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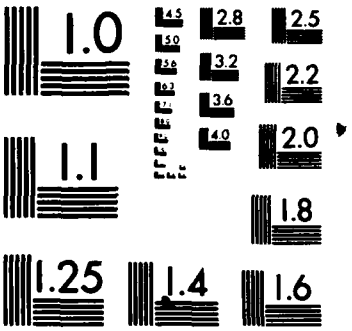

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Crystallization and Nucleation in a Polybutadiene-Isotactic Polypropylene Block Copolymer and the Corresponding Blend

by

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A study of crystallization in isotactic polypropylene, a blend of this homopolymer with polybutadiene and a diblock copolymer of isotactic polypropylene and polybutadiene has been carried out. Results indicate significant differences in the mechanisms of crystallization in these three systems even though a polypropylene-like spherulitic morphology is observed in every case.

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INTRODUCTION

The physical behavior of a block copolymer is related to its microphase separated morphology. In the case where one of the blocks is capable of crystallizing, the nucleation and growth of the crystallites may be influenced by the non-crystallizable regions of the chain. Thus, phase separation and properties of a semicrystalline block copolymer should be inter-related with the factors governing crystallization.

This paper reports a study of the crystallization behavior and nucleation phenomena of a recently reported novel polybutadiene-isotactic polypropylene block copolymer and the corresponding homopolymer blend (1). In addition to presenting various crystallization and nucleation data, some qualitative insight is provided regarding the relationship between microphase separation in block copolymers (which requires that the block junction be at the interface) and the driving forces for crystallization (which involves surface free energy difference between the crystal and the melt as well as the difference in the interfacial energies between components in the melt).

EXPERIMENTAL

All experiments were performed with a series of four polymers:

1) Commercial Isotactic Polypropylene (Comm. iPP.)
2) Experimental Isotactic Polypropylene (Exp. iPP.)
3) 60% Exp. iPP/40% Polybutadiene Blend (Blend)
4) 60% iPP - 40% PBD Block Copolymer (Block)

Preparation and characterization of the above samples have been reported elsewhere (1). Thermal analysis results were obtained on a Perkin-Elmer DSC-4 Calorimeter. The resultant isothermal crystallization curves were analyzed using Avrami kinetics. Spherulitic growth and nucleation were studied by means of a polarizing light microscope equipped with a Mettler FP-5 hot stage. The spherulitic growth rate was determined from micrographs taken at various time intervals and the nucleation density was calculated from Avrami kinetics employing the bulk crystallization and spherulitic growth rate constants.

RESULTS AND DISCUSSION

A general summary of the thermal behavior of the materials in this study is given in Table I. According to Avrami kinetics, the crystallization isotherms are described by specifying the bulk crystallization rate constant, K, and the time exponent, n. In the case of these materials, the results show a good agreement with theory when plotted against the proper function of time. For the most part all four samples exhibited a value of $n = 3$ consistent with the known athermal heterogeneous (primary) nucleation and spherulitic growth.

Even though there are numerous effects that can occur by adding a second component to isotactic polypropylene, the spherulitic structure of the iPP exists even when large percentages of the second phase are present. The presence of this secondary dispersed phase does, however, disturb the internal spherulitic structure. (2) The result can be seen in Figures 1 and 2.

Comparison of the curves of Figure 3 brings out two important points. The first of these is the fact that some of the differences between the various samples can be minimized or eliminated by plotting the data as a function of undercooling. Thus, some of the crystallization behavior can be attributed to differences in Tm or to the dependency of nucleation and growth on undercooling.

This dependency is illustrated by the differences in the activation energies for the various processes (see Table I). A second point brought out by Figure 3 is the nature of the differences in crystallization behavior of polypropylene, the block copolymer and the blend. Comparing the experimental iPP with the block copolymer on a basis of constant undercooling shows that the copolymer crystallizes with lower growth rates and higher nucleation rates than the homopolymer. In the blend the reverse is true; the polypropylene in the blend crystallizes with higher growth rates and lower nucleation rates than the corresponding homopolymer alone.

We may speculate at this point about the above mentioned phenomena and the mechanisms of crystallization in these materials. In this regard it is useful to compare the value of $\bar{\sigma} = (\sigma_e \sigma_u^2)^{1/3}$ for various systems (Table I). The symbols σ_e and σ_u represent the end and lateral interfacial energy terms, respectively. Generally for polymers σ_e will be appreciably greater than σ_u since the chains emerge from the crystal face, migrate through the viscous melt, and fold back to produce another crystal layer. The value of σ_e may be expected to depend on the nature of the separation in heterogeneous polymer systems. This effect may be particularly strong for block copolymers where the block junctions are constrained to be at or near the crystal surfaces. Referring again to Table I, it appears that σ_e is smaller for the block copolymer and the blend when compared to the polypropylene homopolymer or alternatively that No. , the number of primary nucleation sites is larger for the block copolymer and the blend.

Reported experimental results on such systems as PEO-PS, PEO-PBD, and PBD-PE illustrate the complexity of the effects of block copolymerization on crystallization (3-7). For the most part, the experimental evidence to date indicates that:

a) The large-scale crystal morphology is the same in the semicrystalline /amorphous block copolymers as in the semicrystalline homopolymer

except that the internal perfection of this morphology is diminished for the case of the copolymer.

b) The crystallization rate depends on the nature of the surfaces produced by phase separation so that the number of chain folds is changed with respect ot the homopolymer crystallization.

c) An increase in the number of chain folds due to the microphase nature of the copolymer leads to smaller, more rapidly formed crystals which results in a lower Tm compared to homopolymer.

d) The difference in the number of chain folds in the block copolymer is directly related to changes in σ_e.

The results of this study are qualitatively consistent with all of the above.

CONCLUSIONS

Based upon the results of this study and those in the literature, it appears that there is a significant relationship between the detailed mechanisms of crystallization and the nature of the phase separation in a heterogeneous polymer system. Thus, in the particular case of a polybutadiene-isotactic polypropylene block copolymer, nucleation phenomena play a much more significant role than for the case of the corresponding homopolymer blend. Spherulitic morphologies are observed in both cases, however. The implications of the observed variations in crystallization behavior on the physical properties of these materials is under investigation.

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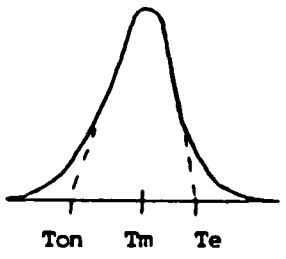
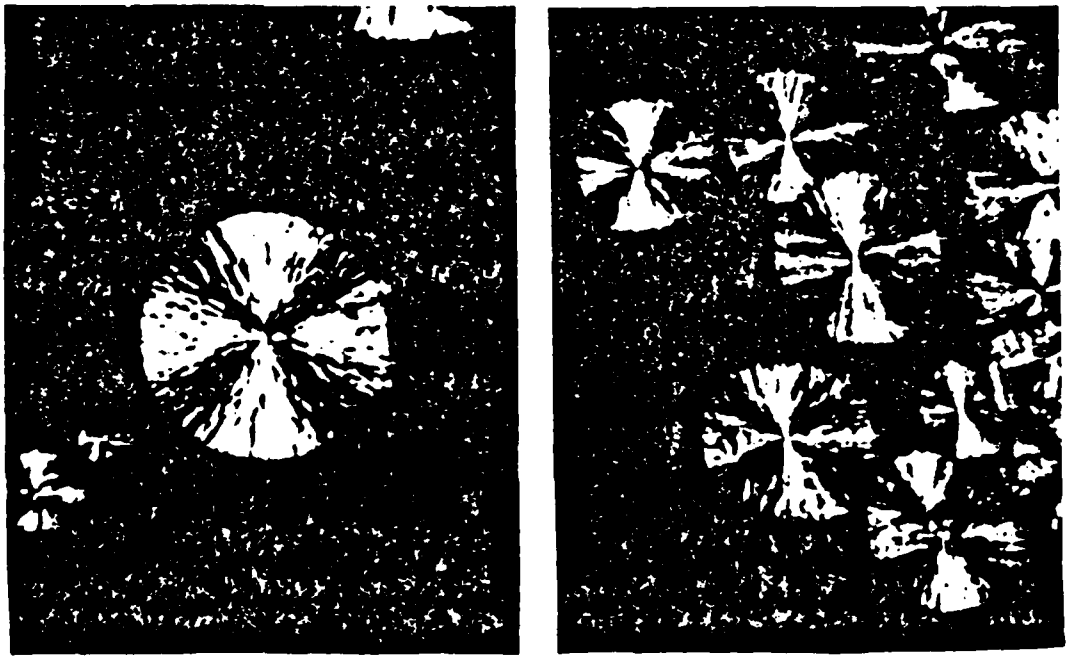
Table I

	Tm[1] (C)	Xc[1] (%)	Te-Ton[1] (C)	Tm°[2] (C)	E(K)[3] (kcal/mole)	E(G)[3] (kcal/mole)	E(N)[3] (kcal/mole	$\bar{\sigma}$[4] (ergs/cm^2)
iPP Comm.	164	50	20	202	160	55	25	12.1
iPP Exp.	154	25	40	192	150	35	35	10.3
Blend	153	12	40	189	150	30	50	9.4
Block	154	25	25	196	130	35	40	9.5



1. Value is the average of three DSC runs on the same sample.
2. $Tm = Tm^{\circ}(1-1/2B) + Tc/2B$ (See: J. I. Lauritzen & J. D. Hoffman, Res. Nat. Bur. Stand. 64 ,73 (1960).
3. $E(X) = R(m)$, where m is the slope of ln X vs. 1/Tc.
4. $\bar{\sigma} = \sqrt[3]{\sigma e \sigma u^2}$ where $\sigma e \sigma u^2 = mR(Hu)^2/_2 - 8\Pi N_o$ and m is the slope from $\ln K$ vs. $(Tm^{\circ})^2/\ Tc(Tm^{\circ}-Tc)^2$.



FIGURES 1 & 2. Commercial iPP & Block Copolymer Spherulites Developed at the Same Degree of Undercooling.

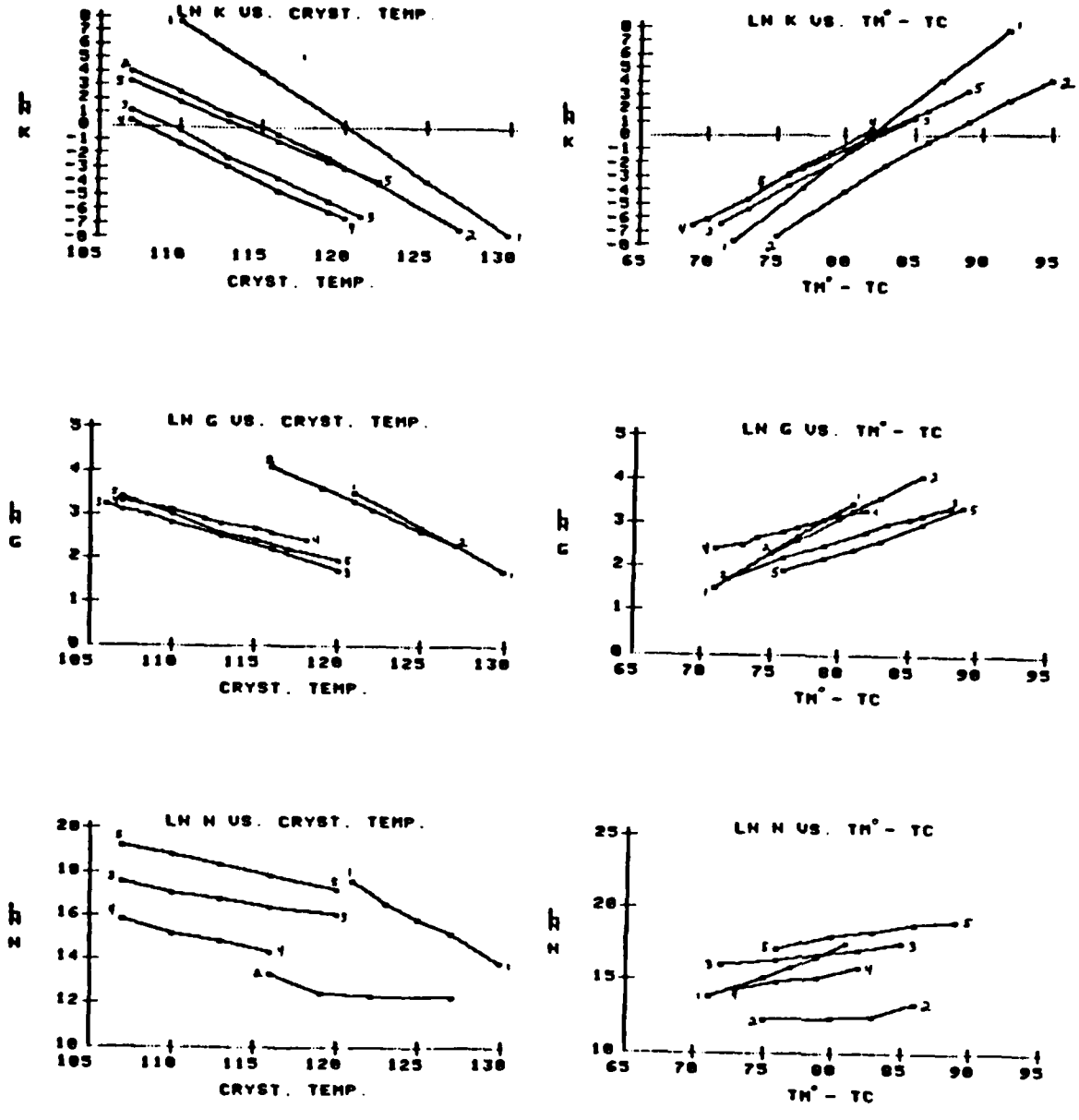


FIGURE 3. Comparison of Various Crystallization and Nucleation Phenomena As a Function of Temperature and Undercooling.

KEY

1. Literature Data iPP (8)
2. Commercial iPP
3. Experimental iPP
4. Blend
5. Block

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