

# Crystallization Characteristics of Polymer Blends. I.

## Polyethylene and Polystyrene

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### Synopsis

Blends of polyethylene and polystyrene have been prepared to study the effect of the morphology on their crystallization characteristics since the polymers are known to phase separate. The polymer component present in least amount formed a dispersed phase of discrete spherical particles whose number and size altered with blend composition. However, close to 50% composition cylindrical rods of polyethylene dispersed in polystyrene were observed. With polyethylene in excess the kinetics of crystallization were insensitive to the morphology, but with polyethylene present as the dispersed phase they became dependent on the size and number of the spheres, and in particular on the nucleation density. When the number of spherical particles exceeded that of heterogeneous nuclei, larger supercoolings, and so presumably homogeneous nucleation, were required for crystallization to develop further. The degree of crystallization of the blends then became dependent on the temperature of crystallization rather than on time, and the isothermal crystallization appearing to be instantaneous.

### INTRODUCTION

In a recent study<sup>1</sup> of the crystallization of ethylene block copolymers it was observed that the development of crystallinity was independent of time and dependent on the crystallization temperature only. This behavior was totally unlike that exhibited by polyethylene or its random copolymers, and was considered to be due to phase separation of the two blocks in the melt and to nucleation density control of the crystallization of the isolated domains.

Analogous behavior was to be expected in polyethylene blends for which a similar domain structure has been observed, and which is dependent on blend composition. The general effect of melt morphology on the crystallization kinetics has been studied by varying blend composition, the morphology being observed directly on the crystallized samples by electron microscopy.

### EXPERIMENTAL

Commercial polymer samples were used—Carinex SR61 polystyrene and Rigidex 50 polyethylene—as obtained from Shell Chemical Co. Ltd., and B. P. Chemical Co. Ltd., respectively. Compositions were made up by weight, by mixing the polymers between the rollers of a Schwabenthan Mill at 150–160°C for 10 min. The mixed crepes were then molded at 160°C under 9 MPa into 1 mm sheets. Standard test specimens were either cut from these sheets or molded directly from the crepe for examination on an Instron tensile tester.

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Fracture surfaces were examined on a Cambridge Instruments scanning electron microscope (Stereoscan-600).

Crystallization characteristics were determined by differential scanning calorimetry, Perkin-Elmer DSC-2, using 25 mg samples encapsulated in aluminum. The calorimeter was calibrated with zone-refined stearic and benzoic acids, and ultrapure metals, indium and tin. The thermal response was calibrated assuming the enthalpy of fusion of indium to be  $6.80 \text{ cal g}^{-1}$ .

## RESULTS AND DISCUSSION

### General Characteristics

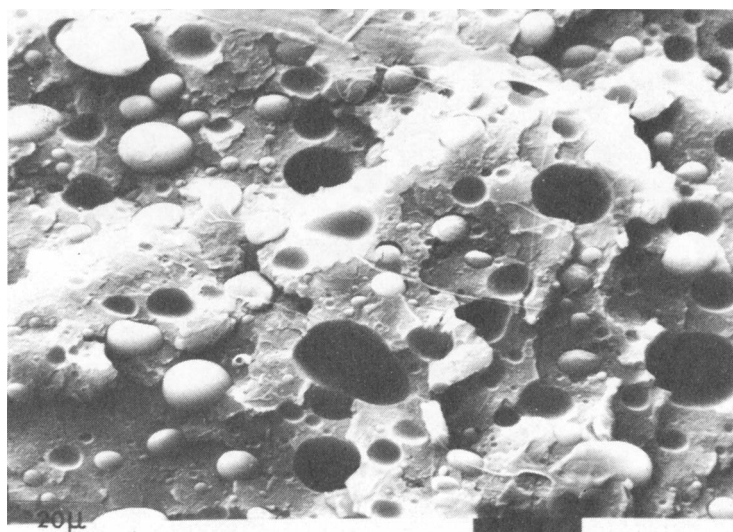
The mechanical properties of the molded specimens changed progressively with composition, falling between those of the parent polymers (see Table I). The properties were consistent with little or no interaction between the polymers, each acting as an inert filler for the other. Examination of the surfaces formed by fracture at low temperature confirmed that phase separation had taken place. At low composition of either polymer, i.e., below 30%, isolated spherical domains were observed (Fig. 1) whose number and size changed with composition (Table II). The smooth surfaces of the holes left in the matrix when a spherical particle had been prised out in the fracturing process and the apparent gaps between the spheres and the matrix are consistent with complete segregation of the polymers and no interaction between the two separated domains. Crystallization of polyethylene is followed by considerable volume contraction, about 10%, and this would be sufficient to account for the gaps between the spheres of polyethylene and the polystyrene matrix [Fig. 1(a)].

At higher composition, i.e., about 50%, the morphology changed to that of parallel packed rods, alternating polyethylene/polystyrene. This change is consistent with a lowering of the contact surface area as required by the reduced weight fraction. Thus, decreasing the composition from bulk polystyrene caused changes from a continuous matrix of polystyrene with discrete polyethylene spheres embedded in it, to a discontinuous one of alternating cylinders, and finally to polystyrene spheres embedded in a polyethylene matrix.

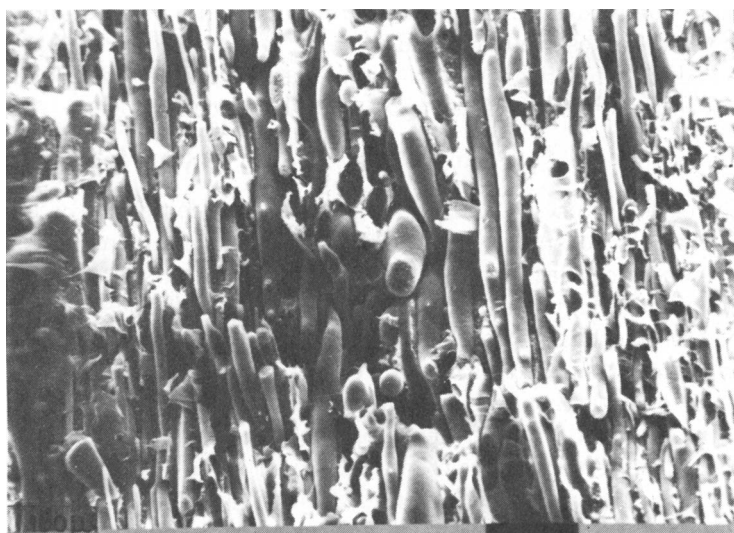
The discrete polyethylene spheres embedded in the polystyrene matrix increased in number and decreased in size as the polyethylene composition decreased (Table II).

TABLE I  
Mechanical Properties of Blends

Blend composition (wt% PS)	Young's modulus ( $\text{nm}^{-2}$ )	Fractional elongation to break
100	1.66	0.20
90	1.61	0.17
80	1.37	0.21
50	1.04	0.10
20	0.87	0.39
10	0.84	0.82
0	0.72	1.00



(a)

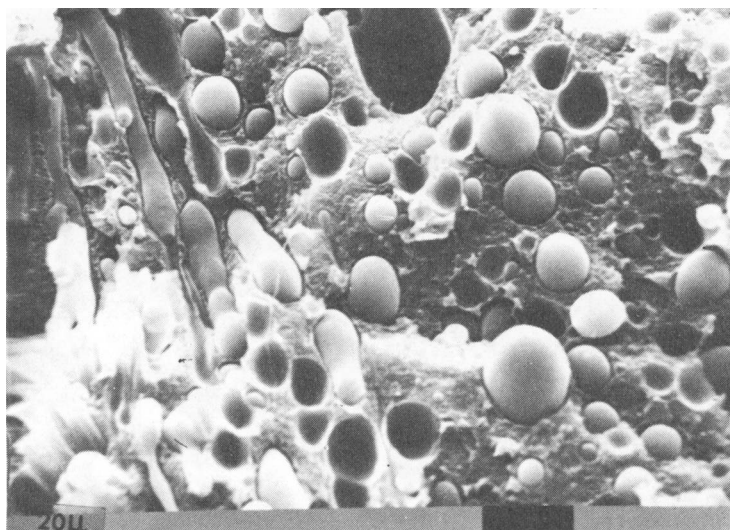


(b)

Fig. 1. Micrographs of the fracture surfaces of blends. (a) 20% Polyethylene; (b) 50% polyethylene; (c) 80% polyethylene.

### Crystallization Characteristics

Thermal analyses of the blends (Fig. 2) revealed the presence of both a glass transition of polystyrene, at 105°C, and melting of polyethylene, at 137°C. The temperature of both these transitions were independent of the blend composition, provided correction was made for thermal lag by extrapolation to zero rate of heating, and were the same as those determined separately on the parent ho-



(c)

Fig. 1. (Continued from previous page)

mopolymers. Only the intensities of the transitions varied with blend composition. The degree of crystallinity of the polyethylene phase, measured from the heat of fusion, and assuming  $70 \text{ cal g}^{-1}$  for completely crystalline material, decreased with composition (Table III).

The crystallization rate characteristics of the polyethylene rich blends were studied isothermally and analyzed by the Avrami equation:

$$-\ln(1 - X_t) = Zt^n \quad (1)$$

relating the extent of crystallization  $X_t$  at time  $t$  to a composite rate constant  $Z$  and a mechanistic constant  $n$ . Provided the polyethylene formed a continuous phase, it was observed that the crystallization rate characteristics were insensitive to the blend morphology (Table IV) and there was no evidence of the crystallization mechanism changing from three-dimensional to one-dimensional growth. Avrami indicated<sup>2</sup> that the constant  $n$  would decrease from 4 or 3, to 2 or 1 for homogeneous or heterogeneous nucleation, respectively, if the mechanism of crystallization changed from the development of spherulites to rodlike growth. Accordingly, the observed change in morphology at about 50% composition must be too gross compared with the diameters of the spherulites to appreciably alter the crystallization characteristics.

It was not possible to measure the isothermal crystallization rates for those blends containing low concentrations of polyethylene. Although crystallization

TABLE II  
Distribution of Polyethylene Spheres

Blend composition (wt% PE)	Sphere diameter ( $\mu\text{m}$ )	Number ( $\text{cm}^{-3}$ )
1	0.1–0.3	$10^{11}$ – $10^{12}$
5	0.3–0.5	$10^{10}$ – $10^{11}$
10	2.0–3.0	$10^7$ – $10^8$
20	5.0–10.0	$10^6$ – $10^7$

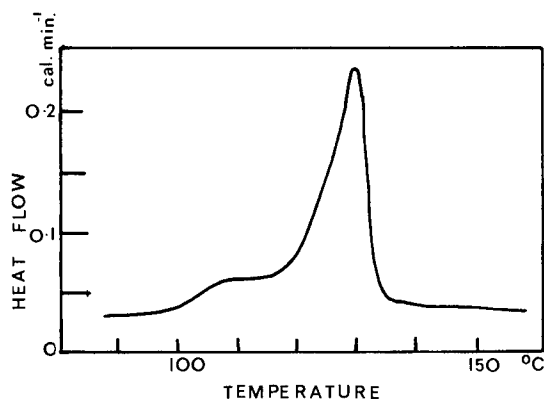


Fig. 2. Thermal analysis of a blend. 10% Polyethylene; heating rate  $10^{\circ}\text{C min}^{-1}$ ; 25 mg sample.

did develop to a limited extent as determined by subsequent measurement of the heat of fusion, it all occurred within a very short initial time period of less than 1 min, and within the equilibration time period of the calorimeter. Crystallization did not develop further with time at that temperature, but it did increase on cooling. The final extent to which crystallization developed was determined by the lowest temperature to which the sample was cooled. This

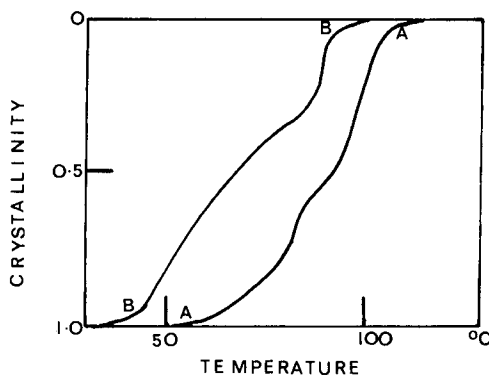


Fig. 3. Dependence of relative crystallinity on crystallization temperature. AA: 20% Polyethylene blend; BB: 10% polyethylene blend.

TABLE III  
Crystallization Characteristics

Blend composition (wt% PE)	Heat of fusion ( $\text{cal g}^{-1}$ )	Degree of crystallinity $X_t$	$T_m$ ( $^{\circ}\text{C}$ )	$T_g$ ( $^{\circ}\text{C}$ )
5	39	55	135	105
10	38	54	137	105
20	44	63	138	104
50	49	70	137	106
100	56	80	136	...
Standard deviations	3	0.5	2	2

TABLE IV  
 Crystallization Rate Characteristics

Blend composition (wt% PE)	Temperature (°C)	$-\log K$	$n$	$t_{1/2}$ (min)	Degree of fit
100	122	0.51	1.57	2.1	0.987
	123	0.96	1.86	2.4	0.974
	124	1.76	2.29	4.4	0.978
	125	2.54	2.44	9.0	0.987
	126	3.11	2.26	19.0	0.992
50	122	0.62	1.88	1.6	0.967
	123	0.79	1.94	2.1	0.985
	124	1.58	2.32	3.8	0.985
	125	2.64	2.59	7.4	0.985
	126	3.22	2.36	15.0	0.975

temperature dependence of the degree of crystallinity was explored by melting the specimens in a standard way, heating to 175°C at 10°C min<sup>-1</sup>, and cooling to the crystallization temperature at 160°C min<sup>-1</sup> or quenching. The degree of crystallinity developed was independent of the dwell period at the isothermal temperature. It was determined from the heat of fusion on subsequent melting (Fig. 3) and expressed as a fraction of that obtained after storing the samples at room temperature, 20°C. In general, the temperature dependence was complex with two distinct temperature regions in which the crystallinity developed. At low degrees of supercooling there was a higher dependence on temperature; and at high degrees of supercooling a slow development of crystallinity with temperature was observed with supercoolings of 100°C or more. A similar dependence was observed by Price and co-workers<sup>3</sup> in polyethylene droplets dispersed in a nonsolvent and attributed to a change from heterogeneous nucleation to homogeneous nucleation of the droplets at high supercooling. This change in nucleation mechanism occurred when the number of droplets in the system exceeded the number of heterogeneous nuclei with the correct characteristics for growth, such that on the average there were some droplets with no active heterogeneities present which could nucleate the crystallization. Under these conditions, crystallization of these droplets will not occur until much higher degrees of supercooling, when homogeneous nuclei can form. At low supercoolings, in the regime of heterogeneous nucleation, the temperature dependence of the degree of crystallinity reflects the size distribution of these nucleating heterogeneities in the polyethylene. At higher supercooling, in the regime of homogeneous nucleation, the temperature dependence of the degree of crystallinity is determined by the free energy of formation of the critical-size nucleus. The break in the temperature dependence-crystallinity plot was taken as the change from one form of nucleation to the other.

The relatively small size of the droplets formed in the blends and the comparatively high degrees of supercooling involved in the observed crystallizations require that the development of crystallinity within a droplet is essentially instantaneous at each crystallization temperature.

On the basis of these conclusions we are lead to conclude that polyethylene normally crystallizes from heterogeneous nuclei, and that, for example, there are 10<sup>7</sup> nuclei cm<sup>-3</sup> present in the Rigidex 50 sample used in the present study.

This is consistent with the observed spherulite diameter, 0.2 to 5  $\mu\text{m}$ ,<sup>4</sup> and the great difficulty in "seeding" the crystallization.

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