The parameters c, d, and λ are f-dependent dimensionless constants that are tabulated in ref 14. For a symmetric diblock, ϵ has the value $8.11N^{-1/3}$ at the MST.

After this paper was completed, the author received a preprint from A. Onuki[17] that has a brief discussion of the form birefringence of diblock melts. Because of slightly different assumptions, he finds results qualitatively similar to those reported here, but they differ in quantitative detail.

Acknowledgment. The author wishes to express his gratitude to R. Larson and G. Fuller for enlightening discussions.

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Correlation between Crystallinity and Ethylene Content in LLDPE and Related Ethylene Copolymers. Demonstration of the Applicability of a Simple Empirical Relationship

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ABSTRACT: Calorimetric data on six distinct series of ethylene copolymers have been examined and shown to fit the empirical relationship log $(\Delta H_m) = \log k + n \log x_E$, where ΔH_m is the heat of fusion, k a constant, n the critical sequence length for crystallization, and x_E the mole fraction of ethylene. For olefin copolymers values of $n = 8$–16 are observed, whereas a series of vinyl chloride copolymers shows a value of $n = 5$. These are generally in accord with literature data. The analysis of co- and terpolymers based on a range of olefinic comonomers strongly suggests that the number and distribution of noncrystallizable units are more important than size in the inhibition of crystallization.

Introduction

The copolymer melting of polyethylene is a fascinating topic which has been studied for many years and has attracted attempts to provide some quantitative theoretical basis.[1-3] The development of the commercial ethylene copolymer LLDPE has led to a renewed interest in this topic, and recently several calorimetric studies of ethylene copolymers have been published.[4-10] A common feature of all of these studies is that the level of crystallinity, as measured by the enthalpy of fusion (ΔH_m), decreases as the level of comonomer is increased. In an earlier publication[8] we proposed a simple empirical relationship for the dependence of crystallinity of the mole fraction of ethylene in the copolymer and showed it to be applicable to calorimetric data on one series of LLDPE samples. We now wish to provide further results and an analysis of published data to show that the proposed relationship has general applicability to a wide range of ethylene copolymers.

Experimental Section

The parent polyethylene and derived 4-methyl-1-pentene copolymers were prepared with a $TiCl_3$ 1.1 Stauffer catalyst by procedures to be described elsewhere.[11]

Calorimetric measurements were made with a Perkin-Elmer Model DSC-2C instrument on 5-mg samples as detailed earlier.[8] Samples were inserted into the instrument at 310 K and heated at 20 K/min over the range 310–450 K (as-polymerized samples). Subsequently the cooling curve was obtained by cooling the sample at 20 K/min with data acquisition (*cooling run*). Finally the sample was rescanned over the temperature range 310–450 K (*rerun sample*).

Results and Discussion

For the purpose of analysis an ethylene copolymer may be treated as being composed of crystallizable ethylene units and noncrystallizable comonomer units. Long sequence runs of ethylene are presumed to crystallize whereas short sequences are inhibited from so doing. The lamellar thickness of the formed crystallites will be determined in part by the sequence length of ethylene units providing that the comonomer unit is excluded from the structure. It is known that the melting point of the crystallites is related to the lamellar thickness and it follows therefore that at any given temperature there is a certain minimum thickness required to provide a stable crystallite. Consequentially it is not unreasonable to suppose that there is also a corresponding critical ethylene sequence length (n) below which chains will not crystallize.

In an earlier publication[8] it was suggested that for a random copolymer the enthalpy of fusion (ΔH_m) should be related to the ethylene mole fraction (x_E) by the relationship

$$\Delta H_m = k x_E^{\,n} \tag{1}$$

where k is a constant related to the enthalpy of fusion of the parent homopolymer. The constant k is likely to be affected by parameters such as MW and MWD, heterogeneity of copolymer composition, thermal history of sam-

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Table I
Comparison of Results on DSC Studies of LLDPE Samples

copolymer	thermal history	(slope) n	n'	intercept (k), cal/g	ref
1-butene (slurry)	rerun[a]	11	9	43.2	
(high pressure)	rerun[a]	8	6	37.3	Kimura et al.[4]
1-butene, 1-hexene, 1-octene, 1-decene	as polymerized[e]	10	7	44.6	Seppala[6]
propene, 1-butene 4-methyl-1-pentene	as polymerized	14	12	58.6	Burfield et al.[8]
hydrogenated polybutadiene	rerun[b]	7	5	35.5	Krigas et al.[7]
4-methyl-1-pentene	as polymerized	12	9	42.8	
	rerun[c]	16	13	35.2	this study
	cooling	18	16	27.5	
vinyl chloride	as synthesized[d]	5	3.5	43	Bowmer et al.[13]

[a] Cooled from the melt at 5 K/min to 298 K before rerunning. [b] Cycled at 10 K/min between 113 and 423 K. [c] Cooled from the melt at 20 K/min to 310 K. [d] Heated from 223 K. [e] From 253 to 473 K at 10 K/min.

ples, and presence of nucleating impurities, since all of these parameters are known to influence the crystallization of polyethylene samples and hence the enthalpy of fusion. For copolymers prepared with the same catalyst under similar process conditions and purified in a similar manner we may reasonably expect k to be constant and then eq 2, the logarithmic form of the above relationship, provides a convenient basis for evaluation:

$$\log (\Delta H_m) = \log k + n \log x_E \qquad (2)$$

In the earlier calorimetric studies of ethylene copolymers ΔH_m has been measured in terms of unit mass of copolymer. However, if the comonomer does not contribute toward crystallization it may be regarded as an inert filler and then it is appropriate to define a new heat of fusion ($\Delta H_m'$) such that

$$\Delta H_m' = \Delta H_m / W_E \qquad (3)$$

where W_E is the weight fraction of ethylene in the copolymer. In this case eq 2 now becomes

$$\log (\Delta H_m') = \log k + n' \log x_E \qquad (4)$$

The new critical sequence length n' should be more equivalent to the values derived from spectroscopic derivations where the presence of the comonomer units are effectively neglected.

The applicability of these equations to the range of ethylene copolymers is now briefly presented and discussed.

Analysis of Current and Literature DSC Data. DSC analysis of a series of ten LLDPE samples containing from 0 to 4.6 mol % of 4-methyl-1-pentene has been made under the three distinct conditions described above. In each case the enthalpy of fusion or crystallization decreases with increasing comonomer content showing progressive disruption of the crystallization process. The logarithmic plot according to eq 2 is shown in Figure 1 and reveals a good fit for each of the series of results. It is evident that the thermal history of the sample affects the slope of the plot and hence the value of n'—the critical sequence length of ethylene units (Table I). This minimum sequence length is seen to increase in the order as polymerized < rerun < cooling run. This is to be expected as the as-polymerized samples will have effectively been annealed at ambient temperatures for long periods, thus allowing the crystallization of the shortest ethylene sequences. Conversely, the samples studied during the cooling scan are allowed minimum time for crystallization and hence only the more stable crystallites are formed.

We have recently reported[8] DSC studies of ethylene copolymers of propene, 1-butene, and 4-methyl-1-pentene. Reevaluation of these results according to eq 2 gives as anticipated a linear correlation (Figure 2) with a slope of $n = 14$ for the as-polymerized samples. The equally good fit for the different comonomers again emphasises the determinant nature of the ethylene run sequence, rather than the size of the irregularity, in limiting crystallization.

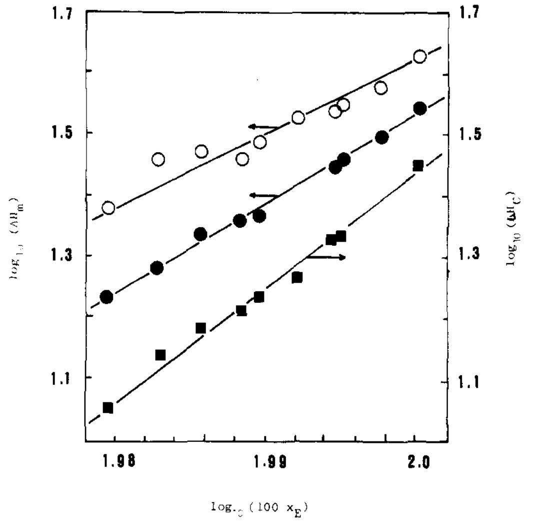

Figure 1. Logarithmic plot of ΔH_m or ΔH_c versus mol % ethylene: (○) as polymerized; (●) rerun; (■) cooling run.

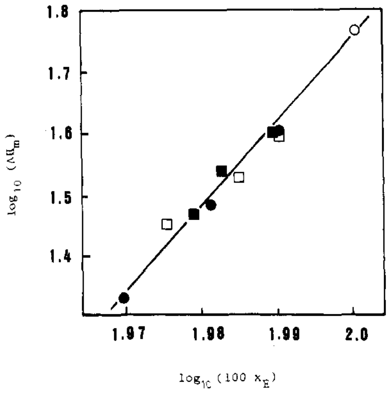

Figure 2. Logarithmic plot of ΔH_m versus mol % ethylene. Data from Burfield et al.:[5] (○) homopolymer; (●) propene; (□) butene; (■) 4-methyl-1-pentene.

Kimura et al.[4] have carried out a comprehensive DSC study of ethylene–1-butene copolymers prepared with the same supported titanium catalyst system but under two distinct conditions—a slurry (SP) and high-pressure (HP) process. Fractionation of the two polymers provided a series of samples of varying molecular weight, butene content, and heat of fusion. The evaluation of this data according to eq 2 is shown in Figure 3. A good fit is

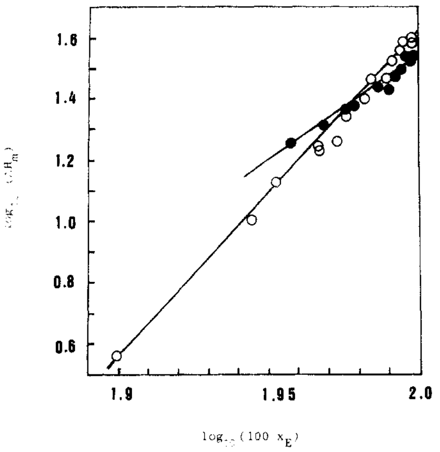

Figure 3. Logarithmic plot of ΔH_m versus mol % ethylene. Data from Kimura et al.,[4] Table II: (○) SP sample; (●) HP sample.

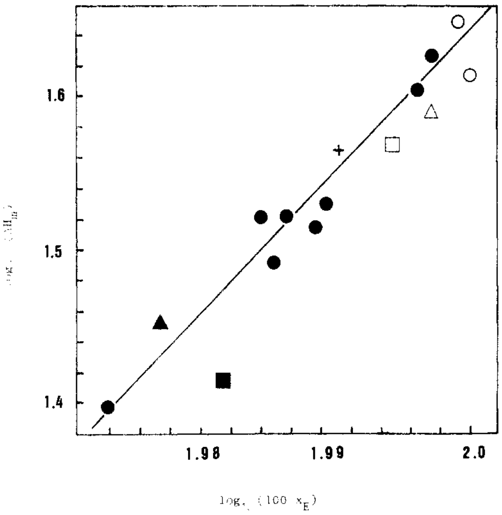

Figure 4. Logarithmic plot of ΔH_m versus mol % ethylene. Data from Seppala[6] Table II. Copolymers: (+) butene; (□) hexene; (△) octene; (○) decene. Terpolymers: (■) butene/hexene; (▲) butene/octene; (●) butene/decene.

observed for both data sets which span the range from 0.5 to 21 mol % butene. The effect of process conditions on crystallization in the form of distinct values of *n* and *k* is clearly evident and may reflect differences in MW and MWD as well as heterogeneity of comonomer incorporation. Nevertheless, within each data set the dependence upon ethylene sequence length is clearly demonstrated.

Similarly, Seppala[6] has prepared and characterized, by DSC, a series of co- and terpolymers of ethylene with α-olefins such as 1-butene, 1-hexene, 1-octene, and 1-decene. The polymers were prepared with a conventional aluminum-activated $TiCl_3$ catalyst in a slurry process. The application of an eq 2 type analysis for the whole series of co- and terpolymers is shown in Figure 4. Although the scatter is more accentuated than the fractionated samples discussed above, the trend very clearly shows that crystallization inhibition is more dependent on number than size of the disrupting groups.

In an alternative approach to the understanding of ethylene–1-butene copolymers, Krigas et al.[7] have prepared such polymers through the hydrogenation of polybutadiene samples of distinct initial 1,2-unit content. The rather limited number of data points provided by that study again show a fairly good linear correlation for the logarithmic plot (Figure 5).

The examples cited above are restricted to ethylene copolymers with α-olefins. More recently the preparation and characterization of random ethylene–vinyl chloride copolymers have been described.[10,12,13] Copolymers containing more than 60 mol % of ethylene units exhibit measurable crystallinity by DSC measurement[10] and the data from these samples is shown (Figure 6) to fit eq 2. It is of some interest that the calculated value of *n'* for these samples is 3.5 which is very close to the value of 3 estimated for the minimum crystallizable ethylene sequence length by both calorimetric[10] and IR evaluation[13] for the same samples.

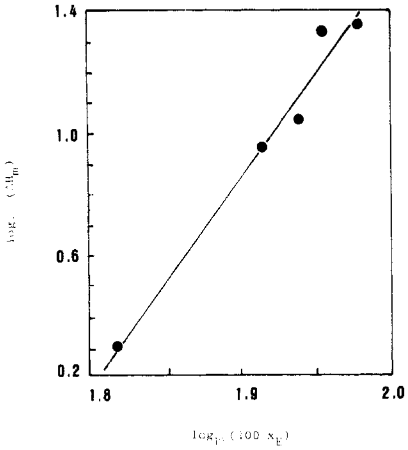

Figure 5. Logarithmic plot of ΔH_m versus mol % ethylene. Data from Krigas et al.[7]

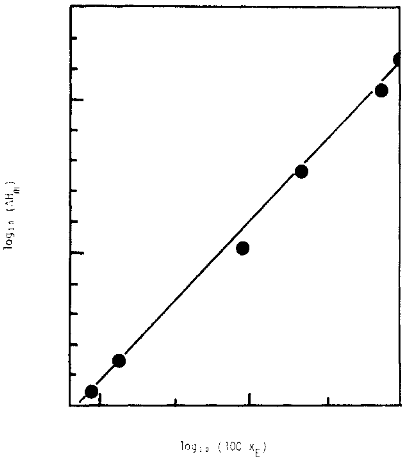

Figure 6. Logarithmic plot of ΔH_m versus mol % ethylene. Data from Bowmer and Tonelli.[13]

Overall Comments

The results analyzed in this paper are drawn from six different studies representative of widely different ethylene copolymers. However, in each case the data have been shown to fit the formalism of eq 2 and 4. Furthermore, in the sole case where direct comparison is possible, the calculated value of *n'* is closely similar to the literature evaluation. This evaluation shows that the proposed relationship provides a useful empirical fit for calorimetric data and suggests that there may be some merit in the rather simplistic postulates put forward[8] as the basis for the derivation of eq 1.

The calculated values of the critical ethylene sequence length, *n* and *n'*, are summarised in Table I. It is apparent that a considerable range in values is observed but this may perhaps largely be explained by the thermal pretreatment of the samples. Thus, even the same set of 4-methyl-1-pentene copolymers shows a *n'* range of 9–16 depending on the sample pretreatment and mode of calorimetric measurement. In this connection Table II summarizes the

Table II
Relationship of the Critical Ethylene Sequence Length to Sample Pretreatment Temperature and the Melting Points of Simple Alkanes

copolymer	n'	T,[a] K	ref
α-olefins	12	310	8
4-methyl-1-pentene	9–13	310	this study
1-butene	6–9	298	4
α-olefins	7	253	6
vinyl chloride	3.5	223	13
1-butene	5	113	7
alkanes			
n-octadecane	8	301	
n-hexadecane	7	291	
octane	3	216	

[a] The starting temperature for the DSC run.

n' values with corresponding minimum temperatures for the DSC measurement, together with the melting points of simple hydrocarbons which may be considered as guides to the thermal stability of small PE crystallites. The general trend is clear. The observed n' value decreases with lowering of the DSC starting temperature. This presumably arises since the very small crystallites arising from short sequence lengths will be unstable at slightly higher temperatures and hence will not contribute to the observed heat of fusion.

The comparison with the alkene models is striking. Thus the data for octadecane suggests that ethylene sequence lengths of eight units will only form stable crystallites at temperatures below 301 K. The prediction appears to correspond approximately to the situation presented here, since for the copolymers studied at 310 K and above, only sequence lengths >8 are observed. It is also worthy of note that the observed values of n' for the olefin copolymers are in the range 6–13, which is of the same order of magnitude as the range 8–15 observed by authors using IR[14] and melting point data[15,16] in studies of propylene copolymers. The significantly lower values observed for the vinyl chloride copolymers might be related to additional stabilization brought about by the more rigid chain structure of the comonomer, as evidenced by higher T_g values.

Registry No. (1-Butene)(ethylene) (copolymer), 25087-34-7; (1-butene)(ethylene)(1-hexene) (copolymer), 60785-11-7; (1-decene)(ethylene)(1-octene) (copolymer), 110661-50-2; (1-butene)-(ethylene)(propylene) (copolymer), 25895-47-0; (ethylene)(4-methyl-1-pentene) (copolymer), 25213-96-1; (ethylene)(vinyl chloride) (copolymer), 25037-78-9.

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Thermal Properties of Poly(ethylene oxide) Complexed with NaSCN and KSCN

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ABSTRACT: The melting behavior of series of solvent-cast mixtures of a low molecular weight ($\bar{M}_n = 4 \times 10^3$) poly(ethylene oxide) (PEO) with NaSCN and KSCN has been studied by DSC and optical microscopy. The results show great similarities between the two systems. Their common characteristics are first the formation of a single solid compound, $P(EO_3{\cdot}NaSCN)$ and $P(EO_{\sim 4}{\cdot}KSCN)$, that melts incongruently to yield the solid salt and a peritectic liquid and second a liquid–liquid miscibility gap occurring at the melting point of the pure salt. Both systems exhibit a nearly vertical salt liquidus curve, indicating that complex formation also takes place in the liquid phase. The stoichiometry of the solvate is close to 4/1 for NaSCN and 5/1 for KSCN. The mixtures with NaSCN were highly crystalline over the whole composition range while those with KSCN showed either partial crystallinity or the absence of crystallinity at PEO contents above that of the solid compound. Because of the peritectic reaction, in either system the solid compound cannot participate in the formation of a eutectic mixture with the solid salt. In turn, it can form a eutectic mixture with solid PEO. In the case of the PEO–NaSCN system for which the construction of a complete phase diagram was possible, the eutectic composition is close to 93% by weight in PEO with a corresponding tie line located 4 °C below the melting point of pure PEO. The analysis of the $P(EO_3{\cdot}NaSCN)$ liquidus curve in terms of the Flory–Huggins thermodynamic concepts indicates the presence of a strong exothermic interaction ($\chi = -1.2$), associated with the solvation of $P(EO_3{\cdot}NaSCN)$ by PEO yielding the solvate $P(EO_4{\cdot}NaSCN)$. For either system, the reverse path of the peritectic reaction is not quantitative for a mixture having the composition of the solid compound. In either case, melt recrystallization yields a material that contains the solid salt in addition to the solid compound.

Introduction

Poly(ethylene oxide) (PEO) is known to form crystalline ionic complexes with several inorganic compounds, including mercuric halides,[1,2] ammonium salts,[3] and alkali-metal salts.[3-8] In the last 10 years, a great deal of interest has been generated for the ionic complexes of PEO with

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