Crystallization of low molecular weight fractions of poly(octamethylene oxide)

C. Marco, J.G. Fatou, A. Bello and A. Blanco
Sección de Física y Fisicoquímica de Polímeros, Instituto de Plásticos y Caucho, C.S.I.C., Juan de la Cierva 3, Madrid 6, Spain

Poly(octamethylene oxide) fractions ranging in molecular weight from 3400 to 9000 have been isothermally crystallized in the interval 61–70°C. From the dilatometric isotherms, the Avrami exponent is an integral number, 4, and is independent of temperature and molecular weight; the total crystallinity ranges from 78% for M = 3400 to 51% for M = 9000. The crystallization temperature coefficient was studied using the three-dimensional nucleation theory and it was found that the basal interfacial free energy changes from 3700 cal/mol to 2200 cal/mol, decreasing with molecular weight. When the change of the interfacial free energy is considered, the crystallization is described by a unique function of the free energy for nucleation.

INTRODUCTION

The crystallization kinetics of polyoxides, with the repeat unit $-[(CH_2)_m-O]_n-$, have been previously investigated for the lower members of this series, especially poly(ethylene oxide).[1–7] More recently the effect of molecular weight on the crystallization kinetics of poly(hexamethylene oxide)[8] and poly(decamethylene oxide)[9] has been published.

However, poly(octamethylene oxide), POMO, has been analysed, although Tadokoro *et al.*[10] determined the crystal structure of this polymer.

POMO presents two crystalline modifications: polyethylene or orthorhombic, and polytetrahydrofuran or monoclinic, types. The orthorhombic type is predominant when the polymer is crystallized from solution, whereas the monoclinic type also occurs in the crystallization from the melt. The chain conformation is planar zig-zag in both crystalline forms.

In order to analyse the relation between the crystallization conditions and the crystalline forms, we present the results of the crystallization kinetics of several fractions of POMO, ranging in molecular weight from 3400 to 9000. This analysis has been carried out by dilatometry at relatively low undercoolings.

EXPERIMENTAL

Materials

POMO was obtained by polycondensation of 1, 8-octanediol using sulphuric acid as catalyst.[11] The whole polymer was fractionated at 50°C by using the benzene-methanol solvent-nonsolvent system. The fractions were washed with methanol and dried by liofilization. The number average molecular weights were determined in a Hitachi-Perkin-Elmer 115 vapour pressure osmometer.

Crystallization

The crystallization kinetics were followed using dilatometric techniques previously described.[12,13] About 190-220mg of bubble-free polymer films were used in the dilatometers, which were built with 0.6 mm diameter precision bore tubing.

Previous to crystallization the influence of the melting temperature on the kinetics was analysed. The method for this analysis has been previously described.[8] Briefly, before crystallization, the dilatometers were melted for different periods of time at a series of predetermined temperatures. When the melting temperature is $\geqslant 125$°C, the temperature of the melt and time held there have no influence on the ensuing crystallization isotherm.

This observation is in agreement with previous studies on poly(hexamethylene oxide)[8] and poly(decamethylene oxide).[9]

The specific volume of the partly crystalline sample and the degree of crystallinity were calculated assuming the additivity of the specific volumes of the amorphous and crystalline portions.

The specific volume – temperature relationship for the amorphous polymer was determined in the melted state by using in the dilatometer a sample of known density at 25°C. The relationship was given by:

$$\bar{V}_L = 1.039 + 6.864 \times 10^{-4} t$$

where t is the temperature in (°C).

The relationship for the specific volume of the completely crystalline polymer was given by:

$$V_C = 0.962 + 3.0 \times 10^{-4} t$$

taking 0.971 as the specific volume of the crystalline polymer at 25°C[8] and assuming the expansion coefficient to be the same as that in polyethylene.[14]

All the fractions were crystallized after melting at 125°C for 20 min, at temperatures from 61-70°C, depending on molecular weight.

X-ray diffraction

X-ray diffraction diagrams for the crystallized samples were obtained with a Geiger counter X-ray diffractometer, made by Philips. The diagrams were recorded in the 2θ range between 4° and 35° with Ni-filtered CuKα radiation

0032-3861/79/101250-05$02.00
© 1979 IPC Business Press

and with an amplification varying with the absorption by the sample.

The samples were prepared by moulding the polymer at a temperature above the melting point, and then isothermally crystallized at different temperatures between 63°C and 67°C. After crystallization the samples were cooled at room temperature and then the X-ray diagrams were recorded. In another set of experiments, the isothermally crystallized samples were annealed at 66–67°C for a period of 20h, before obtaining the X-ray diagrams.

RESULTS AND DISCUSSION

Quantitative kinetic data could be obtained in the molecular weight range from 3400 to 9000, and in the temperature interval 61–70°C. At higher temperatures the rates become too slow to be measured in a reasonable period.

In both the Avrami equation[15] and the free-growth analysis or the Göler–Sachs approximation,[16] the same behaviour is found. The Avrami exponent, the slope of the double logarithmic plot of the extent of the transformation against t, is found to be independent of temperature and molecular weight in the range analysed and it corresponds to 4 (*Figures 1* and *2*).

Experimental results according to the Göler–Sachs equation are described in a double logarithmic plot of crystallinity against time. Again, a linear relation is obtained in the first part of the total transformation, with a slope of 4 (*Figures 3* and *4*).

The simplest interpretation of the exponent $n = 4$ is the occurrence of a homogeneous nucleation accompanied by three-dimensional growth. The same value, 4, has been found for low-molecular-weight linear polyethylene,[17] poly(hexamethylene oxide)[8] and poly(decamethylene oxide).[9]

After the deviations from linearity develop, the experimental results for a given molecular weight form a common straight line and this fact indicates that the degree of crystallinity after very long periods is independent of the crystallization temperature.

The crystallinity of the various molecular-weight fractions after isothermal crystallization at three different temperatures is plotted in *Figure 5*. The maximum crystallinity is reached for $M = 3400$ (78.4%) and the crystallinity decreases monotonically with increasing molecular weight to a value of 51.3% for $M = 9000$. These variations are closely connected with the influence of molecular weight on crystallization.

Moreover, the influence of molecular weight on the time scale of the crystallization is very pronounced. In the low-molecular-weight range, the crystallization time decreases as the molecular weight is increased and a minimum is reached for $M = 7000$. At the highest molecular weights the crystallization time increases again (*Figure 6*). The observation of a minimum in time which corresponds to a

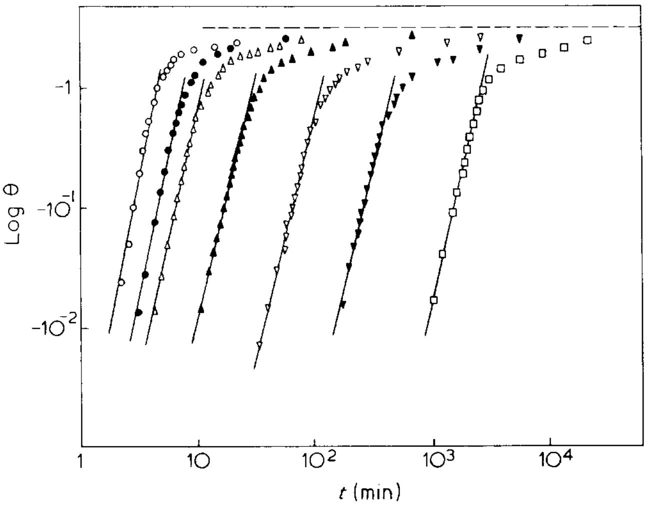

Figure 1 Double logarithmic plot of θ against time for fraction $M = 3400$ at indicated temperatures, O, $T_c = 61°C$; ●, 62°C; △, 63°C; ▲, 64°C; ▽, 65°C; ▼, 66°C; □, 67°C

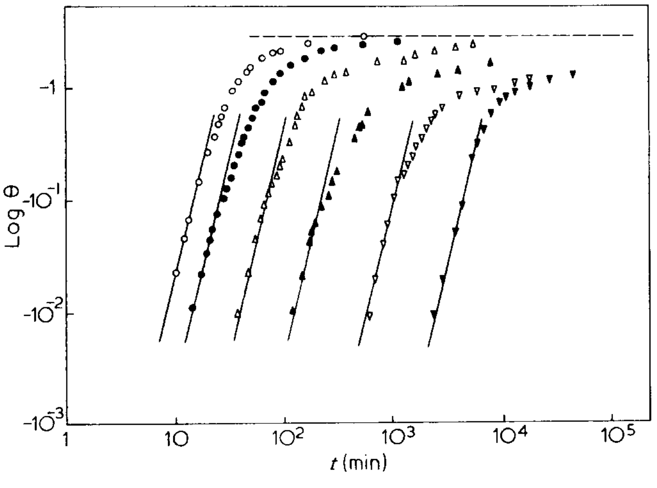

Figure 2 Double logarithmic plot of θ against time for fraction $M = 9000$ at indicated temperatures. O, $T_c = 64°C$; ●, 65°C; △, 66°C; ▲, 67°C; ▽, 68°C; ▼, 69°C

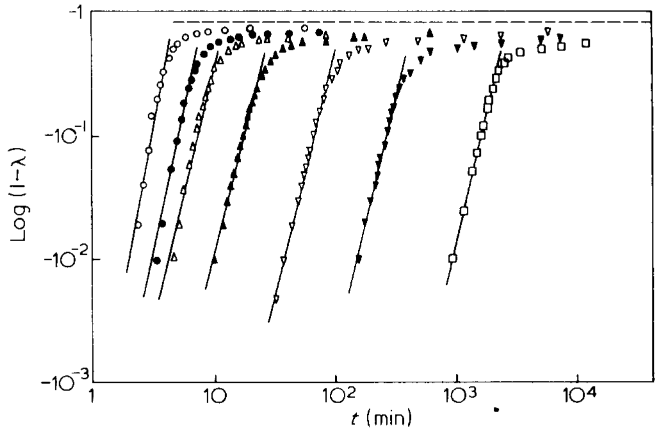

Figure 3 Double logarithmic plot of $1 - \lambda$ against time for $M = 3400$ at indicated temperatures. O, $T_c = 61°C$; ●, 62°C; △, 63°C; ▲, 64°C; ▽, 65°C; ▼, 66°C; □, 67°C

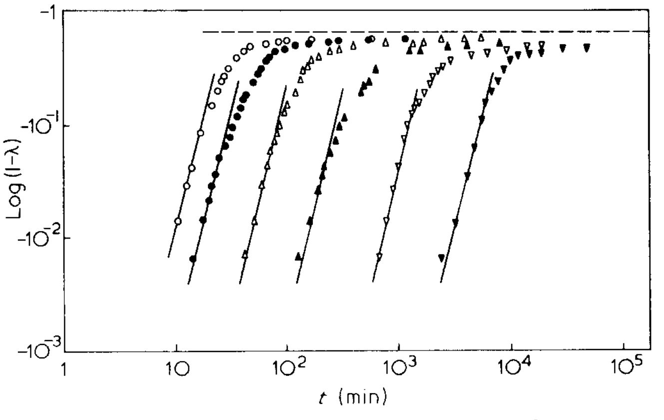

Figure 4 Double logarithmic plot of $1 - \lambda$ against time for $M = 9000$ at indicated temperatures. O, $T_c = 64°C$; ●, 65°C; △, 66°C; ▲, 67°C; ▽, 68°C; ▼, 69°C

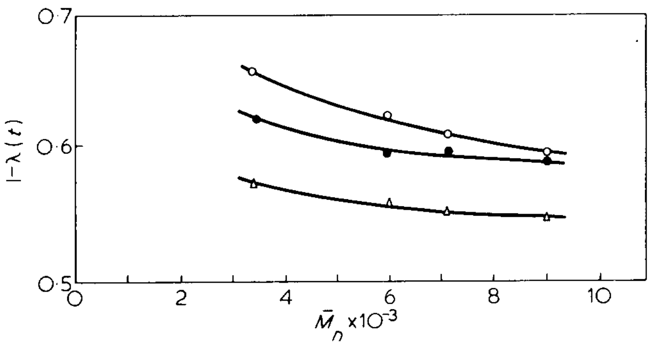

Figure 5 Crystallinity against molecular weight at different crystallization temperatures: O, 65°C; ●, 66°C; △, 67°C

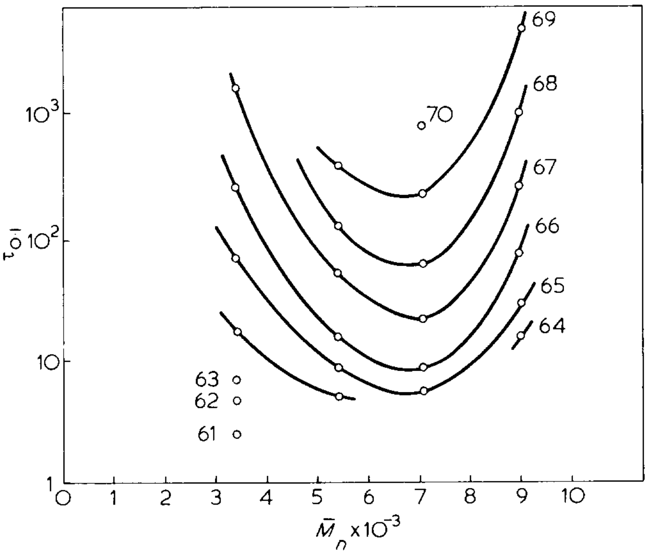

Figure 6 Double logarithmic plot of $\tau_{0,1}$ against molecular weight for indicated crystallization temperatures

maximum in the crystallization rate is a general characteristic of other polymers.[17–19]

The crystal structure of POMO has been determined by Tadokoro *et al.*[10] and according to their results both the orthorhombic and monoclinic structures are formed from methanol solutions, and only the monoclinic structure is found when the polymer is crystallized from the melt. The same results have been shown by Yoshida *et al.*[20] by measuring the heat capacity for POMO crystallized from solution and from the melt.

All the observed reflections of POMO can be indexed with the monoclinic unit cell. The X-ray curves of POMO show strong reflections at Bragg angles $2\theta = 195°$, 24° and no reflection at 21.7°, corresponding to the (110) reflection of the polyethylene-type lattice. This is independent of the crystallization temperature and molecular weight in the analysed range. Moreover, annealing of the samples confirmed that the crystalline structure remains unchanged (*Figure 7*).

On the other hand, the isothermal crystallization rate for the crystallization from the melt can be expressed by the general equation[21]

$$\ln(\tau_{0.1})^{-1} = \ln(\tau_{0.1})_0^{-1} - \frac{E_D}{RT} - \frac{\Delta F}{RT_c} \qquad (1)$$

where T_c is the crystallization temperature, ΔF the free energy for forming a stable nucleus and E_D is the transport term.

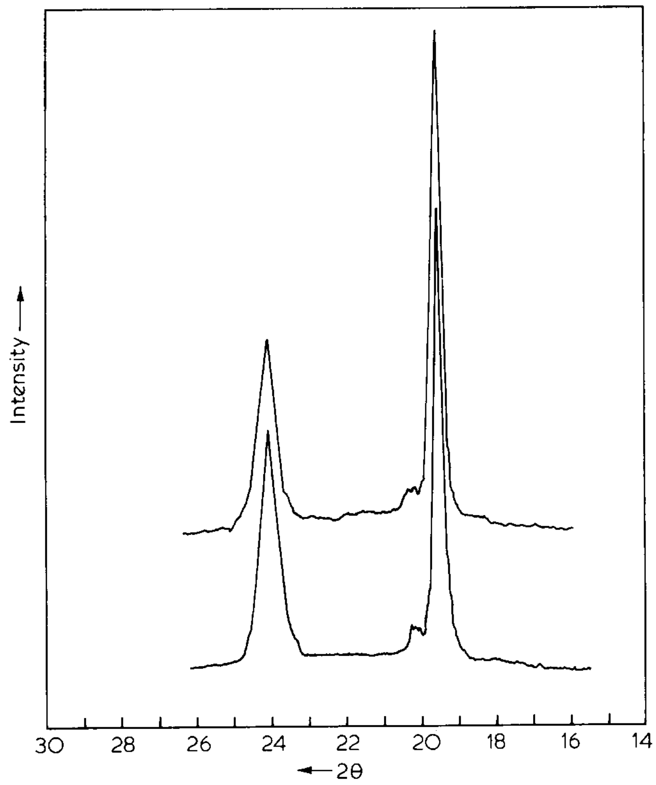

Figure 7 Wide angle X-ray diffraction patterns of POMO, $\bar{M}_n = 7100$. A, sample annealed; B, sample crystallized from the melt at 67°C

The nucleation theories developed for finite chains by Mandelkern *et al.*[23,24] show that the free energy for nucleus formation is dependent on molecular weight, and for the case of a cylindrical nucleus, it has been shown that

$$\Delta F = \pi^{1/2}\,\xi^*\,\rho^{*1/2}\,\sigma_u^2 \qquad (2)$$

where ξ^* and ρ^* are the critical dimensions of the nucleus and σ_u is the lateral interfacial free energy per structural unit.

The critical dimensions for a finite chain, x, are given by the expressions[22]

$$\xi\left[2\left(\Delta f_u - \frac{RT}{x}\;\; \frac{RT}{x-\xi+1}\right)\right]^{-1} = 2\sigma_e - RT_c \ln\frac{x-\xi+1}{x} \qquad (3)$$

and

$$\rho^{1/2} = 2\pi^{1/2}\sigma_u\left(\Delta f_u - \frac{RT_c}{x} - \frac{RT_c}{x-\xi+1}\right)^{-1} \qquad (4)$$

where σ_e is the interfacial free energy per unit area in the basal plane and Δf_u is the free energy of fusion per repeating unit for a chain of infinite molecular weight.

Analysing the data according to the conventional manner, $\ln(\tau_{0.1})^{-1}$ is plotted against $T_m^2/\Delta T^2$ in *Figure 8*. The analysed fractions give straight lines and the slopes of these lines vary with the molecular weight, the lower the molecular weight, the lower the slopes are, and variations in the slopes represent a change in the value of σ_e or σ_u or both. Assuming that σ_u is constant,

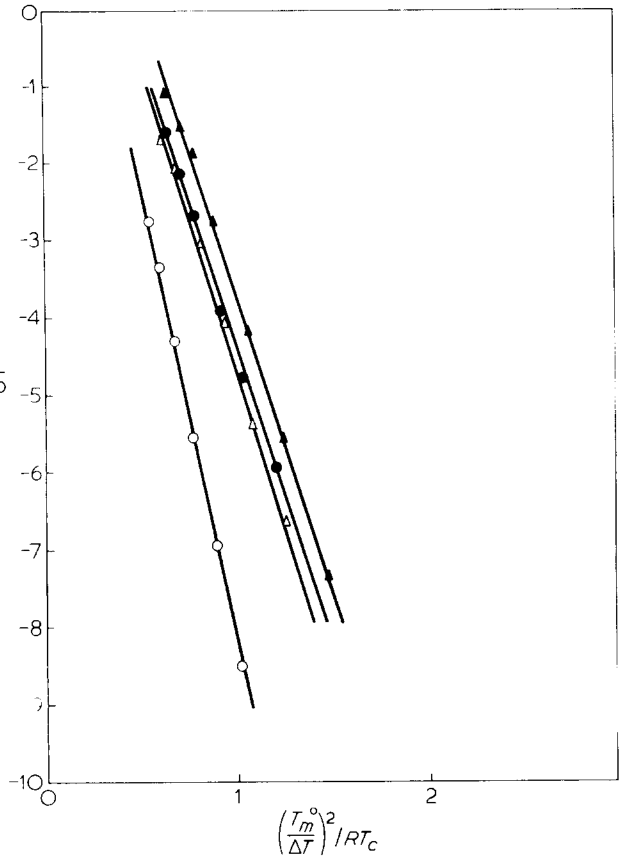

Figure 8 Plot of log $(\tau_{0,1})^{-1}$ against $(T_m/\Delta T)^2/RT_c$ for indicated molecular-weight fractions: O, 9000; △, 7100; ●, 5900; ▲, 3400

σ_u = 10 cal/mol, the values of σ_e for each molecular weight can be established.

These values are indicated in *Table 1* and change from 3700 cal/mol to 2200 cal/mol in the molecular weight range 9000-3400. *Table 1* includes the equilibrium melting temperatures, obtained independently from the extrapolation of T_m against T_c in experiments involving low crystallinity.[24]

The variation in σ_e with molecular weight has been shown in the analysis of polyethylene[19,25] and polyethers.[8,9] Only in the case of poly(ethylene oxide) has the dramatic decrease of σ_e with decreasing molecular weights not been shown.[26]

The value of 3700 cal/mol for M = 9000 is lower than the value of 4600 cal/mol for high-molecular-weight polyethylene and lower than the value of 4300 cal/mol for M = 35 500 for poly(hexamethylene oxide). However, when the values obtained for POMO are compared with PHMO on the basis of the same molecular weights, the agreement is excellent.[8]

Analysis of the temperature coefficient according to equation (1) requires the specification of T_m^0 and ΔH_u. Both parameters have previously been determined;[24] ΔH_u corresponds to 7700 cal/mol and T_m^0 are indicated in *Table 1*. According to equation (2), ΔF^* can be calculated for each fraction with the corresponding σ_e, and the plot of $\ln(\tau_{0.1})^{-1}$ *versus* $\Delta F^*/RT_c$ gives a unique straight line with slope one according to equation (1) (*Figure 9*). The fairly common assumption that both the initiation and the growth have the same temperature coefficient has been used.

Table 1 Interfacial free energy (σ_e cal/mol) for POMO

Molecular weight	T_m^0 (K)[a]	σ_e
3400	351.0	2200
5900	354.5	2300
7100	355.0	2600
9000	356.0	3700

[a] Equilibrium melting temperatures.[24]

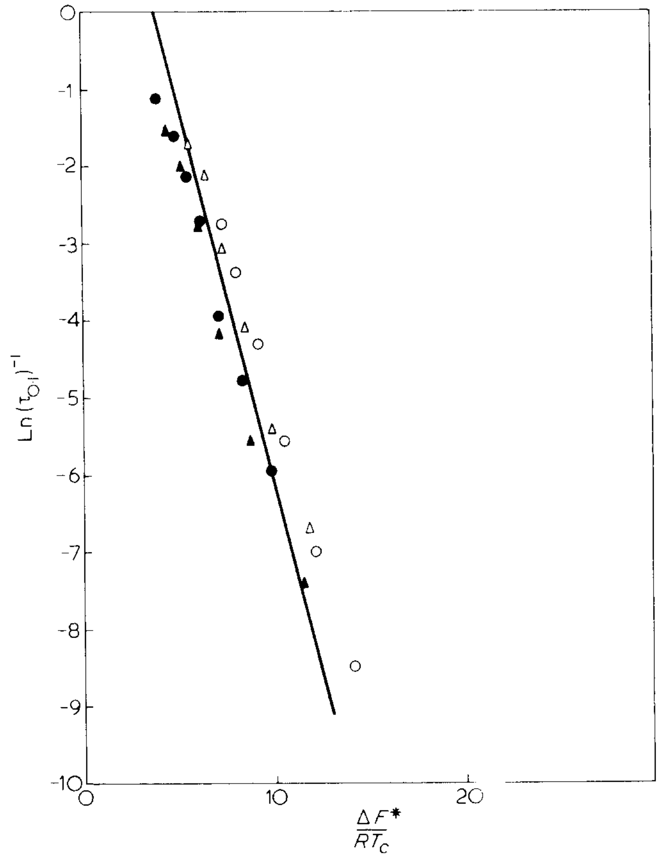

Figure 9 Plot of log $(\tau_{0,1})^{-1}$ against $\Delta F^*/RT_c$ for indicated molecular weight fractions: O, 9000; △, 7100; ●, 5900; ▲, 3400

REFERENCES

1 Mandelkern, L., Quinn, F.A. and Flory, P.J. *Appl Phys* 1954, **25**, 830
2 Banks, W., Gordon, M., Roe, R.J. and Sharples, A. *Polymer* 1963, **4**, 61
3 Vidotto, G., Levy, D. and Kovacs, A. *J Kolloid Z Z Polym* 1969, **230**, 289
4 Beech, D.R., Booth, C., Dosgson, D.V. and Hillier, I.H. *J Polym Sci (A-2)* 1972, **10**, 1555
5 Godovsky, Y., Slonimsky, G.L. and Garbar, N.M. *J Polym Sci (C)* 1972, **38**, 1
6 Kovacs, A.J. and Gontheir, A. *Kolloid Z Z Polym* 1972, **250**, 530
7 Maclaine, J.Q.G. and Booth, V. *Polymer* 1975, **16**, 191, 680
8 Marco, C., Fatou, J.G. and Bello, A. *Polymer* 1977, **18**, 1100
9 Tinas, J. and Fatou, J.G. *An Fis Quim* (Spain) 1978, in press
10 Kobayashi, S., Tadokoro, H. and Chatani, Y. *Makromol Chem* 1968, **112**, 225
11 Marco, C., Bello, A. and Fatou, J.G. *An Quim* 1977, **73**, 41
12 Flory, P.J., Mandelkern, L. and Hall, H.K. *Am Chem Soc* 1951, **73**, 2352

13 Mandelkern, L. and Flory, P.J. *Am Chem Soc* 1951, 73, 3206

14 Chiang, R. and Flory, P.J. *J Am Chem Soc* 1961, **83**, 2857

15 Avrami, M. *J Chem Phys* 1939, 7, 1103

16 Göler, V., Sachs, F. and Sachs, G. *Z Phys* 1932, 77, 281

17 Ergoz, E., Fatou, J.G. and Mandelkern, L. *Macromolecules* 1972 **5**, 147

18 Mandelkern, L., Fatou, J.G. and Ohno, K. *J Polym Sci (B)* 1968, **6**, 615

19 Fatou, J.G. and Barrales, J.M. *J Polym Sci (A-2)* 1969, 7, 1755

20 Yoshida, S., Suga, H. and Seki, S. *Polymer Journal* 1973, **5**, 33

21 Mandelkern, L. 'Crystallization of Polymers' McGraw-Hill, New York, 1964

22 Mandelkern, L., Fatou, J.G. and Howard, C. *J Phys Chem* 1964, **68**, 3386

23 Mandelkern, L., Fatou, J.G. and Howard, C. *J Phys Chem* 1965, **69**, 956

24 Marco, C., Fatou, J.G., Bello, A. and Blanco, A. (unpublished results)

25 Devoy, C. and Mandelkern, L. *J Polym Sci (A-2)* 1969, **7**, 1883

26 Beech, D.R., Booth, C., Hillier, I.H. and Pickles, C.J. *Eur Polym J* 1972, **8**, 799