{\ln \Phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)(1 - \phi_2) + \chi(1 - \phi_2)^2\right] \tag{2}$$

where V_i and m_i are respectively the molar volume and the number of repeating units along the chain for the component i. χ is the polymer–second component interaction parameter and R the gas constant. The melting point depression of a semicrystalline polymer in the presence of a second compatible component, as mentioned before, is evaluated by setting the free energy of mixing of the two components equal to the free energy of melting of the crystals. At the melting temperature:

$$\frac{1}{T_{\mathrm{m}}^{0}(\phi_2)} - \frac{1}{T_{\mathrm{m}}^{0}} = -\frac{RV_2}{\Delta H V_1}\left[\frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)(1 - \phi_2) + \chi(1 - \phi_2)^2\right] \tag{3}$$

where $T_{\mathrm{m}}^{0}(\phi_2)$ is the equilibrium melting temperature of infinite crystals in a mixture of concentration ϕ_2.

It is widely accepted that the interaction parameter, χ, between polyethylene and n-paraffins decreases with increasing the number of carbon atoms of the n-alkane, approaching a value close to zero for $n > 18$ (refs 13–16, 18). Therefore the mixing of PE with n-paraffins, which are two chemically identical species, should be athermal, and strong combinatorial entropy contributions due to the short chains of paraffins are expected. On the other hand the degree of polymerization, the number of repeating units along the chain, for the polymeric component is quite high so $1/m_2$ is negligible and equation (3) reduces to:

$$\frac{1}{T_{\mathrm{m}}^{0}(\phi_2)} - \frac{1}{T_{\mathrm{m}}^{0}} = \frac{R}{\Delta H}\frac{1}{m_1}(1 - \phi_2) \tag{4}$$

where we have taken $V_1 = V_2$.

In the real case crystals grow and melt under non-equilibrium conditions. In the case of laterally large lamellae, the only surfaces contributing significantly to the free enthalpy of the crystals are the basal ones, so that the equilibrium melting temperature can be calculated from the Thomson–Gibbs equation:

$$T_{\mathrm{m}}(l) = T_{\mathrm{m}}^{0}\left(1 - \frac{2\sigma_{\mathrm{e}}}{\Delta H l}\right) \tag{5}$$

where σ_{e} is the top and bottom specific surface free energy, l the lamella thickness and $T_{\mathrm{m}}(l)$ is the melting temperature of the metastable crystals. The surface free energy is not expected to be modified when the composition of the blend is varied, so we can rewrite the melting point depression equation as:

$$\left(1 - \frac{2\sigma_{\mathrm{e}}}{\Delta H l}\right)\frac{1}{T_{\mathrm{m}}(\phi_2)} - \frac{1}{T_{\mathrm{m}}^{0}} = \frac{R}{\Delta H}\frac{1}{m_1}(1 - \phi_2) \tag{6}$$

The use of equation (3), which was first derived by Nishi and Wang[1] for two dissimilar polymers, in a binary system involving two chemically identical polymers has been criticized by Mandelkern and co-workers[16,17]. The argument presented has been that the thermodynamic interaction parameter, which enters the later equation, does not seem to be suitable in a mixture of two similar species that constitute an athermal system. However, the final expression for the m.p.d. equation (6) in our work, based upon the combinatorial term and that reported by Mandelkern *et al.*[16] are identical.

EXPERIMENTAL

The samples studied in this work were a commercial PE fraction from the Societé National of Paris Aquitaine ($M_{\mathrm{w}} = 1.3 \times 10^4\,\mathrm{g\,mol^{-1}}$; $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.12$) and two paraffin fractions $C_{22}H_{46}$ and $C_{40}H_{82}$ synthesized by Montedison. PE single crystals were grown from a 0.5% w/v solution in *p*-xylene. After dissolving the polymer at 130°C, the solution was transferred to a silicone oil bath at 80°C and the polymer was allowed to crystallize for 24 h. The single crystals were then separated from the solvent by centrifugation and the excess clear xylene was removed. Finally, the PE single crystals were dispersed in the paraffin matrix at 60°C and several mixtures containing 15, 20, 30, 40, 50 and 75% by weight of paraffin were prepared. As a last step, the slurry mixtures were placed into aluminium differential scanning calorimetry (d.s.c.) pans and fully dried in a vacuum oven at 60°C. Thermograms of the investigated samples were recorded by a Perkin-Elmer DSC4 calorimeter at heating rates of 10, 20 and 40°C $\mathrm{min^{-1}}$. Indium was used as a calibration standard for the instrument.

RESULTS AND DISCUSSION

In *Figure 1* the experimental melting thermograms of the pure PE and a PE/n-$C_{22}H_{46}$ blend of 50% composition at a heating rate of 40°C $\mathrm{min^{-1}}$ are compared. Two main

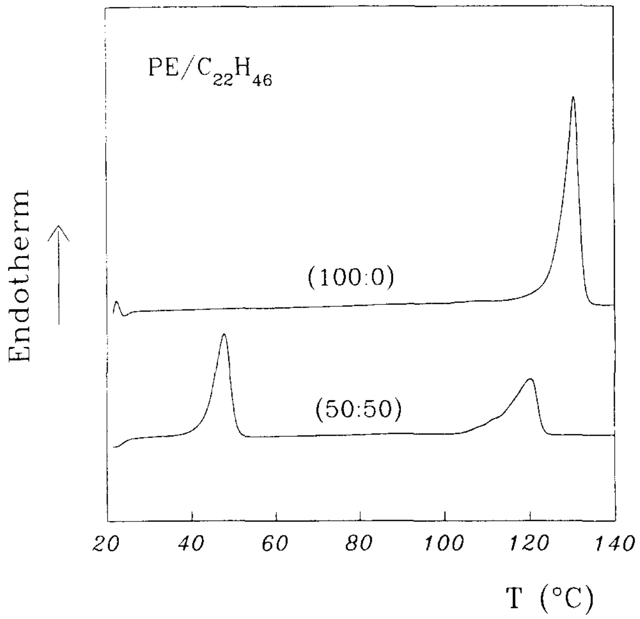

Figure 1 D.s.c. thermogram for pure PE and a PE/$C_{22}H_{46}$ blend with a composition of 50%. Heating rate 40°C min^{-1}

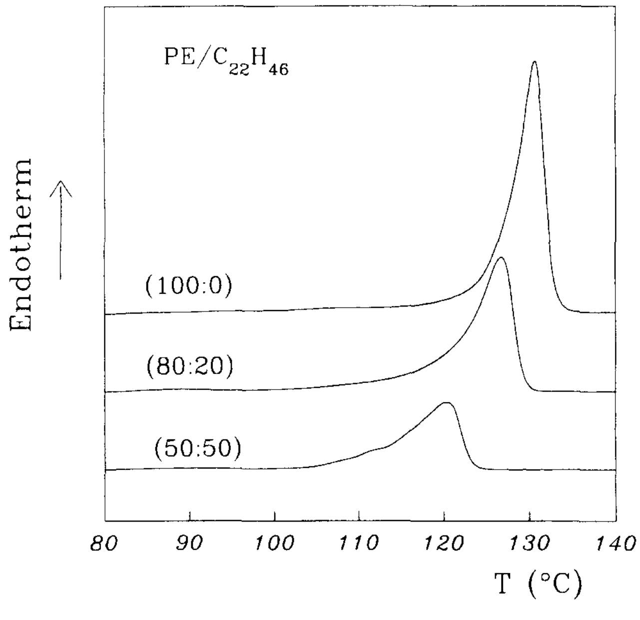

Figure 2 PE melting curves for PE/$C_{22}H_{46}$ blends of different composition: 0, 20 and 50%. Heating rate 40°C min^{-1}

peaks are observed for the PE/n-$C_{22}H_{46}$ mixture: the low temperature peak corresponds to the melting of the paraffin, and the high temperature peak is associated with the melting of the PE single crystals. While the position and the shape of the low temperature peak remains essentially constant with composition, the PE melting curves show a broadening with increasing paraffin content and shift towards lower temperatures, as shown in *Figure 2*. In the first part of this section, the melting point depression of the PE single crystals in the presence of paraffins by means of the Flory–Huggins relation will be analysed. The second part will be mainly concerned with the kinetics of melting of the systems under study.

For the m.p.d. analysis, temperatures of the beginning of melting (T_{onset}), the maximum (T_{max}) as well as the end of melting (T_{final}), i.e. the temperature at which the last trace of melting is observed, have been studied. Each temperature was calibrated by means of the corresponding melting temperature of the n-paraffin pure sample. The main reason for using the n-paraffins instead of indium, the instrument calibration standard, is the fact that the heat conduction of the PE crystals is much more similar to paraffins. On the other hand, the crystallization and melting of the paraffin crystals are not affected by the presence of PE single crystals, so the melting temperature of the n-paraffins can be used as an inner calibration in each mixture.

The major difficulty in using the experimental temperature for the equilibrium melting determination, equations (5) and (6), is the instability of the small crystals[19]. Small lamellae anneal on heating, thus giving a higher experimental melting temperature corresponding to a thicker crystal. Fast melting, so that not enough time remains to reorganize, has been used to minimize the annealing of polymers[19]. Under fast melting conditions a temperature representative of the initial metastable crystals is expected to be obtained. However, there are two main limitations in using the fast melting method. The first is the possibility of superheating, which is observed when heat is supplied to the crystals faster than they can melt, so that the inner portion of the crystals is heated above the melting temperature before actual melting. This effect is more relevant to large crystals, extended chain crystals, or to crystals containing a large number of tie molecules. Fortunately this effect can be ignored for small metastable crystals as in our case. The other limitation of fast heating is the rate of heat conduction through the bulky sample before reaching the crystal surface. This second effect can be minimized by using small samples. In the present work samples weighing about 1 mg were used.

The reciprocal of the experimental melting temperature, $1/T_m$, for PE/$C_{40}H_{82}$ as a function of paraffin content and at a heating rate of 10°C min^{-1}, is plotted in *Figure 3a*, where the onset, the maximum and the final melting reciprocal temperatures are compared. The dashed line in this figure has the same slope as the calculated melting temperature as a function of paraffin content according to equation (6). Up to the maximum composition studied in this work, i.e. $\phi_2 > 0.25$, the end of melting data lie on the calculated straight line. However, there is a clear enhancement of the melting point depression for the onset and the maximum as compared to the combinatorial entropy dashed line. This effect will be discussed later. The melting point depression data for the same system at a heating rate of 40°C min^{-1} are plotted in *Figure 3b*. Again, the final melting temperature fits quite well with the expected values, while there are large deviations for the onset and the melting maximum. For the slower heating rate, 10°C min^{-1}, some annealing of the single crystals seems to take place during the heating process and the melting temperatures are shifted towards higher values. But, as mentioned before, the final melting temperature depression for the two heating rates, within experimental error, have the same slope as predicted by the Flory–Huggins lattice model and the kinetics of annealing of PE single crystals for the lower heating rate do not seem to be affected by the presence of n-paraffin. From *Figures 3a*

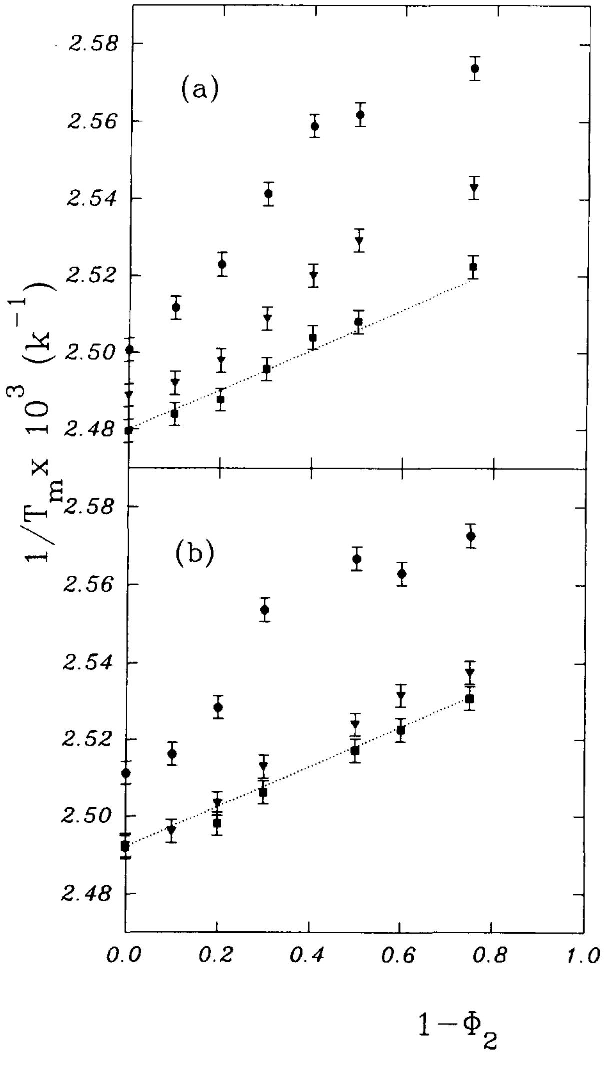

Figure 3 Reciprocal of the experimental melting temperatures (T_{onset}, T_{max}, T_{final}) of PE single crystals as a function of the paraffin content for the PE/$C_{40}H_{82}$ system. The dashed line corresponds to the theoretical values derived from equation (6). Heating rates: (a) = 10°C min^{-1}; (b) = 40°C min^{-1}

and *b* one can conclude that the final melting temperature is an adequate magnitude for m.p.d. analysis. To avoid as much as possible both the annealing and superheating effects, we have taken the final melting temperature at a heating rate of 40°C min^{-1} as the more representative experimental melting point of the metastable crystals. Similar behaviour is obtained in the PE/$C_{22}H_{46}$ system.

In *Figure 4* the melting point depressions, $1/T_m^0(\phi_2) - 1/T_m^0$ as a function of paraffin content for the two hydrocarbons are compared. The equilibrium melting temperature for the pure PE was calculated according to Broadhurst's equation[20] and the crystal thickness, *l*, for the pure PE was calculated by means of equation (5). Finally, the value of *l* thus obtained was used to calculate the equilibrium melting temperature of the PE single crystals embedded in the paraffin matrix, $T_m^0(\phi_2)$. As observed in this figure, a good agreement between experimental and theoretical data, the solid line, is obtained. The melting point depression is enhanced for the PE/$C_{22}H_{46}$ system where the difference in the chain length of the constituent molecules is higher and therefore the entropic effect larger.

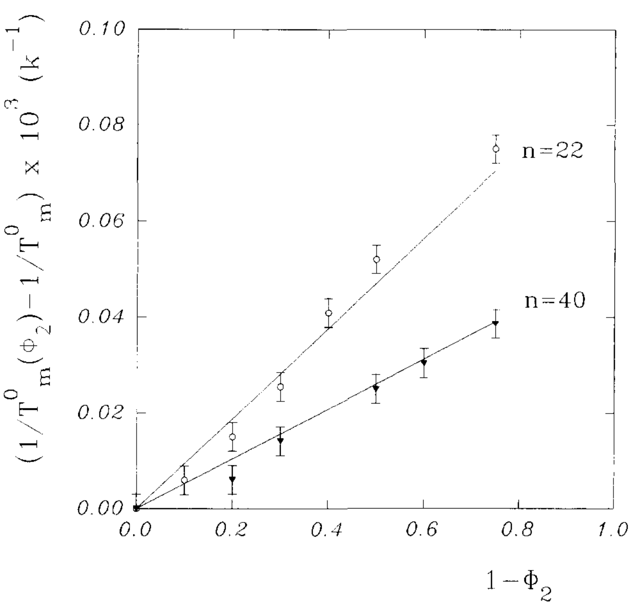

Figure 4 Influence of the paraffin length on the melting point depression. Symbols correspond to the experimental final melt and the continuous lines are the expected values from the Flory–Huggins expression. Heating rate 40°C min^{-1}

The other problem concerning this study is whether the kinetics of melting of the PE single crystals is modified by the paraffin matrix. As seen in *Figure 2* there is a continuous broadening of PE melting curves as the paraffin content in the blend is increased. This effect can also be detected easily if one compares the slopes of $1/T_m$ *versus* $(1-\phi_2)$ curves for the beginning of melting, the melting peak and the end of melting (see *Figures 3a* and *b*). The broadening of the melting curves for the two heating rates, once corrected for the heat conduction effect, is quite similar and thermal conductivity problems in the paraffin matrix can be discarded. It is worth mentioning that for concentrations of paraffin greater than 50%, there is a levelling off in the $1/T_m$ *versus* $(1-\phi_2)$ curves for both the onset and the maxima. This effect might be thought to be due to the existence of a distribution of single crystals, where the smallest ones thicken upon heating and produce more stable crystals, thus raising the melting point. In this case, under fast melting the annealing effects should be minimized. On the other hand, as seen above from the end of melting data, the annealing of the PE single crystals upon heating is not affected by the presence of the paraffin. A possible explanation for this phenomenon is that melting is a local process, initiated at suitable surface sites and it is a question of crystal size and the melting rate as it takes the crystal melt interface to reach a given superheated crystal volume. The presence of paraffin at the surface of the PE crystals might enhance the mobility of the PE molecules, reducing the effective time for them to reach the pure molten phase. This fact can be understood in terms of the diffusion coefficient of the PE/n-paraffin mixtures obtained according to Brochard *et al.*'s expression[21,22]. The diffusion coefficient increases as the paraffin content is increased, going through a maximum located at a polymer concentration ϕ_2 of ≈ 0.7. On the other hand as the number of carbon atoms of the n-paraffin is decreased, a major increase of the diffusion coefficient of the PE crystals in the blend is expected. Our experimental results on PE/n-$C_{22}H_{46}$ and PE/$C_{40}H_{82}$ are in accordance with the theory predictions. However, for a quantitative description of the process a more detailed study as well as the use of additional techniques would be required.

CONCLUSIONS

The use of PE single crystals in a mixture with n-alkane is an elegant and effective method of studying the effect of paraffin upon the melting behaviour of the polymer crystals. The final melting temperature at the highest heating rate studied has been shown to be the closest value to the actual melting temperature of the metastable crystals. The experimental values thus obtained fit very well with the melting point depression deduced from the combinatorial term of the Flory–Huggins approximation. Moreover, at a fixed heating rate the kinetics of melting of the crystals in the mixture is largely affected by the presence of the paraffin. This effect, which is qualitatively observed as an increase of the asymmetry of the melting curves towards lower temperatures as the paraffin content is increased, might be explained by the enhancement of molecular mobility of PE at the surface melting.

ACKNOWLEDGEMENT

We wish to thank the CICYT (grant MAT94-0825) for their kind support of this investigation.

REFERENCES

1 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**, 909

2 Flory, P. J. 'Principles of Polymer Chemistry'. Cornell University Press, Ithaca, NY, 1953

3 Scott, R. L. *J. Chem. Phys.* 1949, **17**, 279

4 Utracki, L. A. in 'Polymer Alloys and Blends', Hanser Publishers, New York, 1989

5 Hoffman, J. D., Davis, G. T. and Lauritzen Jr, J. I. in 'Treatise on Solid State Chemistry' (Ed. N. B.. Hannay), Vol. 3, Plenum Press, New York, 1976, p. 473

6 Conde Braña, M. T., Iragorri, J. I., Terselius, B. and Gedde, U. W. *Polymer* 1989, **30**, 410

7 Martinez-Salazar, J., Canalda, J. C. and Vallejo, B. *Macromol. Symp.* 1994, **78**, 95

8 Alfonso, G. C. and Rusell, T. P. *Macromolecules* 1986, **19**, 1143

9 Martinez-Salazar, J., Sanchez Cuesta, M. and Plans, J. *Polymer* 1991, **32**, 2984

10 Plans, J., Sanchez Cuesta, M. and Martinez-Salazar, J. *Polymer* 1991, **32**, 2989

11 Canalda, J. C., Hoffman, Th. and Martinez-Salazar, J. *Polymer* 1995, **36**, 981

12 Ke, B. *J. Polym. Sci.* 1961, **50**, 79

13 Nakajima, A. and Hamada, F. *Kolloid Z.Z. Polym.* 1965, **205**, 55

14 Smith, P. and St. John Manly, R. *Macromolecules* 1979, **12**, 483

15 Smith, P. and Gardner, K. H. *Macromolecules* 1985, **18**, 1222

16 Mandelkern, L., Smith, F. L. and Chan, E. K. *Macromolecules* 1989, **22**, 2663

17 Mandelkern, L. in 'Comprehensive Polymer Science. Vol. 2, Polymer Properties' (Eds C. Booth and C. Price), Pergamon Press, Oxford, 1989, Ch. 11

18 Flory, P. J., Orwell, R. A. and Virj, A. *J. Am. Chem. Soc.* 1964, **86**, 3515

19 Wunderlich, B. in 'Macromolecular Physics', Vol. 3, Academic Press, New York, 1980

20 Broadhurst, M. G. *J. Res. Natl Bur. Std* 1966, **70A**, 481

21 Brochard, F., Jouffroy, J. and Levinson, P. *Macromolecules* 1983, **16**, 1638

22 Brochard, F., Jouffroy, J. and Levinson, P. *Macromolecules* 1984, **17**, 2925