Crystallization kinetics of polyethylene—paraffin mixtures

E. Riande and J. G. Fatou

Sección de Física y Fisicoquímica, Instituto de Plásticos y Caucho, CSIC, Juan de la Cierva 3, Madrid 6, Spain

The crystallization kinetics of polyethylene—paraffin mixtures with volume fractions of polymer, v_2, from 0.90 to 0.0098 have been investigated by dilatometric and calorimetric methods. For all concentrations and temperatures the isotherms are well expressed by the free growth approximation, with exponent $n = 3$ for the lower undercoolings and $n = 4$ for the higher undercoolings. When the weight fraction of the polymer and the crystallization temperature increase, the discrepancy between theory and experiment occurs at progressively lower levels of crystallinity. The overall rate temperature coefficient was analysed using the theory pertinent to polymer—diluent mixtures, and it was found that the usual plot $\ln(\tau_{0.1})^{-1}$ vs. $T_m/T\Delta T$ was not linear. At the high crystallization temperature the data are linear and parallel for the different concentrations, and the interfacial free energies are found to be independent of concentration. At the lower crystallization temperatures the data also lie in parallel lines, but a much smaller slope is obtained, about half that corresponding to high temperature crystallization.

INTRODUCTION

Since the crystallization of polymers is a process involving phase equilibrium, the addition of a second low molecular weight component alters the crystallization kinetics and significantly modifies the resulting thermodynamic and morphological properties. For the specific system polyethylene—normal paraffin mixtures, it is known that the diluent does not enter into the crystalline phase[1], so that is present in the non-crystalline or interzonal regions in high concentration. As a consequence, the effective diluent concentration relative to the non-crystalline chain units, will be much greater than the nominal concentration as the crystallization proceeds.

There are major differences between the thermodynamic properties of polyethylene samples crystallized from the pure melt and those crystallized from polymer—diluent mixtures. In both cases, however, the crystallite size in the chain direction is governed by the nucleation process. In other words, the kinetic aspects of the crystallization play an important role in the final properties of the crystallized samples.

Much attention has been paid in the past to the effect of diluents on the crystallization of polymers. The crystallization kinetics[2-5], the relation between the crystallite size and the crystallization temperature[6,7] and between the dissolution temperature and the mature crystal[8-11] have been studied for very dilute polyethylene solutions. However, almost no attention has been given to the crystallization kinetics of polyethylene—normal paraffin systems.

Thermodynamic and morphological properties of polyethylene crystallized from a concentrated mixture of the polymer with the n-hydrocarbon $C_{32}H_{66}$ have been analysed after removing the diluent at room temperature, subsequent to the crystallization[12-14]. It has been demonstrated from these data that there are major differences between the thermodynamic properties of samples crystallized from the pure melt and those crystallized from diluent mixtures of moderate concentration.

Moreover, the temperature coefficient of the overall crystallization rate of molecular weight fractions of linear polyethylene has been extensively analysed by Ergoz et al.[15] and the results for the very high molecular weights appear to indicate a constant value for the slopes, which is similar to that for the high temperature range of the lower molecular weights. However, in the intermediate molecular weight range two different slopes were found which intersect at $129°-130°C$. More recently, Mandelkern et al.[16-18] have reported that different morphologies can be developed in molecular weight fractions of linear polyethylene and the influence of polydispersity and solvents has also been explored.

The two major objectives of this work are therefore: (a), to examine the crystallization kinetics of the system polyethylene—n-paraffins within the scope of the polymer—diluent theory, with special emphasis on the influence of the weight fraction of diluent at crystallization temperatures where the paraffin is melted and is acting as a diluent: and (b) to analyse the temperature coefficient of the overall rate over a very wide range of crystallization temperature, to see if the behaviour is similar to that of the pure polymer where a change in this coefficient is suggestive of changes in the growth mechanism.

EXPERIMENTAL

Materials

The polyethylene fraction used in this work was obtained from Marlex 50 (a linear unfractionated polyethylene manufactured by Phillips Petroleum Company) by elution column techniques[19]. The viscosity average molecular weight of the fraction, calculated from viscometric data using the
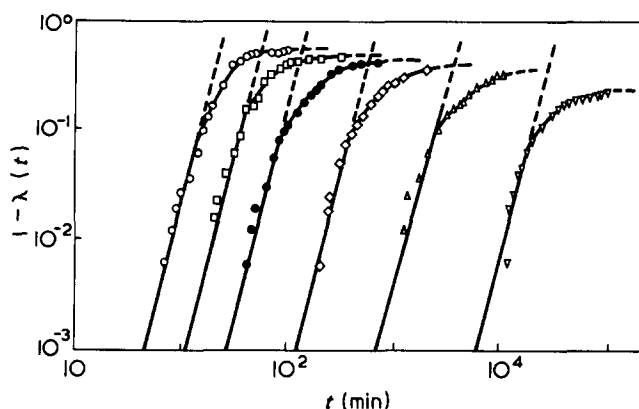
Figure 1 Double logarithmic plot of degree of crystallinity against time at different crystallization temperatures for $v_2 = 0.10$. Temperatures $\bigcirc$, 117°; $\square$, 118°; $\bullet$, 119°; $\Diamond$, 120°; $\triangle$, 121°; $\odot$, 122°C

relation given by Chiang[20], was 160 000. Pure normal paraffins (Humphrey Chemicals) were used as diluent.

Homogeneous mixtures were prepared by dissolving appropriate amounts of the polymer and paraffins in p-xylene at a concentration of about 0.3%. The homogeneous solution was kept at 130°C for 2 h under a nitrogen atmosphere, after which it was quenched in dry ice—isopropyl alcohol. The p-xylene was then removed from the solution by freeze drying. A known amount of the mixture was then transferred to the bulb of a dilatometer, which was sealed and filled with mercury on a high vacuum line. The composition of each mixture, on a volume basis, was calculated at the respective melting temperature of the mixture from the specific volumes reported for n-paraffins by Flory *et al.*[21] and for the polymer in the liquid state at the appropriate temperature, assuming additivity of volumes[19]. Five mixtures were studied in which the volume fraction of polymer v_2 was 0.0096, 0.098, 0.313, 0.704 and 0.90. The first of these fractions was obtained using n-$C_{44}H_{90}$ as diluent and the other four fractions using n-$C_{38}H_{78}$.

Crystallization

An accurately weighed amount of polymer was introduced into the bulk of the dilatometers, which were constructed so that after introducing the mixtures the bulb was sealed and filled with mercury on a high vacuum line[2]. Prior to the initiation of the crystallization the polymer—diluent mixtures were heated at 170°C to remove all traces of crystallinity. The dilatometer was then transferred to an oil bath, thermostatically controlled to within ±0.01°C.

The crystallization kinetics of these samples were analysed at high undercooling using a Perkin—Elmer calorimeter Model DSC-1B. The method used was that previously described[22,23]. The weight of the samples ranged between 5 and 14 mg and the instrument was calibrated on the basis of the melting temperatures of indium, benzyl, phenacetin, benzanilide and the melting enthalpy of indium.

RESULTS AND DISCUSSION

General results

In earlier work related to the crystallization kinetics of very dilute polyethylene solutions[3,4] it has been observed that the crystallization rates depend on the thermal history of the systems. In most cases, at any given temperature, reproducible isotherms are obtained when the solutions are

heated well above their solution temperatures. Although this behaviour also occurs in many polymers crystallized from the bulk[15,24—26], it is unusual for polyethylene of molecular weight lower than 10^6, where completely reproducible isotherms are obtained as long as the sample is rendered totally molten[15]. However, for molecular weights higher than 10^6, the reproducibility of the isotherms and the independence of the prior thermal history is not easily obtained. The mixtures used in this work behave, as far as the influence of the previous thermal history on the crystallization rate is concerned, like polyethylene crystallized from the bulk. That is, reproducible isotherms are obtained when the mixtures are melted at the temperature of the undiluted polyethylene. The experiments were carried out over a wide range of crystallization temperatures, depending on the weight fraction of paraffin in the mixture. Thus, for the two most concentrated systems, $v_2 = 0.9$ and 0.70, isotherms were obtained from 119° to 130°C; for the mixtures in which $v_2 = 0.3$ and 0.1 experiments were carried out in the interval 110° to 125°C; finally for the more dilute system, data were obtained from 116° to 120°C.

The kinetic data were examined using the Göler—Sachs 'free growth' approximation[27]. The theory suggests that for the initial part of the transformation, the double logarithmic plot $1 - \lambda(t)$ *versus* t is linear. Plots of this kind for the dilatometric data are given in *Figure 1*. We note from this Figure that there is a relatively good fit of the experimental data to the theoretical approach. For any given concentration, the slopes of the linear portion are found to be independent of temperature. Of great importance is the fact that these slopes have the same value, 3, similar to that obtained with pure polyethylene of the same molecular weight crystallized from the bulk[15]. However, a puzzling result is found when we analyse the calorimetric data at high undercoolings. As an example, we have plotted these data in *Figure 2* according to the theory for the mixtures in which $v_2 = 0.90$. We observe that a good adherence of the data to the theory is obtained, but the slope of the linear portion is now 4. The simplest interpretation of the slope $n = 3$ is the occurrence of a homogeneous nucleation accompanied by two-dimensional growth, while the slope $n = 4$ means a homogeneous nucleation followed by three-dimensional growth. This last slope was also found for the crystallization of very dilute polyethylene solutions using xylene and tetraline[4] as solvent as well as for low molecular weight samples of polyethylene ($M = 10 000$) crystallized from the bulk[15]. This result cannot easily be explained since the three-dimensional growth cannot be reconciled with the lamellar-like crystallites which are observed. Furthermore, the crystallization of poly(ethylene oxide)—xylene mixtures, analysed over a wide composition range[5], has shown that the slopes also depend on concentration, in sharp contrast with the present experimental results. The possibility of some concomitant changes in the primary morphological forms which develop with the changes in n, has been investigated by Ergoz *et al.*[15]. These authors focussed their attention on the changes in exponent associated with molecular weight in polyethylene samples crystallized from the bulk and found that in all the cases the lamella-like crystallite is the primary morphological structure of bulk crystallized samples. They conclude that the differences in the crystallization kinetics cannot be attributed to any major differences in the basic crystallite morphology.

The method of presenting the data in *Figure 1* is very insensitive to the higher levels of crystallinity where tangible deviations from the free growth approximation manifest

themselves. In order to remove this insensitivity, it is usual to represent the data, covering the complete composition range, as linear plots of the degree of crystallinity as a function of log t. In *Figure 3* the dilatometric isotherms for each composition were superposed upon one another by shifting
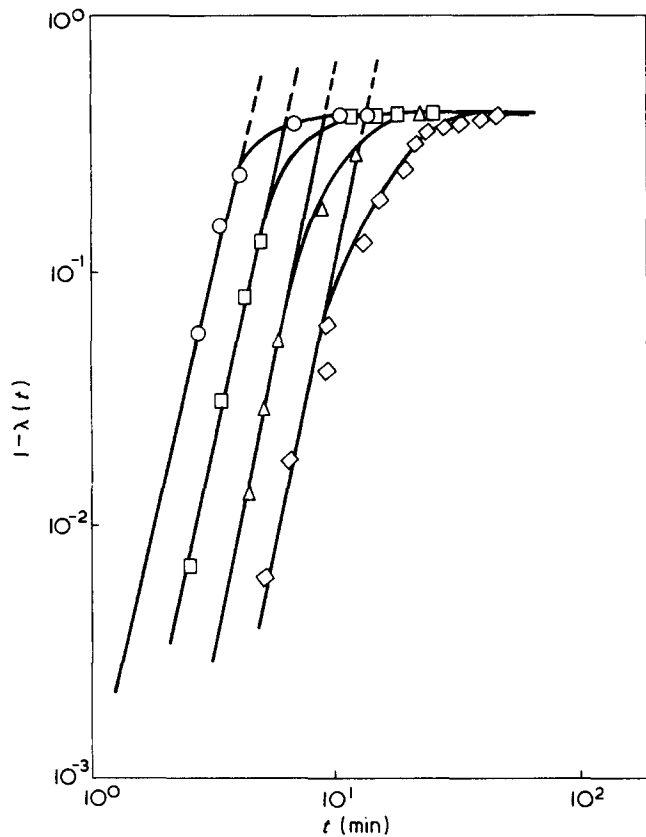

Figure 2 Double logarithmic plot of degree of crystallinity against time at high undercooling. (Calorimetric data) for v_2 = 0.10. Temperature (°C) of crystallization ○, 106° ; □, 107° ; △, 108° ; ◇, 110°C

each one along the log time axis until the best composite curve was obtained. We observe the general autocatalytic nature of the process at the beginning of the crystallization, followed by a very marked retardation in the crystallization rate in such a way that the increase in crystallinity with time proceeds very slowly. Within each composition, the higher is the crystallization temperature the lower is the crystallinity level at which the retardation occu rs. This behaviour contrasts with that of polyethylene crystallized from the bulk[15]. In this case the retardation of crystallization rate is more prominent in the low temperature region. The isotherms of each mixture are not superposable over the complete extent of the transformation, the deviations from the superposition being more important in the more dilute solution. This means that the temperature coefficient of the process in the tail portion of the isotherms is not the same as for the initial part of the transformation. Moreover, when the different mixtures are compared, the extent of the transformation at which the crystallization rate becomes retarded is also dependent on composition in a way which is more apparent in moderate and highly concentrated system. In *Figure 3* we have also drawn the theoretical Avrami isotherms with the composite curves. Since in the early stages of the transformation the Avrami formulation reduces to the Göler—Sachs treatment, we have used the slope of the double logarithm plot $1 - \lambda(t)$ against t as Avrami exponent. As occurs with other systems, the agreement of the experimental data with the Avrami representation is about the same as with the free growth approximation, so that devia tions from either of the theories takes place at the same crystallinity level.

It is important to examine the influence of the concentration of diluent on the final level of crystallinity. We can note that the earlier the retardation in the crystallization rate occurs, the lower is the level of crystallinity which is attained. For the more dilute mixture, crystallinities of about 90 % are obtained at the lower crystallization temperatures. However, as the fraction of diluent decreases in
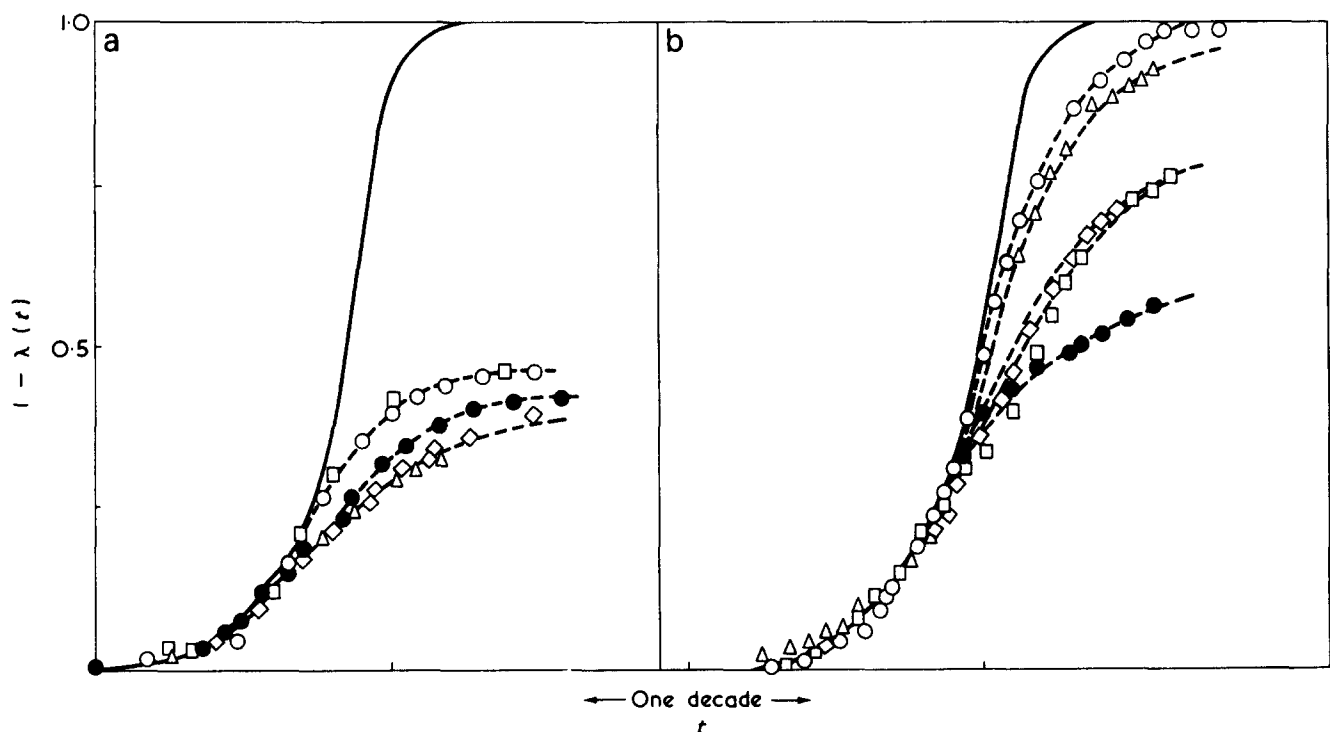

Figure 3 Superimposed plots of 1 − λ against log t at different crystallization temperatures: A, for v_2 = 0.10; ○, 118° ; □, 119° ; ●, 120° ; ◇, 121° 121° ; △, 122°C. B, for v_2 = 0.01; ○, 116° ; △, 117° ; ◇, 118° ; □, 119° ; ●, 120°C
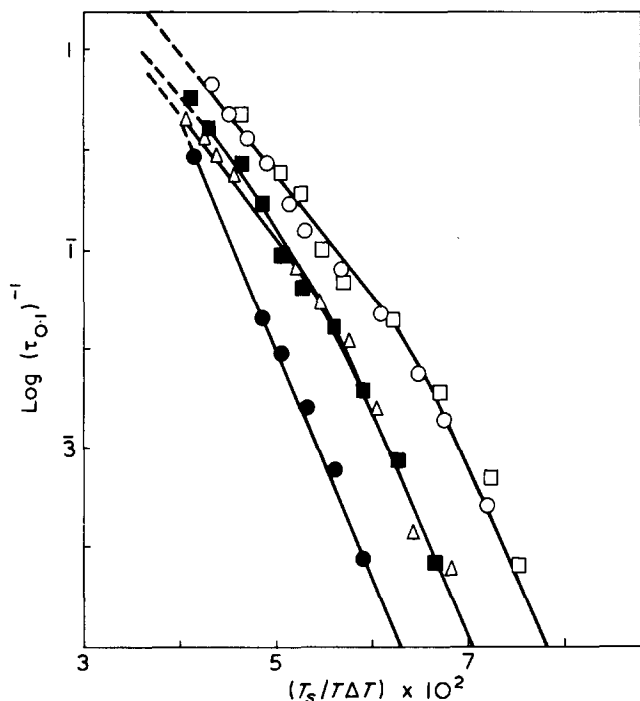
Figure 4 Plot of log $(\tau_{0.1})^{-1}$ against $(T_s^0/T\Delta T)$ for different polymer concentrations: $\odot$, $v_2 = 0.90$; $\square$, $v_2 = 0.70$; $\blacksquare$, $v_2 = 0.30$; $\triangle$, $v_2 = 0.10$; $\bullet$, $v_2 = 0.01$

the mixtures, the final level of crystallinity also decreases reaching a value of 50%, slightly lower than that found for polyethylene of molecular weight similar to that used in this study (~65%). The experimental data also seem to indicate that for moderate and highly concentrated mixtures, the final level of crystallinity is the same.

Temperature coefficient

The crystallization rate depends strongly on temperature and composition, showing a large negative temperature coefficient for each composition[28]. It is usual to discuss the rate—temperature relationship in terms of the nucleation theory, according to the equation[2-5]:

$$(\tau_{0.1})^{-1} = (\tau_{0.1})_0^{-1} \exp\left(-\frac{\Delta F}{RT}\right) \qquad (1)$$

where $\tau_{0.1}$ is the time necessary to achieve 10% crystallity, $(\tau_{0.1})_0^{-1}$ is constant over the temperature range considered and ΔF is the free energy for forming a critical size nucleus. Equation (1) can be written in the following way:

$$\ln\left(\tau_{0.1}\right)^{-1} = (\ln \tau_{0.1})^{-1} - \frac{2\sigma_e\sigma_u}{\Delta H_u} \frac{T_s^0}{T\Delta T} \qquad (2)$$

where T_s^0 is the equailibrium-melting temperature or dissolution temperature, T is the crystallization temperature and ΔT is the undercooling, σ_e and σ_u are the basal and lateral interfacial free energies respectively. The plots of log $(\tau_{0.1})$ against $T_s^0/T\Delta T$ should be a straight line provided the rate controlling step is the formation of a monolayer nucleus. In order to analyse the temperature coefficient, it is necessary to know T_s^0. However, as has been widely discussed[28] this quantity has evaded direct experimental determination. Therefore, the evaluation of T_s^0 was carried out using Flory relationship[29] which permits us to calculate the

depression of temperature by the presence of diluents:

$$1/T_s^0 - 1/T_m^0 = (RV_u/\Delta H_u V_1)v_1(1 - \chi v_1) \qquad (3)$$

This equation can only be used for concentrated solutions in any solvent and for very dilute solutions in sufficiently poor solvents, where excluded volume effects are negligible.

With these limitations in mind, and taking the same value for interaction parameter, χ_1, as that given for n-hexadecane $(\chi_1 = 0.16)$[10,11] we find the values given in *Table 1* for T_s^0. We should stress that for the paraffins used here the exact value of χ_1 is not important as for other diluents, owing to the large molar volume which significantly reduces the effect of χ_1 in the depression of temperature.

In the analysis of the temperature coefficient we have taken the nucleation mode to be bidimensional and plots of log $(1/\tau_{0.1})$ against $(1/T)$ $(T_s^0/T\Delta T)$ are shown for this case in *Figure 4*. Before examining these representations in detail it is necessary to point out that with the present dilatometric and calorimetric data, any attempt at discriminating between the two possible modes of nucleation would be unsuccessful, since it has been amply shown in the past that this treatment cannot accomplish this task. Previous work on polyethylene—solvent mixtures[4] and on poly(ethylene oxide)—xylene[5] have shown linear relations in the plots $\ln(\tau_{0.1})^{-1}$ vs. $T_s^0/T\Delta T$, which are parallel for different concentrations and it was concluded that the product $\sigma_e\sigma_u$ is independent of the concentration over the whole range of crystallization temperatures. However, the general character of these plots in the polyethylene—paraffins system is non-linear. It is possible to draw two straight lines which intersect at a critical crystallization temperature, T_{cc}: the value of T_{cc} decreases with increasing weight fraction of diluent, as is shown in *Figure 4*.

A striking feature of these plots is that the experimental data for the highly concentrated mixtures ($v_2 = 0.70$ and 0.90) can be fitted to a unique straight line in the region of low undercoolings ($T \gg T_{cc}$). In the same way, another single straight line is obtained for the moderately concentrated mixtures ($v_2 = 0.10$ and 0.30). All these lines seem to be parallel to that of the lower concentration mixtures and the exact values of their slopes calculated by least square analysis, are given in *Table 1*. If we average all these quantities we obtain a value of 210 ± 13% for the slope of these plots. It may be worthwile to compare this slope with that obtained for high molecular weight polyethylene crystallized from the bulk. Here, for fractions of molecular weight between 47 000 and 660 000 the data behave as those of the mixtures, that is, the plots are non-linear[15]. The temperature at the intersection of the two straight lines, corresponding to high and low undercoolings, is 129°C for a fraction of molecular weight M = 175 000 similar to that

Table 1 Crystallization temperature T_{cc}, above which there are significant changes in the temperature coefficient

v_2	T_{cc}	Slope $(T > T_{cc})$	Slope $(T < T_{cc})$	T_s^0
0.0098[b]	—	238	—	411
0.092	117	210	146	410.5
0.313	121	210	146	414
0.704	125	182	125	416
0.90	127	182	125	417.6
1.0	129	205	80	

[a] Slope average 210 ± 13%; [b] this mixture prepared with $C_{44}H_{90}$; the others prepared with $C_{38}H_{78}$

of the mixtures. Moreover, the slope at the high crystallization temperature is 205 which agrees very satisfactorily with the averaged slope obtained for the mixtures.

In the low crystallization temperature region the data for concentrated mixtures also lie in a line parallel to the straight line drawn through the data corresponding to the moderately concentrated solutions. Although a much smaller slope is obtained for the data in this region, its value is significantly higher than that of the polymer crystallized from the bulk.

The temperature coefficients for either the high or low temperature regions are, within experimental error, independent of the concentration of polymer. The results for low undercoolings indicate that the product of the lateral interfacial free energy σ_u and the apparent basal free energy σ_e is independent of the composition of the mixture and has a value 2.37×10^5 cal^2/mol^2, similar to that reported for the polymer crystallized from the bulk[15] and from very dilute solutions[3,4]. The presence of another set of data which fits a straight line of smaller slope appears to indicate that although the very strong negative temperature coefficient still gives strong support to the importance of the nucleation process, this is not as simple as has been previously postulated. Mandelkern *et al.*[16-18] have recently investigated the influence of the crystallization temperature on supermolecular structure of polyethylene fractions crystallized from the bulk by small-angle light scattering; they found that these structures are strongly dependent on molecular weights. For these molecular weight fractions crystallized in bulk, the usual plot $\ln(\tau_{0.1})^{-1}$ vs. $T_m/T\Delta T$ is no longer linear as stated before, except for the higher molecular weights. The slopes for the high molecular weights and the high temperature lower molecular weights are the same. At low molecular weights a rod-like morphology was observed at all temperatures and at intermediate molecular weights there is a crystallization temperature T_{cc} where the morphology changes from spherulitic to rod-like morphology. Hoffman *et al.*[30] studied the growth kinetics of the different morphological forms that they observed in polyethylene and found that the temperature coefficient of the axialites was twice that of the coarse granied spherulites.

To summarize, the analysis of the crystallization on polyethylene—paraffin mixtures has shown that at low undercoolings the temperature coefficient and the basal free energy is independent of the composition of the mixtures. However at higher undercoolings, the temperature coefficient for the overall crystallization rate is about half that corresponding to high temperature crystallization. This point was not previously reported in the kinetic analysis of polymer—diluent mixtures[2-5], where higher undercoolings could not be used, and it is similar to that found in bulk polyethylene. This very interesting fact suggests that morphological changes may be associated also in the crystallization of polyethylene—paraffin mixtures. Further work is in progress to clarify this point.

REFERENCES

1   Nakajima, A. and Hamada, F. *Kolloid Z.* 1965, **205**, 55
2   Fatou, J. G., Riande, E. and Valdecasas, R. G. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, **13**, 2103
3   Riande, E. and Fatou, J. G. *Polymer* 1976, **17**, 99
4   Riande, E. and Fatou, J. G. *Polymer* 1976, **17**, 795
5   Riande, E., Fatou, J. G. and Alcazar, J. C. *Polymer* 1977, **18**, 1095
6   Devoy, C., Mandelkern, L. and Bourland, L. *J. Polym. Sci. (A-2)* 1970, **8**, 869
7   Ergoz, E. and Mandelkern, L. *J. Polym. Sci. (Polym. Lett. Edn)* 1973, **11**, 73
8   Jackson, J. F. and Mandelkern, L. *Macromolecules* 1968, **1**, 546
9   Sharma, R. K., Mandelkern, L. and Jackson, J. F. *Am. Chem. Soc. Meeting, New York,* 1969
10   Nakajima, A., Hamada, F., Hayashi, S. and Sumida, T. *Kolloid Z.* 1968, **222**, 10
11   Nakajima, A., Hayashi, S., Korenaga, T. and Sumida, T. *Kolloid Z.* 1968, **222**, 124
12   Keith, H. D., Padden, F. J. and Vadimsky, R. G. *J. Polym. Sci.* 1966, **4**, 267
13   Keith, H. D., Padden, F. J. and Vadimsky, R. G. *J. Appl. Phys.* 1966, **37**, 4027
14   Devoy, C., and Mandelkern, L. *J. Polym. Sci. (Polym. Lett. Edn)* 1968, **6**, 141
15   Ergoz, E., Fatou, J. G. and Mandelkern, L. *Macromolecules* 1972, **5**, 147
16   Go, S., Mandelkern, L., Prud'homme, R. and STein, R. *J. Polym. Sci. (Polym Phys. Edn)* 1974, **12**, 1485
17   Mandelkern, L., Go, S., Peiffer, D. and Stein, R. S. *J. Polym. Sci. (Polym. Phys. Edn)* 1977, **15**, 1189
18   Maxfield, J. and Mandelkern, L. *Macromolecules* 1977, **10**, 1141
19   Fatou, J. G. and Mandelkern, L. *J. Phys. Chem.* 1965, **69**, 71
20   Chiang, R. *J. Polym. Sci.* 1959, **36** 91
21   Flory, P. J., Orwoll, R. A. and Vrij, A. *J. Am. Chem. Soc.* 1964, **86**, 3507
22   Fatou, J. G. and Barrales-Rienda, J. M. *J. Polym. Sci. (A-2)* 1969, **7**, 1755
23   Barrales-Rienda, J. M., and Fatou, J. G. *Polymer* 1971, **13**, 407
24   Jadraque, D. and Fatou, J. G. *Anal. Quim. (Spain)* 1977, **73**, 639
25   Marco, C., Fatou, J. G. and Bello, A. *Polymer* 1977, **18**, 1100
26   Tinas, J. and Fatou , J. G. *Anal. Quim. (Spain)* 1978 , **74**, in press
27   Göler, V., Sachs, F. and Sachs, G. *Z. Phys.* 1932, **77**, 28 1
28   Mandelkern, L., 'Crystallization of polymers' McGraw–Hill, New York, 1964
29   Flory, P. J. 'Principles of Polymer Chemistry' Cornell University Press, Ithaca, New York, 1953
30   Hoffman, J. D., Frolen, L. J., Ross, G. S. and Lauritzen Jr, J. I. *J. Res. Nat. Bur. Stand. (A)* 1975, **79**, 671