Phase Separation in *n*-Hexatriacontane–*n*-Hexatriacontane-d_{74} and Polyethylene–Poly(ethylene-d_4) Systems[1a]

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ABSTRACT: Phase separation, melting temperature, and crystallization rate measurements have been made on hydrocarbon–deuteriocarbon systems to assess the extent of fractionation that can occur when such mixtures crystallize. Selective partitioning of *n*-$C_{36}H_{74}$ and *n*-$C_{36}D_{74}$ between the crystalline and liquid phases occurs when the two paraffins crystallize from the melt or from benzene solution. The partitioning of the two paraffins is caused by the fact that the melting point of $C_{36}H_{74}$ is *ca.* 4° greater than that of $C_{36}D_{74}$. The equilibrium melting temperature of polyethylene (PEH) is demonstrated to be greater than that of poly(ethylene-d_4) (PED) by about the same amount. Because of this difference in melting temperatures, PEH crystallizes much more rapidly from dilute solution than PED. The relevance of these observations to recent interpretations of the infrared spectra of PEH-PED mixed crystals is discussed. From such spectra it has been concluded that adjacent reentry along certain fold planes occurs in both solution-crystallized and melt-crystallized polyethylene. However, because of the possibility of severe composition heterogeneity occurring in the preparation of hydrocarbon–deuteriocarbon mixed crystals, the data presented to date cannot be unequivocally interpreted.

Polymers crystallized from dilute solutions characteristically form lamellar crystals in which the polymer chain axes are oriented normal or nearly normal to the broad faces of the lamellae. It has been proposed that the wide surfaces of the lamellae have a highly regular structure with adjacent reentry of chains into the crystal.[2–4] Alternatively, it has been proposed that the surfaces have an irregular structure with essentially random reentry of chains into the crystal.[5–7] Most of the physical–chemical evidence that has been presented supports this latter point of view.[7] Crystals prepared from the polymer melt also typically have a lamellar habit. The regularity of the wide faces of the lamellae and the type of reentry of chains in such crystals is also controversial.[4,8]

Krimm and coworkers recently suggested a new approach to determining the type of reentry occurring in polyethylene crystals.[9] From a comparison of infrared measurements made on cocrystals of *n*-$C_{36}H_{74}$–*n*-$C_{36}D_{74}$ and of polyethylene–poly(ethylene-d_4), it was concluded that chain folding with adjacent reentry occurred both in solution-cast films and in melt-crystallized polyethylene.[10,11] However, this conclusion is based on the tacit assumption that the composition distribution of cocrystals obtained in the crystallization of polyethylene–poly(ethylene-d_4) mixtures is similar to the composition distribution of cocrystals obtained in the crystallization of *n*-$C_{36}H_{74}$–*n*-$C_{36}D_{74}$ mixtures.

In this paper we present results on the melting temperatures, phase separation, and crystallization rates of hydrocarbon–deuteriocarbon systems. From these results an alternate interpretation of the infrared data is suggested.

Experimental Section

Paraffin Experiments. A partial phase diagram for the *n*-$C_{36}H_{74}$–*n*-$C_{36}D_{74}$ binary system was constructed from data obtained with a Perkin-Elmer differential scanning calorimeter (dsc). *n*-$C_{36}H_{74}$ (99.5% purity) was obtained from Lachat Chemicals, Inc., and *n*-$C_{36}D_{74}$ with isotopic purity of 99.6% by mass spectrometric analysis was obtained from Merck Sharpe and Dohme, Ltd. The latter compound was prepared under conditions that ensure the absence of branched isomers. The quantity of impurities in each of the two paraffins detectable by gas chromatographic and mass spectrometric analysis was less than 0.2%. Mixtures of $C_{36}H_{74}$ and $C_{36}D_{74}$ were placed in a sealed dsc cup, the mixture was heated at 150° for 10 min, and the cup was then vigorously shaken to promote good mixing of the two constituents. The sample was cooled to room temperature at 1.25°/min, and the thermogram was subsequently recorded at a heating rate of 1.25°/min. Peaks in the thermograms were taken to be the transition temperatures. More prolonged heating in the melt and more vigorous mixing conditions did not affect the transition temperatures obtained. Precision of the transition temperatures was *ca* 0.2°.

Attempts to determine the equilibrium solidus curve for the $C_{36}H_{74}$–$C_{36}D_{74}$ system were unsuccessful because the fibrous crystals that formed could not be cleanly separated from the liquid for analysis. However, the necessary experiments could be performed in the $C_{36}H_{74}$–$C_{36}D_{74}$–benzene system. Phase separation experiments were made by slowly cooling solutions containing 98.5 mol % benzene and varying ratios of the two paraffins. When small quantities of crystals had precipitated, they were separated from the liquid solution by filtration at the crystallization temperature, 39 ± 1°. The extent of crystallization was between 15 and 21 wt % in each of the runs, and the quantity of liquid solution retained on the crystal mat was so small that subsequent crystallization of the paraffins contained in the retained solution did not measurably affect the composition analyses. Quantitative analyses were made in carbon tetrachloride solvent by infrared spectroscopy using bands at 2932 and 2200 cm^{-1} for $C_{36}H_{74}$ and $C_{36}D_{74}$, respectively. Measurements made on mixtures of known composition in the range from 40 to 60% $C_{36}H_{74}$ had a standard deviation of 1.0% from the true values. Infrared examination also showed that benzene was not incorporated into the crystalline phase. Melting temperatures of $C_{36}H_{74}$–benzene and of $C_{36}D_{74}$–benzene mixtures, each mixture containing *ca.* 98.5 mol % benzene, were obtained using hermetically sealed dsc cups by procedures similar to those given above.

Polymer Experiments. Polyethylene (PEH) and poly(ethylene-d_4) (PED) samples, synthesized under similar conditions, were obtained from Merck Sharpe and Dohme, Ltd. Number-, weight-,

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[1] (a) This work was supported in part by a grant from the Army Research Office (Durham); (b) Esso Research and Engineering Co.; (c) Florida State University.

[2] P. H. Geil, "Polymer Single Crystals," Interscience, New York, N. Y., 1963, pp 79 ff.

[3] A. Keller, *Phil. Mag.*, **2**, 1171 (1957).

[4] A. Keller, *Kolloid.-Z. Z. Polym.*, **231**, 386 (1969).

[5] P. J. Flory, *J. Amer. Chem. Soc.*, **84**, 2857 (1962).

[6] E. W. Fischer and G. Schmidt, *Angew. Chem.*, **74**, 551 (1962).

[7] L. Mandelkern, *Progr. Polym. Sci.*, **2**, 165 (1970).

[8] L. Mandelkern, *Polym. Eng. Sci.*, **9**, 1 (1967).

[9] M. Tasumi and S. Krimm, *J. Polym. Sci., Part A-2*, **6**, 995 (1968).

[10] M. I. Bank and S. Krimm, Preprints of Scientific Papers, IUPAC International Symposium on Macromolecular Chemistry, Toronto, 1968, Vol. 1, Paper No. A6.18.

[11] M. I. Bank and S. Krimm, *J. Polym. Sci., Part A-2*, **7**, 1785 (1969).

and z-average molecular weights of PEH by gel permeation chromatography were 17,000, 620,000, and 1,100,000, respectively. Corresponding values for PED were 67,000, 510,000, and 1,200,000, respectively. Dsc melting points of the pure polymers were obtained at a heating rate of 1.25°/min on samples that had been cooled from the melt at 0.625°/min. Isothermal crystallizations for both PEH and PED polymers were made from 0.08% *p*-xylene solutions, following procedures described previously.[12] Lamella thickness of the crystals was determined by low-angle X-ray diffraction.

In another type of experiment, mixtures with various PEH/PED ratios were crystallized from 0.08% *p*-xylene solution at 89°. For a given set of conditions, a number of parallel crystallizations were conducted, and the compositions of the precipitate and the supernatant liquid were determined as a function of time. The analyses were performed by molding the samples into films of about 1–3 mils thickness. These films were analyzed on a Beckman IR-12 spectrophotometer in the linear absorption mode. Integrated absorptivities were measured for the CH_2 rocking mode (*ca.* 720–730 cm^{-1}) and the analogous CD_2 mode (*ca.* 525 cm^{-1}). Calibration was effected using pure PEH, pure PED, and a mixture containing equal weights of the two polymers.

Results

Phase Separation in the $C_{36}H_{74}$–$C_{36}D_{74}$ Binary System. Transition temperatures *vs.* liquid composition curves for the $C_{36}H_{74}$–$C_{36}D_{74}$ system are shown in Figure 1. Two peaks were detected in pure $C_{36}H_{74}$ and in all $C_{36}H_{74}$–$C_{36}D_{64}$ mixtures examined. The low-temperature peak corresponds to the conversion of the orthorhombic to the hexagonal crystal form,[13] which occurred at 73.4° in pure $C_{36}H_{74}$. The high-temperature peak corresponds to the melting of the hexagonal crystal form[13] and occurred at 75.4° in pure $C_{36}H_{74}$. As the concentration of $C_{36}D_{74}$ increased, the melting point decreased monotonically to a value of 71.6° for pure $C_{36}D_{74}$. The temperature of the orthorhombic–hexagonal transition showed a similar trend. Only a single somewhat broadened peak was obtained when the thermogram of pure $C_{36}D_{74}$ was obtained in the heating mode. However, two partially resolved peaks separated by 0.4° were obtained in the cooling mode of operation.

The melting temperature–composition curve of Figure 1 clearly indicates that cocrystallization occurs in $C_{36}H_{74}$–$C_{36}D_{74}$ mixtures. If a pure $C_{36}H_{74}$ crystalline phase were formed in $C_{36}H_{74}$-rich mixtures, then the melting point–composition curve would follow curve A. Similarly, if a pure $C_{36}D_{74}$ crystalline phase were formed, then the melting point–composition curve of $C_{36}D_{74}$-rich mixtures would follow curve B.

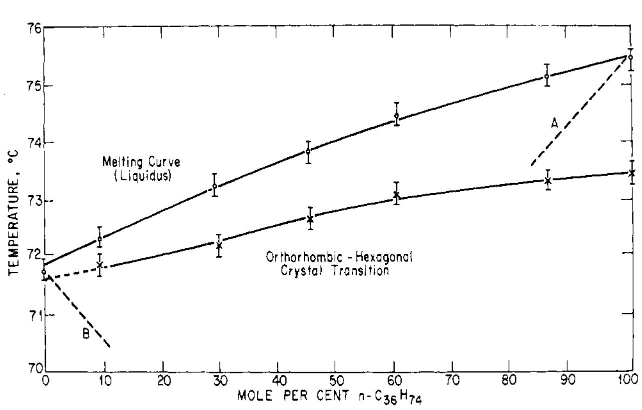

Figure 1. Transition temperatures in binary *n*-$C_{36}H_{74}$–*n*-$C_{36}D_{74}$ mixtures.

TABLE I

CALCULATED COMPOSITION OF LIQUID AND CRYSTALLINE PHASES AT EQUILIBRIUM FOR BINARY *n*-$C_{36}H_{74}$-*n*-$C_{36}D_{74}$ SYSTEM ASSUMING IDEAL LIQUID AND SOLID SOLUTIONS

X_{hl},[a] %	X_{hc},[b] %	Δ, $X_{hc} - X_{hl}$, %
0	0.0	0.0
10	13.5	3.5
20	26.0	6.0
30	37.6	7.6
40	48.4	8.4
50	58.5	8.5
60	67.8	7.8
70	76.6	6.6
80	84.9	4.9
90	92.7	2.7
100	100.0	0.0

[a] Mole per cent $C_{36}H_{74}$ in liquid phase. [b] Mole per cent $C_{36}H_{74}$ in crystalline phase.

The observed melting point–composition curve does not coincide with curves A and B because $C_{36}H_{74}$ and $C_{36}D_{74}$ form a solid solution. However, although cocrystallization occurs in the binary $C_{36}H_{74}$–$C_{36}D_{74}$ system, the composition of the liquid and crystalline mixtures in equilibrium at the melting point must be different. From thermodynamic considerations, it is known that for a two-component system the compositions of two phases can be identical only if (1) ideal liquid and solid solutions are formed and the melting points of the two components are equal or (2) the system is sufficiently nonideal that a maximum or a minimum exists in the liquidus and solidus curves.[14] In the latter case there is only one point at which the compositions of the liquid and solid solutions are equal. The melting points of $C_{36}H_{74}$ and $C_{36}D_{74}$ differ, so the first condition is not fulfilled. The second condition is not met because the liquidus curve in Figure 1 does not have a maximum or a minimum. Consequently, the two paraffins must be selectively partitioned between the two phases at equilibrium.

The composition of the two phases at equilibrium can be calculated from the relation[15]

$$\left(\frac{\gamma_{dc}X_{dc}}{\gamma_{hc}X_{hc}}\right)\Big/\left(\frac{\gamma_{dl}X_{dl}}{\gamma_{hl}X_{hl}}\right) = \exp\left(\frac{\Delta H_{fh}}{RT_{mh}{}^0} - \frac{\Delta H_{fd}}{RT_{md}{}^0} + \frac{\Delta H_{fd}}{RT_m} - \frac{\Delta H_{fh}}{RT_m}\right) \quad (1)$$

where γ_{ij} = the activity coefficient of component i in phase j, X_{ij} = the mole fraction of i in phase j, ΔH_{fi} = the heat of fusion of i, $T_{mi}{}^0$ = the melting point of pure i, and T_m = the melting point of the mixture. The subscripts d and h refer to *n*-$C_{36}D_{74}$ and *n*-$C_{36}H_{74}$, respectively, and the subscripts l and c refer to the liquid and crystalline phases, respectively. Assuming that both the crystalline and solid solutions are ideal solutions, *i.e.*, that all activity coefficients equal one, and that $\Delta H_{fd} = \Delta H_{fh}$, we have

$$\left(\frac{X_{dc}}{X_{hc}}\right)\Big/\left(\frac{X_{dl}}{X_{hl}}\right) = \exp\left[\frac{\Delta H_{fh}}{R}\left(\frac{1}{T_{mh}{}^0} - \frac{1}{T_{md}{}^0}\right)\right] = k \quad (2)$$

Values of X_{hc} corresponding to various values of X_{hl} calculated from (2) using $T_{mh}{}^0$ = 348.6°K, $T_{md}{}^0$ = 344.8°K, $\Delta H_{fd} = \Delta H_{fh}$ = 21,230 cal/mol,[13] *i.e.*, k = 0.71, are listed in Table I. The assumption that ΔH_{fd} equals ΔH_{fh} implies

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(12) J. F. Jackson and L. Mandelkern, *Macromolecules*, **1**, 546 (1968).

(13) M. G. Broadhurst, *J. Res. Nat. Bur. Stand., Sect. A*, **66**, 241 (1962).

(14) A. H. Wilson, "Thermodynamics and Statistical Mechanics," Cambridge University Press, Cambridge, 1957, p 412.

(15) K. Denbigh, "Principles of Chemical Equilibrium," Cambridge University Press, Cambridge, 1961, p 289.

TABLE II
COMPOSITIONS OF LIQUID AND CRYSTALLINE PHASES IN $C_{36}H_{74}$–$C_{36}D_{74}$–BENZENE SYSTEM

Comp of liq phase, %				Comp of cryst phase, %		X_{hc} −	$(X_{dc}/X_{hc})/$
X_{hl}	X_{dl}	X_{bl}[a]	X_{hl}'[b]	X_{dc}	X_{hc}	X_{hl}'	(X_{dl}/X_{hl})
0.514	0.765	98.7	40.2	50	50	10	0.67
0.465	0.689	98.8	40.3	51	49	9	0.70
0.828	0.914	98.3	47.5	45	55	8	0.74
0.791	0.791	98.4	50.0	40	60	10	0.67
0.662	0.624	98.8	51.4	37	63	12	0.62
0.786	0.522	98.7	60.1	31	69	9	0.68
					Av	10	0.68
					Std dev	1.4	0.04

[a] Mole per cent benzene in liquid phase. [b] $X_{hl}' = X_{hl}/(X_{hl} + X_{dl})$; *i.e.*, X_{hl}' is the mole fraction of $C_{36}H_{74}$ in the liquid phase, neglecting the benzene present in that phase.

that the difference in melting points of the pure paraffins is caused by a difference in the entropy of fusion of the two paraffins. However, the assumption that the entropies of fusion of the two paraffins are equal and that the melting point difference is caused by different enthalpies of fusion yields, to an excellent approximation, the same results as those listed in the table.

Examination of Table I shows that, as expected, the crystalline phase is enriched in $C_{36}H_{74}$, the higher melting constituent. For example, the first crystals formed upon cooling an equimolar mixture from the melt would contain 59 mol % $C_{36}H_{74}$. If the temperature is further reduced so that crystallization proceeds to completion, the concentration of the hydrocarbon constituent in the liquid phase decreases, and the instantaneous composition of the crystals formed varies throughout the process. Consequently, the hydrocarbon and deuteriocarbon molecules will not be uniformly distributed among the crystals after completion of the crystallization process. Because of kinetic as well as thermodynamic factors, the composition distribution obtained may depend on the detailed procedures used in the crystallization process.

Since the crystals formed from $C_{36}H_{74}$–$C_{36}D_{74}$ mixtures could not be cleanly separated from the liquid, the calculated composition data in Table I could not be verified directly. However, experimental results given below for the ternary $C_{36}H_{74}$–$C_{36}D_{74}$–benzene system support the validity of the calculated compositions given in Table I.

Phase Separation in the $C_{36}H_{74}$–$C_{36}D_{74}$–Benzene Ternary System. Selective partitioning of $C_{36}H_{74}$ and $C_{36}D_{74}$ between the crystalline and liquid phases was clearly demonstrated in the $C_{36}H_{74}$–$C_{36}D_{74}$–benzene system. Results of these experiments are summarized in Table II. It should be recalled that only a small fraction, 15–21%, of the paraffin has been crystallized in these experiments. Examination of the last column shows that the $C_{36}D_{74}/C_{36}H_{74}$ ratio in the liquid phase is different from that in the crystalline phase. The crystalline phase is relatively rich in the hydrocarbon paraffin. Within experimental error, the quotient $(X_{dc}/X_{hc})/(X_{dl}/X_{hl})$ has a constant value, 0.68, with a standard deviation equal to 0.04.

Since benzene is rejected from the crystal phase, the only thermodynamic effect of the benzene is to lower the free energy of the liquid phase. The compositional relation expressed by eq 1, where T_{mh}^0, T_{md}^0, and T_m are now melting points in 98.5 mol % benzene solution, is applicable. The experimental values for T_{mh}^0 and T_{md}^0 in benzene were 314.4 and 311.2°K, respectively, and T_m was taken to be the observed precipitation temperature, 312 ± 1°K. The right-hand side of (1) then becomes 0.71. Substituting this value and the experimental value, 0.68 ± 0.04, for $(X_{dc}/X_{hc})/(X_{dl}/X_{hl})$, eq 1 becomes

$$(\gamma_{dc}/\gamma_{hc})/(\gamma_{dl}/\gamma_{hl}) = 1.0 \qquad (3)$$

This relation would be satisfied if all activity coefficients were one, but this condition would not be expected to hold in a solution consisting of molecules with widely different molar volumes such as benzene and hexatriacontane. However, the less restrictive condition that $\gamma_{dl}/\gamma_{hl} = 1$ and $\gamma_{dc}/\gamma_{hc} = 1$ also satisfies (3). For the liquid solution it is probable that $\gamma_{dl} = \gamma_{hl} \neq 1$. For the solid solution, which does not contain benzene, it is likely that $\gamma_{dc} = \gamma_{hc} = 1$.

It is noteworthy that the experimental value of $(X_{dc}/X_{hc})/(X_{dl}/X_{hl})$ determined for the ternary system, 0.68 ± 0.04, is similar to the 0.71 value which was calculated for the binary system. The degree of partitioning of the paraffins between phases in these two systems should therefore be similar. This is further illustrated by comparing the data in the last column in Table I with those in the second column from the right in Table II. According to the calculations given in Table I, in the middle range of compositions the $C_{36}H_{74}$ content of the solid phase should exceed by about 8% the $C_{36}H_{74}$ content of the liquid phase with which it is in equilibrium. The experimental results given in Table II show an enrichment of 10%, with a standard deviation of 1.4%, in this composition range. The basis for the partitioning in both systems is, of course, the difference in the melting temperatures of the pure paraffins.

Phase Separation in PEH–PED Systems. It is of interest to extend the preceding phase separation analysis to the corresponding polymers, PEH and PED. Attention is focused on establishing the equilibrium melting temperatures of the two pure polymers, since phase separation behavior is largely governed by these quantities. The difficulties in directly determining the equilibrium melting temperature of any polymer are well known, and indirect procedures have to be employed.[12,16,17] The principal method that we have used is based on an analysis of the relation between the isothermal crystallization temperature and the thickness of the crystallites obtained from dilute solution. According to a variety of experimental observations, the crystallite thickness is nucleation controlled.[17] According to the most general theory,[12] without the need to specify the details of the nucleation act, it is found that

$$1/T_c = 1/T_s^0 + (\kappa/\Delta H_u)(1/\zeta T_c) \qquad (4)$$

Here T_c is the crystallization temperature, T_s^0 the equilibrium melting temperature in dilute solution, ζ the crystallite thickness along the chain axis, and κ a constant determined by the specific features of the nucleation act. Thus, as has been previously demonstrated for polyethylene in a variety of solvents, a plot of $(T_c)^{-1}$ against $(\zeta T_c)^{-1}$ is linear and yields an extrapolated value for T_s^0 that is in good agreement with the value obtained by other methods.[12]

Experimental data obtained from PEH and PED crystals prepared from xylene solutions are shown in Figure 2. The solid line is taken from previously published data obtained using polyethylene molecular weight fractions.[12] The solid

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(16) J. F. Jackson, L. Mandelkern, and O. C. Long, *Macromolecules*, 1, 218 (1968).

(17) L. Mandelkern, "Crystallization of Polymers," McGraw-Hill, New York, N. Y., 1964.

TABLE III
TIME FOR APPEARANCE OF CLOUDINESS IN ISOTHERMAL CRYSTALLIZATION OF PEH AND PED FROM DILUTE *p*-XYLENE SOLUTION

T_c, °C	Time of appearance of cloudiness Poly(ethylene-d_4)	Polyethylene
75.1	4 min	
77.1	6 min	
79.1	9 min	
80.1		5 min
81.1	70 min	
83.1		8 min
85.1	3 hr	17 min
87.1	~24 hr	~45 min
88.1		55 min
89.1	~3 days	2 hr
91.1		14 hr

TABLE IV
COMPOSITION OF CRYSTALS *vs.* TIME FOR CRYSTALS PREPARED FROM PEH–PED-*p*-XYLENE SOLUTIONS WITH VARIOUS INITIAL PEH–PED RATIOS

	Initial PEH–PED weight ratio in solution					
	10:90		50:50		90:10	
	PEH:PED in		PEH:PED in		PEH:PED in	
Time	Ppt	Soln	Ppt	Soln	Ppt	Soln
2.5Θ_i		7:93	99:1	44:56		92:8
5.0Θ_i		5:95	94:6	44:56	100:0	97:3
7.5Θ_i	31:69		100:0	40:60	100:0	92:8
10Θ_i	26:74	4:96	74:26	7:93	95:5	56:44

points, which were obtained on PEH in the present work, are in good agreement with these literature values. The dashed line is drawn through the PED data, which are represented by the open circles. The equilibrium melting temperatures in dilute *p*-xylene solution determined from the intercepts of these lines are 118.6 ± 1.5 and 112.5 ± 1.5 for PEH and PED, respectively. Provided that the polymer–solvent interaction parameters of PEH and PED are equal, these results require that the equilibrium melting temperature of pure PEH be about 6° greater than that of pure PED. The equality of the polymer–solvent interaction parameters is credible in view of the fact that the activity coefficients of *n*-$C_{36}H_{74}$ and *n*-$C_{36}D_{74}$ in benzene are equal. Only a major difference in the interaction parameter, of a magnitude not as yet observed for any of the solvents for polyethylene,[12] could make any serious adjustment to the deduced difference of melting temperature for the pure species.

The experimental observation that the differences in equilibrium melting temperature of PEH and PED is about the same as that of $C_{36}H_{74}$ and $C_{36}D_{74}$ is to be expected from theoretical grounds. Flory and Vrij estimated the equilibrium melting point of polyethylene using melting temperature–molecular weight data on the homologous series of *n*-hydrocarbons.[18] The factors involved in the hydrocarbon series should be manifested also in the deuteriocarbon series. Further experimental evidence that the melting temperature of PEH is greater than that of PED was obtained from dsc measurements made on the pure polymers crystallized rapidly from the melt. Melting temperatures thus determined for PEH and PED were 135.2 and 130.4°, respectively. A similar difference in the melting temperatures of pure PEH and pure PED crystallized from dilute solution was observed when samples with the same lamella thickness were compared.

Because of the influence of nucleation processes on crystallization, the undercooling at which the crystallization is conducted has a very large influence on the rate of crystallization.[17] Consequently, the difference in equilibrium melting temperatures of PEH and PED should cause dramatically different crystallization rates between the two polymers when crystallization is conducted at the same temperature. (This expectation is borne out by bulk crystallization rate measurements, details of which will be reported elsewhere.) This difference in equilibrium melting temperatures manifests itself in a striking way in the crystallization kinetics from dilute solution. This is shown in Table III, where the times for the first appearance of a precipitate at various temperatures are listed. PEH crystallizes much more rapidly than PED, especially at low degrees of undercooling. However, when the *ca.* 6° difference in the equilibrium melting temperatures is taken into account, so that the times for precipitation are compared at the same undercooling, then the two polymers give virtually the same results.

The measured compositions of the precipitate and the supernatant liquid as a function of time for a series of dilute solution crystallizations of PEH–PED mixtures run at 89° are shown in Table IV. Experiments were made using three different initial PEH:PED ratios. Θ_i represents the time at which a precipitate was first observed. The value of Θ_i in each of these experiments was several hours. The experiments were teminated at time 10Θ_i; at this time about 40–50 wt % of the polymer had precipitated. Examination of this table shows that, irrespective of the initial composition, the first crystals formed are greatly enriched in PEH. For example, the first crystals formed from a solution containing a 50:50 weight ratio of PEH and PED are almost pure PEH. At 10Θ_i, when the conversion to crystals is about 40% complete, the average PEH:PED ratio of the precipitate is 74:26. After crystallization to 100% conversion, the average PEH:PED ratio of the precipitate would be 50:50, of course, but the composition distribution of the crystals would be very broad. There is thus a marked partitioning of PEH and PED between the crystalline and liquid phases, and a severe compositional heterogeneity is developed when crystallization proceeds to high conversion.

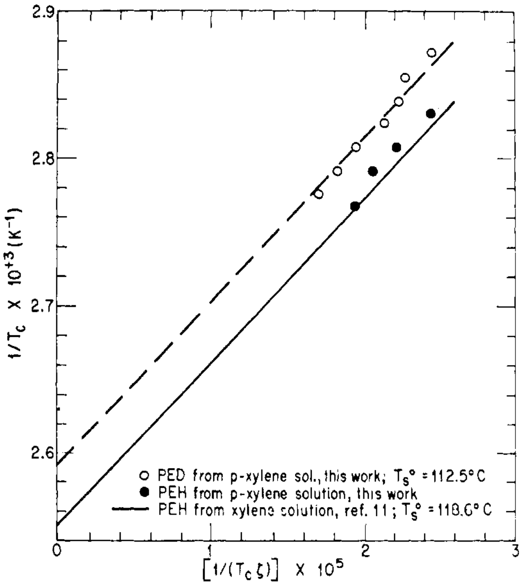

Figure 2. Plot of crystallization temperature–lamella thickness relation for polyethylene and poly(ethylene-d_4) according to eq 4.

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[18] P. J. Flory and A. Vrij, *J. Amer. Chem. Soc.*, **85**, 3548 (1963).

Discussion

The experimental results described above show that the equilibrium melting temperatures of PEH and PED differ by about 6°, a value which is comparable to the difference in the equilibrium melting temperatures of n-$C_{36}H_{74}$ and n-$C_{36}D_{74}$. Consequently, PEH and PED must be selectively partitioned between the crystalline and liquid phases in both binary and ternary mixtures at equilibrium. From purely thermodynamic considerations, broad composition distributions of PEH–PED cocrystals will be obtained upon exhaustive crystallization of mixtures containing both of these polymers. The large differences in the crystallization rates of the two polymers can only enhance the nonuniformity in composition predicted from the thermodynamic data. The extensive compositional heterogeneity that is anticipated from the above arguments is actually demonstrated by the data of Table IV.

Similarly, $C_{36}H_{74}$ and $C_{36}D_{74}$ will segregate upon exhaustive crystallization of $C_{36}H_{74}$–$C_{36}D_{74}$ mixtures. However, monomeric paraffins crystallize at low degrees of supercooling and the segregation caused by kinetic effects may be very different in the paraffin and polymer systems.[19] The actual composition distributions in $C_{36}H_{74}$–$C_{36}D_{74}$ and PEH–PED crystals will depend on the crystallization kinetics and the details of the crystallization procedures. Thus one cannot *a priori* assume that the composition distributions of $C_{36}H_{74}$–$C_{36}D_{74}$ cocrystals and PEH–PED cocrystals obtained after exhaustive crystallization are similar, even though the mixtures have the same nominal or average composition. Indeed, the probability of fortuitously obtaining identical composition distributions in the two systems would appear to be exceedingly small.

The preceding considerations, of interest in themselves, also have an important bearing on the conclusions concerning chain folding in polyethylene based on the spectroscopic examination of mixed crystals. In an elegant theoretical paper, Tasumi and Krimm made normal vibration calculations for various assumed spatial distributions of $(CH_2)_x$ and $(CD_2)_x$ segments in mixed crystals.[9] These calculations showed that the magnitudes of the CH_2 and CD_2 bending and rocking modes depended on the spatial arrangement, or mass distribution, of the two types of chain sequences. Subsequently, infrared measurements were made on solution-cast films and melt-crystallized samples prepared by exhaustive crystallization of mixtures containing PEH and PED in varying proportions.[10,11] These band splittings were compared with those obtained on cocrystals of $C_{36}H_{74}$–$C_{36}D_{74}$ having the same average composition.

At low hydrocarbon/deuteriocarbon ratios, the CH_2 bending and rocking modes in PEH–PED cast film were doublets, whereas in corresponding $C_{36}H_{74}$–$C_{36}D_{74}$ mixtures these modes were singlets. Similarly, for high hydrocarbon/deuteriocarbon ratios, the CD_2 bending mode in the polymer-cast films were doublets, whereas the corresponding paraffin mixtures yielded only singlets.[20] The doublets in the polymer mixed crystals were interpreted in terms of an interfacial structure with adjacent reentry in the 110 plane. In other words, the difference in mass distribution between the polymer mixed crystals and paraffin mixed crystals, which is required to explain the infrared data, was assumed to arise from a regular folded interfacial structure in the polymer crystals. This conclusion, which was based on experiments made on solution-cast films, was also believed to apply to crystals prepared from dilute solution.

The band splittings in melt-crystallized polymer cocrystals were qualitatively similar to those found in paraffin cocrystals having the same average composition. At high hydrocarbon content, the CD_2 bending mode was a singlet in both paraffin cocrystals and in polymer cocrystals. At low hydrocarbon content, the CD_2 bending mode appeared as a doublet in both paraffin and polymer cocrystals. However, the doublet splitting in the polymer crystals was 1-3 cm^{-1} greater than that of the paraffin cocrystals having the same average composition. Following the same line of argument as that given above, these results were interpreted as arising from adjacent reentry in the 200 plane.

It is clear that adjacent reentry along certain fold planes, if it occurs, can account for the greater splittings, in polymer cocrystals compared to paraffin mixed crystals. However, the required differences in mass distribution could also arise from compositional heterogeneity. This possibility has apparently been recognized by Bank and Krimm.[21] In a recent paper they point out that increased splittings can also arise from the presence of some regions in which similar chains are associated with each other rather than mixing with chains of opposite species. If the compositional heterogeneity were large in cast film specimens, then doublet CD_2 bending and rocking modes would be observed even in crystals with high hydrocarbon–deuteriocarbon ratios. The large difference in crystallization rates of PEH solutions and PED solutions and the composition analyses in Table IV indicate that such a broad composition distribution is quite probable. The fact that one of the components may be present in large excess and that the crystallization is done rapidly does not ensure that extensive segregation of the polymer species does not occur. Hence, composition distribution effects rather than adjacent reentry along certain fold planes can be invoked to explain the infrared results obtained on solution-cast films.

The modestly greater spectral splittings in melt-crystallized polymer cocrystals relative to paraffin cocrystals can also be accounted for by composition distribution considerations. The magnitudes of the splittings can be explained by the postulate that segregation of PEH and PED in melt crystallization is (a) less severe than in crystallization of these species from dilute solution, but (b) more severe than the segregation that occurs in the crystallization of $C_{36}H_{74}$–$C_{36}D_{74}$. Irrespective of the validity of this specific hypothesis, the conclusion that adjacent reentry occurs in melt-crystallized polyethylene is highly tenuous because of the qualitative similarity of spectral splittings in melt-crystallized polymer cocrystals and paraffin cocrystals and the lack of any information concerning the composition distribution of the two systems.

Thus, the spectral results presented to date on both solution- and melt-crystallized PEH–PED mixtures do not lend themselves to an unequivocal interpretation, and they therefore do not constitute a strong argument for adjacent reentry. Experiments made on paraffin cocrystals and polymer cocrystals with known composition distributions are required to eliminate the present ambiguity.

Based on spectroscopic evidence, Bank and Krimm recently reported that fractionation occurred when polyethylene–poly(ethylene-d_4) was crystallized at low degrees of supercooling from dilute solution.[21] This observation is in accord with the conclusions drawn above. They attributed the fractiona-

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(19) D. Turnbull and R. L. Cormia, *J. Chem. Phys.*, **34**, 820 (1961).

(20) A more detailed summary of these results is found in Table IV of ref 10.

(21) M. I. Bank and S. Krimm, *J. Polym. Sci., Part B*, **8**, 143 (1970).

tion to a difference in the crystallization rates of the two polymers. The different crystallization rates were, in turn, attributed to a difference in the molecular weights of their samples. However, the difference in melting points of PED and PEH is undoubtedly the major cause of the different crystallization rates of our polymers. This is demonstrated by the fact that the crystallization rates of PED and PEH were virtually identical when compared at equal undercoolings. Moreover, molecular weight has a negligible effect on melting temperature at high molecular weight levels. Consequently, the minor difference in molecular weights of our PEH and PED samples cannot be the cause of the observed difference in melting temperatures.

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Dilute-Solution Theory of Polymer Crystal Growth. Some Thermodynamic and Predictive Aspects for Polyethylene[1a]

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ABSTRACT: The kinetic theory of polymer crystallization from dilute solution is applied to the system polyethylene–xylene. Prerequisite free energy driving forces are derived for crystallization from solution. These naturally depend on bulk thermodynamic properties and three thermodynamic potentials are derived depending on what melt and crystalline properties are assumed. The commonly used $\Delta H \Delta T / T_m^0$ expression is shown to be an upper bound for all materials and a more accurate expression descriptive of polyethylene is used in the actual calculations. Growth rate and lamella thickness are computed as functions of undercooling, concentration, and molecular weight. It is found that the growth rate varies roughly as concentration raised to a power, the value of the power being a function of both molecular weight and temperature. The isothermal lamella thickness increases only slightly with decreasing molecular weight and is even less dependent on concentration. The isothermal growth rate as a function of molecular weight exhibits a broad maximum. An analysis of the temperature dependence of the growth rate is made in terms of classical nucleation theory using calculations of the present theory as data points. This leads to the concept of an apparent $\sigma\sigma_e$ which is seen to vary as a function of molecular weight. The theory makes definitive, as yet unverified, predictions which can be tested experimentally.

I. Introduction

In a preceding paper,[2] hereafter referred to as I, a kinetic theory of polymer crystallization from dilute solution was developed. An interesting hypothesis of this theory is the postulated "self-nucleating" mechanism.[3] Cilia or dangling chain ends, which may be very long, are generated during the course of crystal growth; a very small fraction of these cilia participate in nucleating new growth strips (fold planes) on the crystal face and thus the crystal is quite capable of propagating itself without the benefit of external nucleating species (solution molecules). For a small-molecule nucleation theory, we would expect solution molecules to be the only nucleating species. If the self-nucleating mechanism predominates in dilute-solution crystallization of chain molecules as we suspect, then an anomalous dependence of crystal growth rates on polymer concentration can be anticipated. This topic is discussed in detail in section IIIC.

Two models were considered in I which describe the crystallization of chain molecules of finite length by regular chain folding. Both models can be characterized as "fractional stem rejection" models, since it is assumed that a fractional stem at the end of a folding chain is rejected by the crystal. Fractional stem incorporation causes defects in the crystal, and recent experimental evidence[4] suggests that most chain ends are found outside of the crystal. This assumption can be tested experimentally, as will be shown in section IIID, since the predicted temperature variation of the crystal growth rate should depend on whether or not chain ends are incorporated into the crystal.

In discussing the various predictive aspects of the kinetic theory obtained in I, we will specifically apply the theory to polyethylene (PE) dissolved in xylene.

II. Thermodynamics of Polymer Crystallization

The theory of polymer crystallization from solution requires a knowledge of the free energy difference between the undercooled solution and the equilibrium crystal. The free energy difference in turn is a sensitive function of the melting temperature of the crystalline polymer. The equilibrium melting temperature T_m^0 may be defined as that temperature at which pure *liquid* polymer is in thermal equilibrium with a large crystal—a crystal large enough that surface effects are negligible and one having an equilibrium number of defects. Presumably, the equilibrium crystal is an extended-chain crystal. Similarly, the equilibrium dissolution (melting) temperature T_d^0 may be defined as that temperature at which *polymer solution* is in equilibrium with the equilibrium crystal. Both T_m^0 and T_d^0 depend on the molecular weight of the polymer.

Denoting the molar free energy (chemical potential) of the monomer unit in the crystalline phase and in the pure liquid

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(1) (a) Contribution of the National Bureau of Standards, not subject to copyright; (b) NRC–NAS Postdoctoral Research Associate, 1969–1971.

(2) I. C. Sanchez and E. A. DiMarzio, *J. Chem. Phys.*, **55**, 893 (1971).

(3) I. C. Sanchez and E. A. DiMarzio, *Bull. Amer. Phys. Soc.*, **15**, 377 (1970).

(4) A. Keller and D. J. Priest, *J. Macromol. Sci., Phys.*, **2**, 479 (1968).