

Crystallization Studies on Fire-Retardant Polypropylene

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Synopsis

A study of the effect of a series of fire retardants upon the crystallization behavior and morphology of polypropylene suggests three categories: (1) "Insolubilized nucleating additives"—these remain insolubilized at the premelting temperature of polypropylene, resulting in very high nucleation density which leads to numerous irresolvable small spherulites. (2) "Solubilized nucleating additives"—these are soluble at the premelting temperature of polypropylene but recrystallize before and/or simultaneously with the crystallization of polypropylene; the subsequent lower nucleation density results in medium-size spherulites of a fairly heterogeneous distribution. (3) "Nonnucleating additives"—these remain solubilized in the polymer matrix throughout the course of crystallization of polypropylene. The nonnucleating nature and low viscosity of these solubilized additives results in large volume-filling spherulites crystallized at a much faster growth than the unfilled polypropylene.

INTRODUCTION

It is of technical importance in semicrystalline polymers to control the number and size of the spherulites since they affect the optical properties like light scattering and transparency^{1,2} and mechanical properties like impact strength,³ ultimate tensile strength,⁴ and elongation at break.⁵

The control of spherulite size by adding additives as nucleating agents has been extensively studied by many investigators.⁶⁻¹⁰ Generally, such heterogeneous nucleation serves to increase the overall rate of crystallization and also the total amount of crystallinity which frequently leads to shorter processing cycles and improvement in product properties.

In a previous paper,¹¹ the effect of a series of commercial fire retardants (Dechlorane) and two experimental fire retardants on the dynamic mechanical and thermal properties of polypropylene has been elucidated. The present work investigates their effect on the morphology and crystallization behavior of polypropylene. It is hoped that, from such studies, the effective dispersion and nucleating efficiency of these additives can be inferred so that more homogeneous and efficient FR-PP formulations can be realized.

EXPERIMENTAL

Polypropylene (PP) samples (Exxon CD-100), $\overline{M}_w = 4.08 \times 10^5$, $\overline{M}_w/\overline{M}_n \approx 7.8$, with the formulations listed in Table I were blended on a Steward Bolling mill at 175°C for about 6 min after which they were melt pressed on a Carver

press at 175°C under 10,000 pounds for 1 min to give films of about 1 mil in thickness.

A small piece of film sample, sandwiched between two cover glasses, was premelted at 210°C for 10 min to completely remove any previous orientation, mechanical, and thermal history and then transferred as quickly as possible to a hot stage at 125°C. Crystallization behavior was examined isothermally with a Spencer microscope (American Optics) under crossed polaroids at 150× magnification. Pictures were taken using high speed-type 47 (3¼ in. × 4¼ in.) Polaroid films. The temperature of the sample was monitored by a precalibrated iron-Constantan thermocouple placed near the cover glasses. The growth rate of spherulites, $G = dr/dt$ (r = radius of spherulites), was obtained by measuring the radius of the spherulite as a function of time. The slope of the plot of the radius versus time in the linear region was taken as the average growth rate.

The chemical structures of the fire retardant additives are shown in Table I.

TABLE I
Chemical Structure of the Fire-Retardant Additives

Fire-retardant additives	Structure
Dechlorane "A"	
Dechlorane "B"	
Dechlorane "C"	
Dechlorane "D"	
EFR "A"	
EFR "B"	

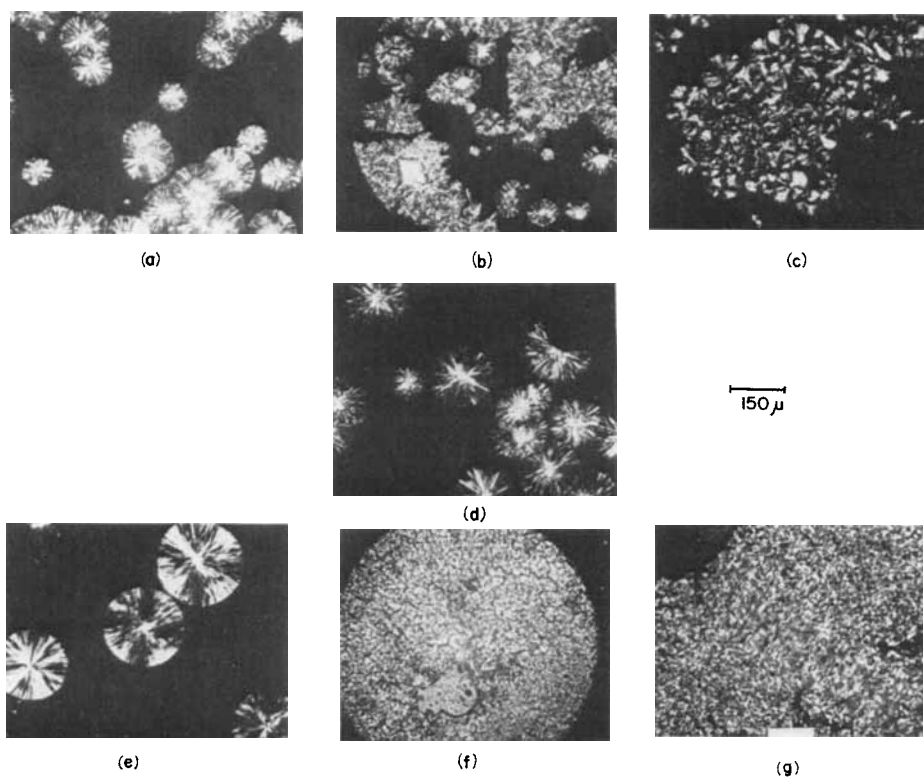


Fig. 1. Crystallization morphology of FR-PP: (a) base PP; (b) PP/Dechlorane "B"; (c) PP/Dechlorane "C"; (d) PP/Dechlorane "D"; (e) PP/EFR "B"; (f) PP/Dechlorane "A"; (g) PP/EFR "A".

RESULTS AND DISCUSSIONS

Rate of Spherulite Growth

Figure 1a–e shows the optical micrographs during the spherulite growth for the samples of PP, PP/Dechlorane "B," PP/Dechlorane "C," PP/Dechlorane "D," and PP/EFR "B," respectively. The plots of the spherulite radius (r) versus time are shown in Figure 2 for all the samples. Data of PP/Dechlorane "A" and PP/EFR "A" systems are not presented because these two fire-retardant additives phase separate at the premelting temperature (210°C); the extremely high nucleation density in these two samples prevents any resolvable spherulites to be formed, thus making accurate determination of the growth rate not possible (Figs. 1f and g).

The measurable growth rate of the spherulites in all the fire-retardant PP samples (Table I) was enhanced irrespective of their type. This can be considered to result from the predominance of the activation energy of diffusion of molecular segments to the growing spherulite front.¹² The cluster of chain segments which make up a crystallite must move in a single direction if it is to participate in spherulite growth. The resistance to the movement of such a cluster is expected to decrease in a less viscous medium. This is in line with the fact that the thermal diffusibility of PP liquid increases, with decreasing viscosity caused by the lower molecular weight additives.

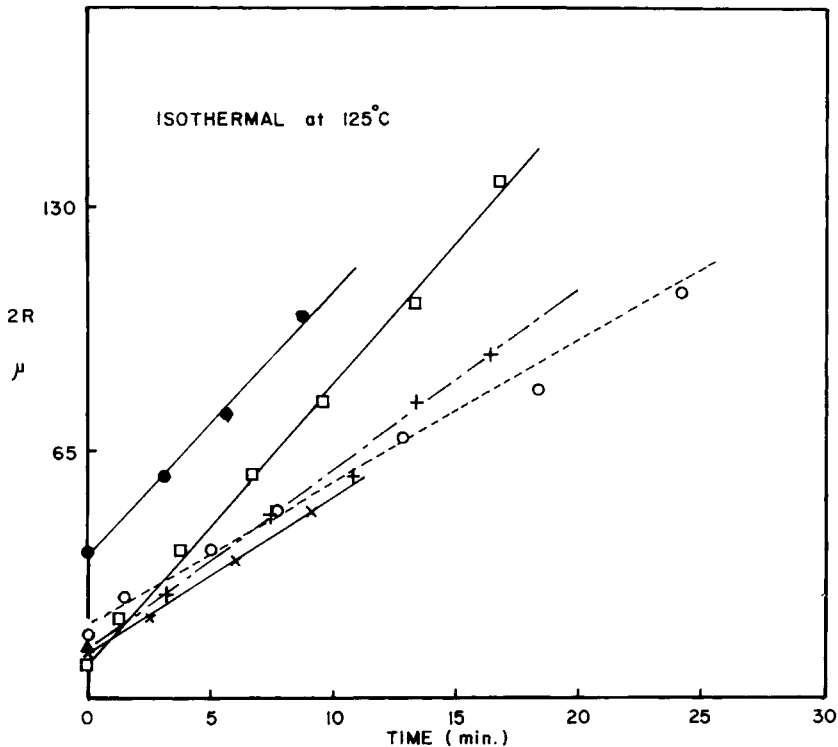


Fig. 2. Spherulite growth rate of FR-PP: (O) base PP; (x) PP/Dechlorane "B"; (+) PP/Dechlorane "C"; (●) PP/EFR "B"; (□) PP/Dechlorane "D".

Morphology of the Crystallized FR-PP Samples

Comparing the different morphologies obtained after crystallization among the seven FR-PP samples, it is apparent that in the presence of the insoluble additives (e.g., Dechlorane "A" and EFR "A"), no well-resolved spherulites were observed. The morphology of the Dechlorane "B"/PP system is unique in that the originally soluble additive recrystallizes to much larger rhombic-shaped crystals which subsequently nucleates the spherulites. In the case of the Dechlorane "C"/PP system, Figure 1c, only a fraction of the additive recrystallizes and nucleates on cooling from the melt, while the remainder is included within the subsequently formed spherulites. Dechlorane "D" and EFR "B" additives which dissolve in PP are accommodated in the volume-filling spherulites of a larger dimension than those from the base PP.

Table II summarizes the spherulite growth rate, average spherulite size after impingement, visual solubility of the additives at 210°C, and their nucleating ability. Assuming that the size of the spherulite is inversely proportional to the nucleation density, the nucleating efficiency of the fire retardants can be arranged in the following order: Dechlorane "A" > EFR "A" > Dechlorane "B" > Dechlorane "C" > EFR "B" ~ Dechlorane "D."

It has been reported previously¹² that Dechloranes "A," "B," "C," and EFR "A" additives act like inert filler and do not affect the melting point and T_g of PP. Such filler properties have been attributed to the phase separation of the

TABLE II
Isothermal Crystallization at 125°C

Sample	Additive mp, °C	Additive wt %	$G = \frac{dr}{dt}, \mu \text{ min}$	Average spherulite diameter after impingement, microns	Visual solubility of additive at 210°C	Nucleating ability of additive
PP-Base		—	1.9	150	—	—
PP/Dechlorane "A"	298.5	9%	not determined ^a	15	insoluble	nucleating agent
PP/Dechlorane "B"	300.0	9%	2.1	75	dissolved	recrystallize and act as nucleating agent
PP/Dechlorane "C"	no melting endotherm; apparent sublimation at 370°C	9%	2.4	100	dissolved	nucleating agent
PP/Dechlorane "D"	181.5	9%	3.7	250	dissolved	nonnucleating
PP/EFR "B"	179.0	9%	3.5	200	dissolved	nonnucleating
PP/EFR "A"	311.0	9%	not determined ^a	30	insoluble	nucleating agent

^a Not determined because of very small spherulite size and high nucleation density.

additive after processing, and the additives apparently also act as nucleating agents as observed in the present studies. On the contrary, for the two low-melting additives (EFR "B" and Dechlorane "D") which melt blend with PP, the incorporation of the additives in the spherulites can be correlated with the pronounced shift in T_m and T_g of PP observed previously.¹¹

CONCLUSIONS

The morphology, spherulite size, and growth rate of FR-PP are strongly dependent upon the nature of the fire-retardant additives. Heterogeneously nucleated crystallization of PP prevails with the high-melting fire retardants which either phase separate at the premelting temperature of PP or recrystallize at the crystallization temperature. Very inefficient heterogeneously nucleated crystallization is suggested for the low-melting fire retardants which remain solubilized throughout the course of crystallization and are incorporated in large volume-filling spherulites. The observed faster growth rate is attributed to the reduced viscosity of the medium.

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