# Phase and Supermolecular Structure of Binary Mixtures of Linear Polyethylene Fractions

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ABSTRACT: The level of crystallinity, the interfacial content, and the supermolecular structure of binary mixtures of linear polyethylenes have been studied. The molecular weights of the parent fractions ranged from $1.3 \times 10^4$ to $8 \times 10^6$. For isothermally crystallized samples, the level of core crystallinity of the mixtures was found to be the same as that of the fractions when compared on the basis of weight-average molecular weight. However, for quenched samples, agreement between the mixtures and fractions is obtained when compared on a number-average basis. Starting with a series of high molecular weight fractions, which display randomly arranged lamellae after rapid crystallization, spherulites begin to form in the mixtures when the number-average molecular weight is in the range $(5-8) \times 10^4$. More regular spherulites develop with a further decrease in the molecular weight. An explanation is offered for the common observation of spherulites in unfractionated systems.

## Introduction

The level of crystallinity, as well as morphological and structural details, of crystalline polymers of flexible chains varies systematically with molecular weight when fractions are used.[1–14] Consequently, microscopic and macroscopic properties which depend on these factors vary over wide limits with molecular weight and crystallization conditions. Several different polymers attest to this general behavior.[1,2,5,10] However, the most extensive studies have been with linear polyethylene fractions. Depending on molecular weight and crystallization temperature, the level of crystallinity that can be attained varies from about 90% to less than 50% for fractions of this polymer. The reasons for the retardation in the crystallinity level can be found in detailed studies of crystallization kinetics[4] and can be attributed in the main to topological restraints in the melt that increase with molecular weight. Chain entanglements are one such example.

The supermolecular structures developed in polyethylene,[6] poly(ethylene oxide),[13] and polypropylene[14] have also been shown to depend on molecular weight and crystallization temperature. It has been found quite generally that spherulite formation, although quite common, is not the universal mode of polymer crystallization. A variety of structures, ranging from sheetlike to spherulites, to the absence of any defined supermolecular organization are found in crystallized flexible chain polymers.

With the wide changes that have been observed in the basic structural parameters and in properties, it is of interest to assess the influence of molecular weight polydispersity on these quantities. As a first step in this direction, we have studied in detail the levels of crystallinity and supermolecular structures of well-defined binary mixtures of fractions of linear polyethylenes that were crystallized under controlled isothermal and nonisothermal conditions. The parent fractions that were used covered a wide range in molecular weights. However, the molecular weights studied were limited to $M \geq 7000$ so that cocrystallization was ensured and fractionation, or segregation, was avoided under all crystallization conditions.[15,16] To complement the study of the binary mixtures, similar properties were also studied for a set of unfractionated polyethylenes.

## Experimental Section

**Materials.** The characteristics of the fractions used in this work are listed in Table I. With just a few exceptions, the fractions were obtained from the Société Nationale des Petroles D'Aquitaine (SNPA) and characterized by GPC. The fractions $M_w$ = 13 600 and 119 600 were NBS reference standards. The high molecular weight fraction, $8 \times 10^6$, was prepared by liquid–liquid phase separation using procedures that have been previously described.[4,17] The pairs of fractions that were used are listed in Table II. The weight fractions of the mixtures were usually in the range of 25–75% of the low molecular weight component. The molecular characteristics of the whole polymers studied are listed in Table III. The molecular weights of these samples were also obtained by conventional GPC. To prepare the binary mixtures of the fractions, weighed amounts of each species were dissolved in a dilute $p$-xylene solution. After stirring, the resulting mixture was rapidly crystallized. A detailed description of the procedure used has been given previously.[15,16] The precipitate thus formed was pressed into a thin film at about 160 °C and cooled to room temperature. These mixtures were used for the controlled crystallizations.

For the isothermal crystallizations about 10 mg of the film was sealed under vacuum in a small glass ampule that was then placed in a beaker of silicone oil contained in an oven at 160 °C for 1 h. The beaker and ampule were then removed from the oven and placed in a thermostatic bath set at a predetermined temperature and controlled to ±0.1 °C. The ampule was rapidly removed from the beaker and placed in the oil bath. After the desired time had elapsed, the sample was then rapidly transferred to an ice–water bath to terminate the crystallization process. The time period for the isothermal crystallization was determined in preliminary studies. It was taken as the time necessary to reach the flat portion in the crystallization kinetic isotherm.

For the rapid crystallization, a thin polymer film was melted in an oven set between 155 and 160 °C and then rapidly submerged into a dry ice–isopropyl alcohol mixture. For molecular weights below 250 000 the samples were held in the oven for about 5 min. For the higher molecular weight the initial time was extended to 10–15 min.

The heats of fusion were measured in a Perkin-Elmer DSC-2 calibrated with indium. To obtain the thermograms, about 3 mg of sample was sealed in an aluminum pan and heated at the rate of 10 °C/min. The melting endotherm was defined by drawing a straight base line from the onset to the conclusion of melting. The measured enthalpy of fusion, $\Delta H_f$, was calculated from the area defined in this manner. The degree of crystallinity

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Table I
Molecular Weight of Fractions

| sample | $M_N$ | $M_w$ |
|---|---|---|
| a | 5 370 | 5 800 |
| b | 6 500 | 6 750 |
| c | 7 940 | 10 000 |
| d | 11 400 | 13 600 |
| e | 20 100 | 23 300 |
| f | 46 500 | 52 600 |
| g | 100 500 | 119 600 |
| g′ | 154 500 | 224 000 |
| h | 265 000 | 316 000 |
| i | 295 200 | 428 000 |
| j | 720 000 | 800 000 |
| k | | 8 000 000[a] |

[a] Viscosity-average molecular weight.

Table II
Binary Mixture Studied

| | |
|---|---|
| series I | 13 600/428 000 |
| series II | 6 750/119 600 |
| series III | 6 750/8 000 000 |
| series IV | 52 600/224 000 |
| series V | 13 600/119 600 |
| series VI | 6 750/428 000 |

Table III
Molecular Weights of Whole Polymers

| | $M_N$ | $M_w$ |
|---|---|---|
| sample A | 22 300 | 188 000 |
| sample B | 22 800 | 53 600 |
| sample C | 18 300 | 53 000 |
| sample D | 39 600 | 183 000 |

determined by this method, $(1 - \lambda)_{\Delta H}$, was calculated from $\Delta H_f$, taking 69 cal/g for the completely crystalline polymer.[15] For the rapidly crystallized samples, and those crystallized at 118 °C, only one endothermic peak was observed. After isothermal crystallizations at 122 and 128 °C two endothermic peaks were observed. The low-temperature peak can be attributed to crystallization upon subsequent cooling. The contribution from this peak was not included in the calculation of the isothermally developed crystallinity level.

The fraction of the sample comprising the interfacial region, $\alpha_b$, was determined from the analysis of the Raman internal modes, using methods previously described.[8,18,19] From the internal modes the fraction of chain units in the ordered core crystallite, $\alpha_c$, and the fraction of chain units in the liquidlike disordered structure, $\alpha_a$, are directly measured. As has been pointed out, their sum does not equal unity.[8,18,19] The fraction of the interfacial region is defined as

$$\alpha_b \equiv 1 - (\alpha_a + \alpha_c) \qquad (1)$$

The supermolecular structures were characterized by small-angle light scattering (SALS) utilizing the photometer previously described.[6] In describing superstructures, the designations a–c represent spherulites with decreasing structural order. The random orientation of the lamellar crystallites, i.e., the lack of any supermolecular structure, is designated by h.[20,21]

## Results and Discussion

The levels of crystallinity $(1 - \lambda)_{\Delta H}$ which were obtained at the isothermal crystallization temperatures of 128, 122, and 118 °C, are plotted against log $M_w$ of the specimens in Figures 1–3, respectively. Crystallization at 118 °C represents the lower limit of isothermal crystallization.[4,22] The open circles in the figures represent the one-component fractions which are given for reference purposes. For each crystallization temperature, the fractions delineate a curve very similar to that previously reported for the linear polyethylenes.[3,23] They also resemble the corresponding curves for poly(ethylene oxide) and poly(tetramethyl-$p$-silphenylenesiloxane).[5,23] The binary mixtures, as well as the whole polymers, fall on the same curves in all of the figures. An extensive molecular weight range, from about $10^4$ to close to $10^7$, is covered by these mixtures. It is important to recognize that these results show that, as far as the levels of crystallinity are concerned, the mixtures behave as fractions with the same value of $M_w$. We can deduce from these results that, because of the time scale involved, the melt has reached its equilibrium or static value prior to the onset of the isothermal crystallization. Previous analysis of the crystallization kinetics in fractions has shown that topological restraints, such as molecular entanglements, play a major role in limiting the crystallinity level that can be attained. The decrease in the attained crystallinity level with increasing molecular weight fractions can be explained in this manner. The entanglement density, and presumably other restraints, is known to depend on $M_w$. Therefore, the limiting crystallinity level would be expected to depend on $M_w$ in the manner that is found in Figures 1–3. The weight-average molecular weight defines the entanglement density of the mixtures and in turn the observed level of crystallinity.

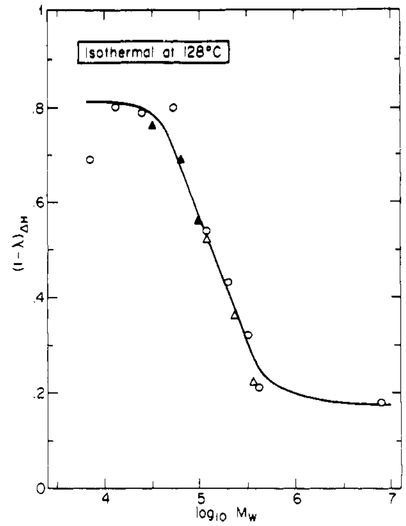

**Figure 1.** Plot of the degree of crystallinity, $(1 - \lambda)_{\Delta H}$, against log $M_w$ for samples isothermally crystallized at 128 °C. Fractions for reference (○). Binary mixtures: (△) series I; (▲) series II.

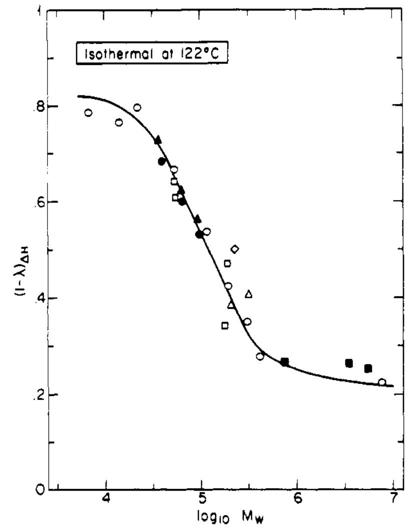

**Figure 2.** Plot of the degree of crystallinity, $(1 - \lambda)_{\Delta H}$, against log $M_w$ for samples isothermally crystallized at 122 °C. Fractions for reference (○). Binary mixtures: (△) series I; (▲) series II; (■) series III; (◇) series IV; (●) series V; (□) whole polymers.

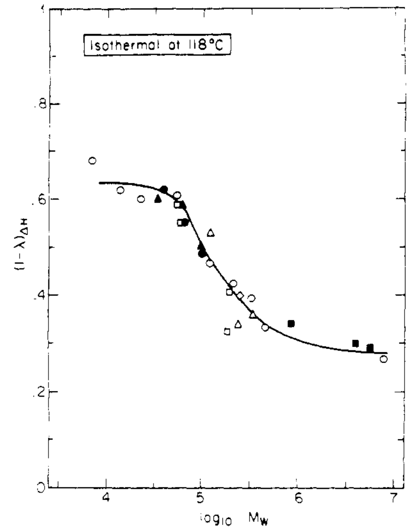

**Figure 3.** Plot of the degree of crystallinity, $(1-\lambda)_{\Delta H}$, against $\log M_w$ for samples isothermally crystallized at 118 °C. Fractions for reference (○). Binary mixtures: (△) series I; (▲) series II; (■) series III; (◇) series IV; (●) series V; (□) whole polymers.

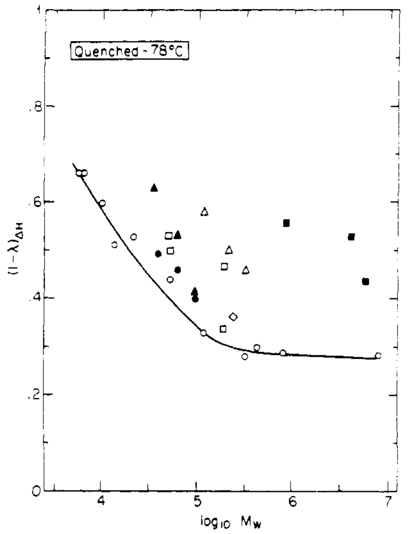

**Figure 4.** Plot of the degree of crystallinity, $(1-\lambda)_{\Delta H}$, against $\log M_w$ for samples quenched at −78 °C. Fractions for reference (○). Binary mixtures: (△) series I; (▲) series II; (■) series III; (◇) series IV; (●) series V; (□) whole polymers.

The crystallinity level $(1-\lambda)_{\Delta H}$ is plotted against log $M_w$ in Figure 4 for rapidly crystallized, quenched specimens. The curve delineated for the fractions is very similar to the one reported.[3,24] However, it is quite clear that neither the binary mixtures nor the whole polymers follow the curve for the fractions when plotted on a weight-average basis. These results obtained for the rapid crystallizations are thus quite different from those obtained after isothermal crystallization. For this mode of crystallization, a specimen with a given $M_w$ develops a much higher level of crystallinity when compared to that of a fraction of the same molecular weight. The binary mixtures, and whole polymers, behave as if they correspond to a much lower average than $M_w$. This effect becomes more accentuated the higher the molecular weight.[25] The strong influence of the lower molecular weight species on the level of crystallinity that is attained after rapid crystallization is illustrated in Figure 5. Here, $(1-\lambda)_{\Delta H}$ is plotted against log $M_N$. When plotted on the basis of $M_N$, there is very close agreement between $(1-\lambda)_{\Delta H}$ for the fractions, binary mixtures, and whole polymers.

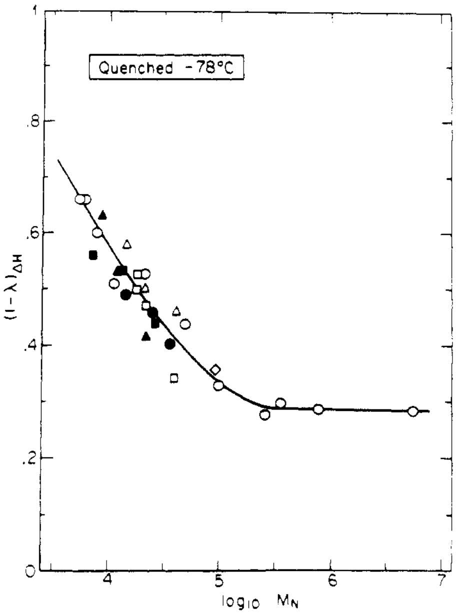

**Figure 5.** Plot of the degree of crystallinity, $(1-\lambda)_{\Delta H}$, against $\log M_N$ for samples quenched at −78 °C. Fractions for reference (○). Binary mixtures: (△) series I; (▲) series II; (■) series III; (◇) series IV; (●) series V; (□) whole polymers.

The temperature from which the crystallization takes place is characterized by an equilibrium melt structure that involves the chain conformation and the distribution of molecular centers. This melt structure develops from the one at the initial temperature at which the sample was held. Because of the time involved prior to the initiation of the transformation, the isothermal crystallization should take place from the equilibrium melt for the specified temperature. However, with rapid cooling crystallization will take place almost instantaneously so that the equilibrium melt structure, consistent with the crystallization condition, cannot be reached from that of the initial molten state. These concepts would indicate that the melt structure prior to crystallization appears to be closer to that typical of the lower molecular weight species. This conclusion is consistent with rheological studies. It has been found that the mutual diffusion coefficient of a binary mixture in the pure melt is controlled by the lower molecular weight species.[26] Also in a mixture the polymer with higher molecular weight relaxes on a time scale that is related to that of the lower molecular weight chains.[27]

In addition to the crystallinity level, another important element of the phase structure of semicrystalline polymers is the interfacial region.[1,2,23] We can examine the influence of molecular weight and polydispersity of this quantity. Figure 6 is a plot of $\alpha_b$ against log $M_w$ for rapidly quenched fractions of linear polyethylene.[28] The data for the binary mixture, series III, $6.75 \times 10^3/8 \times 10^6$ is also plotted in this figure. For this mode of crystallization, the interfacial contents range from about 3% for the lower molecular weight to about 16% for the higher one. The $\alpha_b$ values of the binary mixtures are clearly not the same as the fractions when compared on the basis of the weight-average molecular weight. The mixtures again behave as though they were of much lower molecular weight. The same data are plotted in Figure 7 against log $M_N$. The data for the binary mixtures and the fractions agree quite well with one another when compared in this manner. Thus, following rapid crystallization key elements of the phase structure are influenced by the lower molecular weight species. Consequently, those properties of mixtures that depend on these structural elements should also depend on $M_N$.

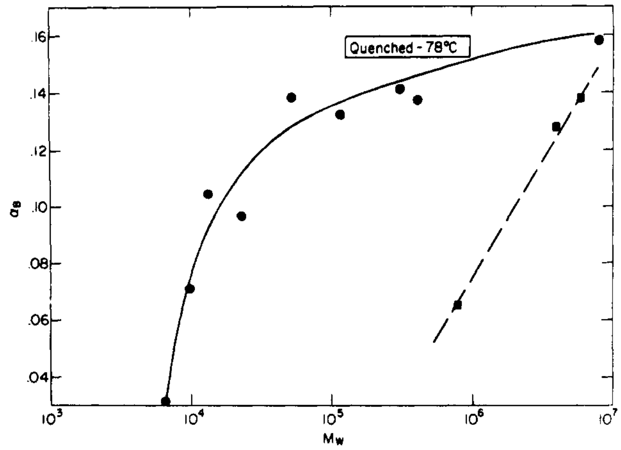

**Figure 6.** Plot of the fraction of the interfacial region, $\alpha_b$, against log $M_w$ for samples quenched to −78 °C. Fractions for reference (●). Binary mixtures: (■) series III.

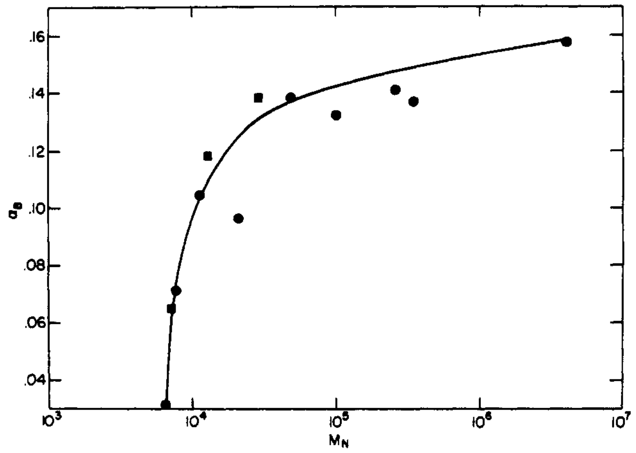

**Figure 7.** Plot of the fraction of the interfacial region, $\alpha_b$, against log $M_N$ for samples quenched to −78 °C. Fractions for reference (●). Binary mixtures: (■) series III.

Light and thin section electron microscopy, as well as small-angle light scattering (SALS), can be used to describe the supermolecular structure, i.e., the arrangement of the crystallites relative to one another. Careful studies with the same specimens under controlled crystallization conditions have shown that concordant results are obtained by these different experimental techniques.[1,29] Hence, the superstructures described here are independent of the specific experimental method used. The particular superstructure that is formed in linear polyethylene, as well as in other homopolymers, depends on the molecular weight and the crystallization conditions.[6,13,14] It is found quite generally that spherulite formation is not a universal mode of polymer crystallization. More specifically, for linear polyethylene, five distinctly different SALS patterns could be observed. These patterns have been related to the different superstructures by the theoretical work of Stein[20] and of Kawai.[21] Three of these patterns represent spherulite structures with progressively decreasing order. They have been designated by the symbols a–c, respectively.[1,6] Another pattern that displays some azimuthal dependence of the scattering and is indicative of lamellae organized as thin rods or rodlike aggregates is designated as d. The fifth pattern shows no angular dependence of the scattering. It can represent either a sheetlike structure designated as g or a collection of randomly oriented lamellae designated as h. Microscopic methods must be used to distinguish between these two morphological forms. The supermolecular structure that develops depends in a systematic manner on the molecular weight and crystallization temperatures. A morphological map that describes the structures that are formed with linear polyethylene fractions as a function of the crystallization or quenching temperature is given in Figure 8.[6,7] In this figure, the almost vertical dashed line represents the demarcation between isothermal and nonisothermal crystallization. The three solid curves represent the boundaries between spherulites and random lamellae (h), spherulites and sheetlike structures (g), and sheetlike structures and rodlike aggregates (d). The dashed curves within the solid curves represent the boundaries between the different types of spherulites a–b–c. The symbols in the figure represent the supermolecular structures of the binary mixtures studied here. The solid symbols represent random lamellae, while the open ones are for spherulites. The morphological map depends on the specifics of sample preparation and details of the crystallization procedure.[31] The experimental procedures followed here for observing the morphology of the binary mixtures correspond to the map presented for fractions.

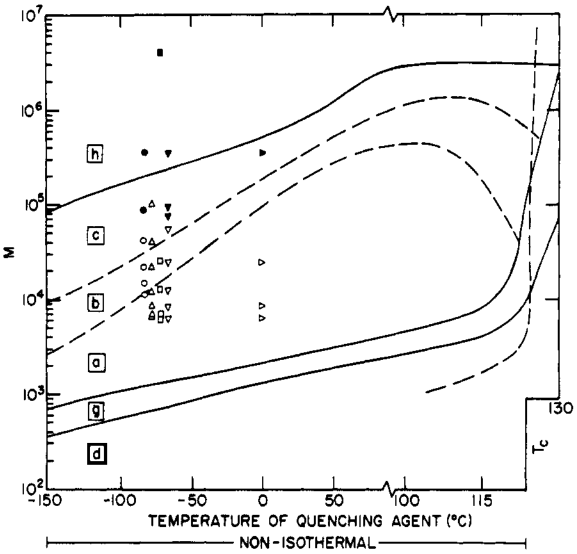

**Figure 8.** Morphological map of linear polyethylene fractions and binary mixtures. Regions delineated by curves for fractions from refs 6 and 7. Symbols are for the binary mixtures. Quenched to −70 °C: (○) series I; (△) series II; (□) series III; (▽) series VI. Quenched to 0 °C: (▷) series VI. Solid symbols represent random lamellae, and open symbols represent spherulites. Letter designations are for supermolecular structures that are described in the text.

The supermolecular structures were studied for mixtures from series I–III and VI. Their representations are plotted according to $M_N$ in Figure 8. The specimens were quenched at either −78 or 0 °C. Each series is displaced slightly on the temperature axis for the purpose of clarity. Plots on the basis of $M_w$ do not show any consistency with the morphological map of the fractions. We can conclude from Figure 8 that the morphological map of the mixtures qualitatively follows that of the fractions when compared on the basis of the number-average molecular weight. Moreover, the demarcation between random lamellae and some type of spherulitic structure is quite clear. This boundary follows the expectations from the results for fractions. For series I (13 600/428 000), the pure high molecular weight species gives randomly arranged lamellae that are maintained in the mixtures until $M_N$ is reduced to 88 500. For mixtures from series VI (6750/428 000), spherulites, although poorly organized, are formed at $M_N$ = 56 000. In series III, although the pure species gives random lamellae, mixtures with an average $M_N$ = 25 900 give well-developed spherulites. In all the mixtures the spherulites became progressively better organized as $M_N$ decreases. We can conclude from these results that irrespective of the high molecular weight component when $M_N$ is in the range of 60 000–80 000, or somewhat less, spherulites will be formed. This influence of the lower molecular weight species on the supermolecular structures formed in polydisperse systems was indicated previously.[32] The more extensive results reported here can account for the very common observation of spherulitic structures in unfractionated polymers of commercial origin, as well as the wide-spread concept that spherulite formation is ubiquitous to polymer crystallization.

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