Memory Effects in Polymers. I. Orientational Memory in the Molten State; Its Relationship to Polymer Structure and Influence on Recrystallization Rate and Morphology

Y. P. KHANNA and A. C. REIMSCHUESSEL, *Corporate Technology, Allied-Signal, Inc., Morristown, New Jersey 07960*

Synopsis

The influence of polymer structure on the orientational memory in the molten state has been studied by observing the crystallization behavior of the molten polymer through differential scanning calorimetry. It is shown that polymers with strong intermolecular forces (e.g., H-bonding) retain the orientation memory even at temperatures above their equilibrium melting temperatures. The retained orientation memory of the polymer melt is shown to influence its recrystallization rate and the morphology.

INTRODUCTION

In order to study the crystallization behavior of a polymer which can be related to the physicochemical characteristics of the polymer, one must eliminate the influence of impurities, additives, nucleating agents, and crystalline memory. The crystalline memory is erased by melting the polymer at a sufficiently higher temperature, for example, above its equilibrium melting temperature (T_m°). If the melting is carried out at lower temperatures that do not completely erase the crystalline memory, traces of crystalline species may persist in the melt, and upon subsequent cooling may nucleate and enhance the crystallization rate.[1] One other factor that influences the polymer crystallization from the molten state is the prior orientation history of the sample.

A detailed analysis of "oriented crystallization in polymers" has been published by Keller and Machin.[2] Among other issues, they have emphasized the phenomenon of "row nucleation" whereby the flow lines originating from stress during melt processing act as centers for nucleation; the subsequent lamellar growth being in the direction normal to these flow lines. Although these authors describe the mechanism and morphology of polymer crystallization under the influence of orientation (stress-induced), phenomena such as (a) the retention of orientation memory at high temperatures (e.g., above the T_m°), (b) its effect on subsequent crystallization rate from the molten state, and (c) the role of polymer structure, appear to be unreported so far. In this article we present our results on the relationship between melt crystallization rate and the orientation history and how this relationship is influenced by polymer structure using differential scanning calorimetry (DSC).

CCC 0021-8995/88/082259-10$04.00

EXPERIMENTAL

Materials

The nylon 6 used was Allied-Signal's 8207F grade pellets of weight-average molecular weight ($\overline{M}w$) of 35,000–40,000. Nylon 6,6 pellets of grade Zytel 101L were obtained from DuPont. An alternating copolymer of ethylene (E)/chlorotrifluoroethylene (CTFE) Halar 500 pellets and a polytetrafluoroethylene (PTFE) powder were obtained from Ausimont-USA. Polyethylene terephthalate (PET) pellets of intrinsic viscosity 0.53 dL/g (at 25°C in 60:40 phenol:tetrachloroethane) were used. Polyethylene (PE) samples 1, 2, and 4 represent Paxon® 4100 grade pellets of Allied-Signal with a $\overline{M}_w$ of 190,000–250,000. PE sample 3 was a powder of high molecular weight, $\overline{M}_w \simeq 5 \times 10^6$ from Himont (Wilmington, DE).

Processing

All the samples were compression molded into about 5-mil thick films except the nylon 6 samples 1 and 3, which were extrusion processed. The films were stretched up to 200–300% on an Instron unit at room temperature. Polyethylene sample 4 was the only film stretched up to 900% at room temperature.

TABLE I

Crystallization Of Polymers From The Molten State With Prior Orientation History

Category	Polymer		% Stretched	Progm. Cryst. Temp. Tcc, °C	Iso. Cryst. Temp. C	Iso. Cryst. Rate $t_{0.5}^{-1}$, min	Change In Cryst. Rate Due To Orientation History
I	Nylon 6	Sample #1	0	182.6 183.2		0.171	Increase
			100	184.9 183.6		0.173	
			200	184.3 184.8		0.182	
			300	186.0, 186.2 186.7, 185.5	200	0.238	
		#2	0			0.094	
			300			0.129	
		#3	0			0.195	
			300			0.248	
	Nylon 66		0	230.7			
			250	232.4			
II	Ethylene/Chlorotrifluoroethylene Copolymer		0	222.2			No Major Change
			200	223.0			
	Polytetrafluoroethylene		0	311.8			
			300	312.6			
	Polyethylene Terephthalate		0	201.3 200.1 201.3			
			300	200.4 199.4 203.2			
III	Polyethylene	Sample #1	0	115.5 116.1			No Change (or possible decrease)
			200	113.7 113.4			
		#2	0	114.3 114.7		0.154 0.138 0.148	
			300	113.0 113.5	123	0.121 0.121	
		#3	0	114.0			
			300	114.0			
		#4	0	111.0 112.3		0.047 0.058	
			900	112.0 112.9		0.046 0.055	

DSC Characterization

A DuPont 9900 DSC was used to obtain crystallization behavior data. Conditions employed were as follows: argon atmosphere, a constant sample size of 10 ± 0.2 mg, 20°C/min heating rate up to a temperature of about 50°C above the polymer melting peak (T_m), followed by 5 min hold and then cooling at a rate of 10°C/min to observe the crystallization peak temperature. It should be noted that $T_m + 50$°C is higher than the T_m° of all the polymers studied presently. Similarly, isothermal DSC experiments were also conducted in which the polymer melt was allowed to cool to an isothermal temperature which produced a crystallization exothermic peak for semiquantitative analysis. Unstretched and stretched samples of a particular polymer were analyzed on the same day to improve reliability of the data and the temperature calibration was assured within ± 0.5°C by analyzing appropriate metal stan-
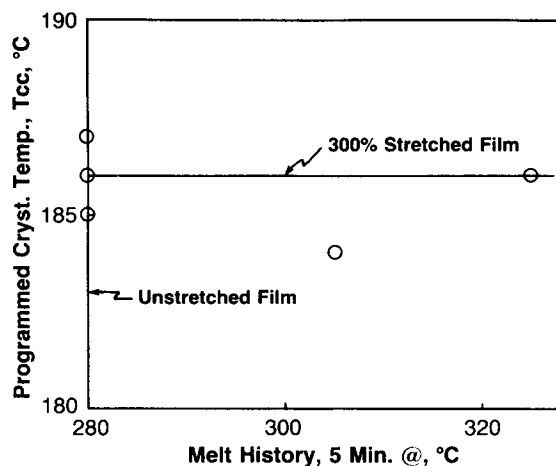
Fig. 1.   Influence of melt history on the relationship between orientational memory and the melt-crystallization behavior of nylon 6.
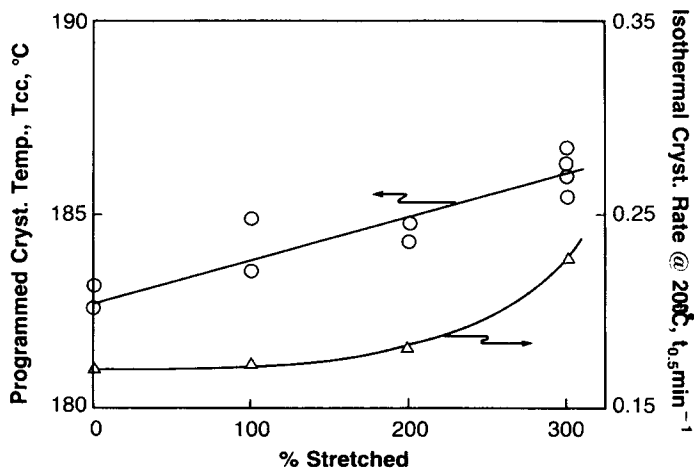

Fig. 2.   Effect of orientational memory in nylon 6 on its crystallization from the molten state.

dards. The isothermal crystallization rate is represented as the reciprocal of the crystallization peak width at half height, that is, $t_{0.5}^{-1}$, min^{-1}.

Optical Microscopy

Samples of nylon 6 and PE isothermally crystallized in the DSC were cross-sectioned and photomicrographs were prepared in transmitted polarized light.

RESULTS AND DISCUSSION

The results are summarized in Table I and illustrated in Figures 1 to 5.

In differential scanning calorimetry, the crystallization temperature upon cooling from the molten state, T_{cc}, is a value characteristic of a particular polymer. However, the T_{cc}, which is related to the overall crystallization rate, can be varied over a narrow range for a particular polymer. For example, addition of a nucleating agent to nylon 6 increases its T_{cc} up to 7°C, whereas every 10,000 increase in molecular weight decreases its T_{cc} by 1°C.[3] Therefore, we have used T_{cc} as a criterion to evaluate the influence of orientation memory on the overall crystallization rate of various polymers. For nylon 6 and PE we have demonstrated the validity of our conclusions by measuring the isothermal crystallization rates and by morphological evaluations.
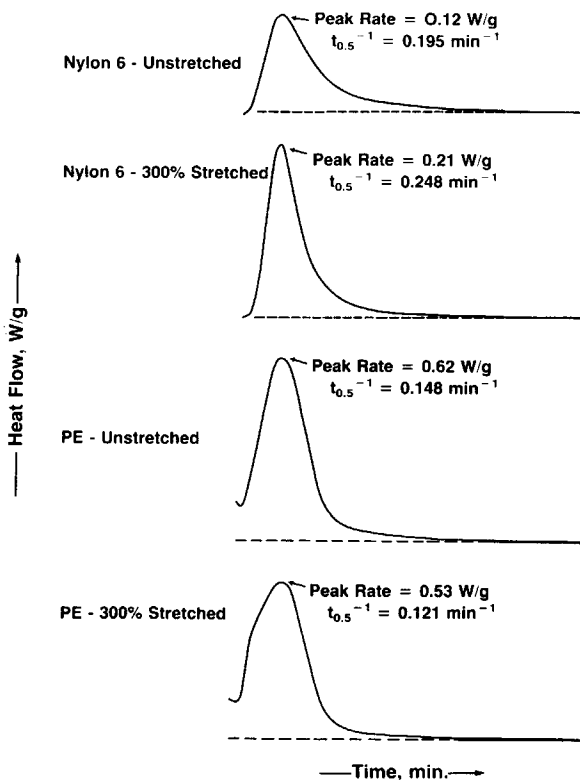

Fig. 3. Isothermal DSC thermograms of nylon 6 (at 200°C) and PE (at 123°C).

For nylon 6, the T_{cc} of the 300% stretched sample is 3° to 5°C higher (see Table I) than that of the unstretched sample even though the samples were treated for 5 min at 280°C prior to crystallization. This suggests (a) that orientation increases the crystallization rate of nylon 6 melt, and (b) the orientational memory persists even after a treatment of 280°C/5 min, which is above the equilibrium melting temperature (260°C) of nylon 6. Figure 1 clearly shows that the orientational memory is not being erased even after a treatment of 320°C/5 min since the T_{cc} of the stretched film is higher than that of the unstretched film. Figures 2 and 3 reveal that the crystallization rate increases with an increase in orientation (related to % stretching) of the nylon 6.

Morphological evaluation of nylon 6 samples isothermally crystallized in the DSC unit supports the conclusions based on DSC crystallization rates. For example, the unstretched nylon 6 exhibits a larger, more well-developed spherulitic structure than that of the stretched nylon 6. Only few "row nucleated" lines are observed in the unstretched crystallized film. These are assumed to be due to some orientation inherent in the film upon extrusion and processing (Fig. 4). The stretched material exhibits more and smaller spherulites, more "row nucleated" lines and, in general, more "nucleation centers." Such behavior is expected in view of the different "overall" crystallization rates of the two nylon 6 materials. [Note: the "overall" or "effective" crystallization rate represents the combined effect of the nucleation rate and of the growth rate processes.] The memory effect in nylon 6 is so strong that even an extruded film can be differentiated from a compression-molded film after the melting/crystallization experiment in the DSC. [Note: the extruded film has only a minor orientation as indicated by a maximum shrinkage of $\simeq 0.2\%$ by thermomechanical analysis. For reference, the maximum shrinkage is $\simeq 16\%$ for the 300% stretched film.] Figure 4 reveals, as stated above, that even after melting and recrystallization of the extruded film, some oriented growth of the spherulitic structure occurs. Although not explored presently, it appears that any high stresses used in processing can give rise to some orientational memory effects. Nylon 6,6, although not explored as well as nylon 6, appears to fall in the same category based on the T_{cc} measurements.

For E/CTFE, PTFE, and PET, we do not find any significant change in the crystallization behavior due to the orientation history (see Table I).

For polyethylene, multiple measurements on samples 1 and 2 suggest the possibility of a slight decrease in the crystallization rate although the morphology of sample 2 shows some indication of oriented growth in the stretched film (Fig. 5). However, these findings cannot be confirmed for samples 3 and 4. At present we are unable to comment on the factors responsible for the variations of the results on polyethylene. For polyethylene, we wish to conclude that the orientation history of the sample has no significant effect on the melt/crystallization rate although the possibility of a slight decrease may not be ruled out until sufficient statistical data become available.

Based on our results it appears that orientation memory effects are dependent on polymer structure. Intermolecular interactions such as H-bonds present in both nylon 6 and nylon 6,6, even at temperatures above their equilibrium melting temperature, preserve stress nucleation sites created on orientation, and therefore enhance the "overall" crystallization rate. Such
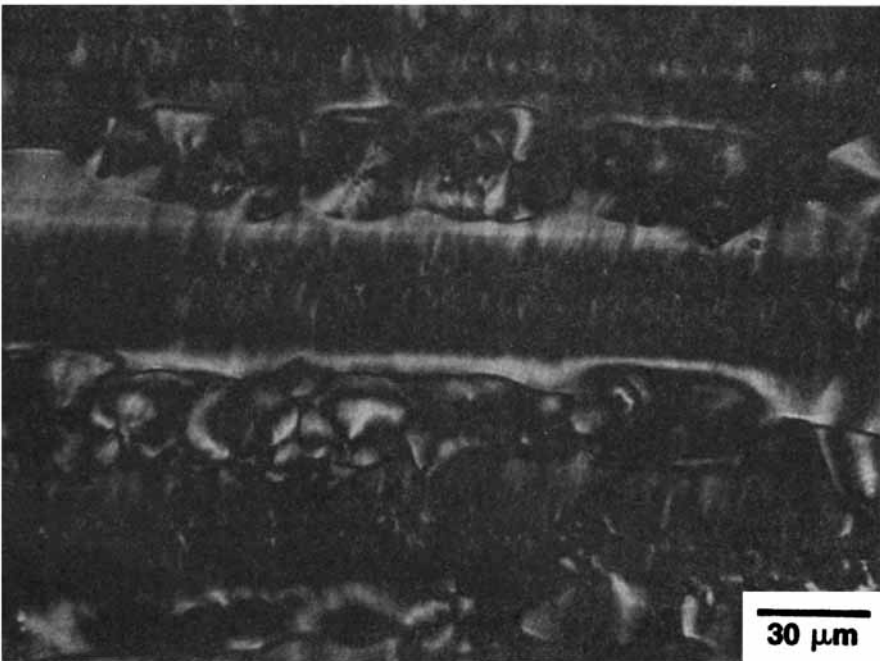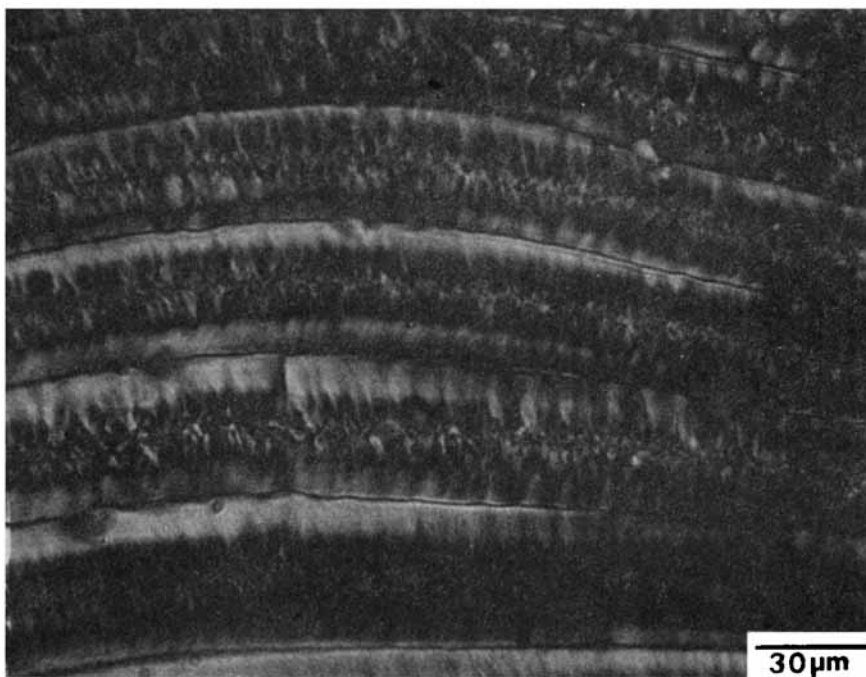
Nylon 6 Film–Unstretched

30 μm

Nylon 6 Film–300% Stretched

30 μm

Fig. 4. Optical micrographs of nylon 6 films isothermally crystallized in the DSC for 1 h at 200°C.

An Extruded Film of Nylon 6

30 µm

A Compression Molded Film of Nylon 6
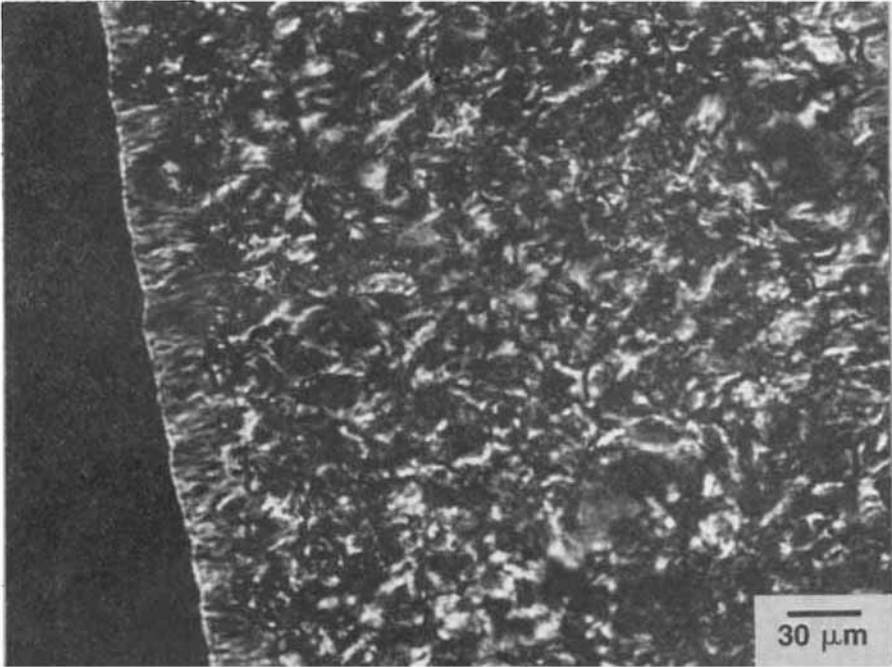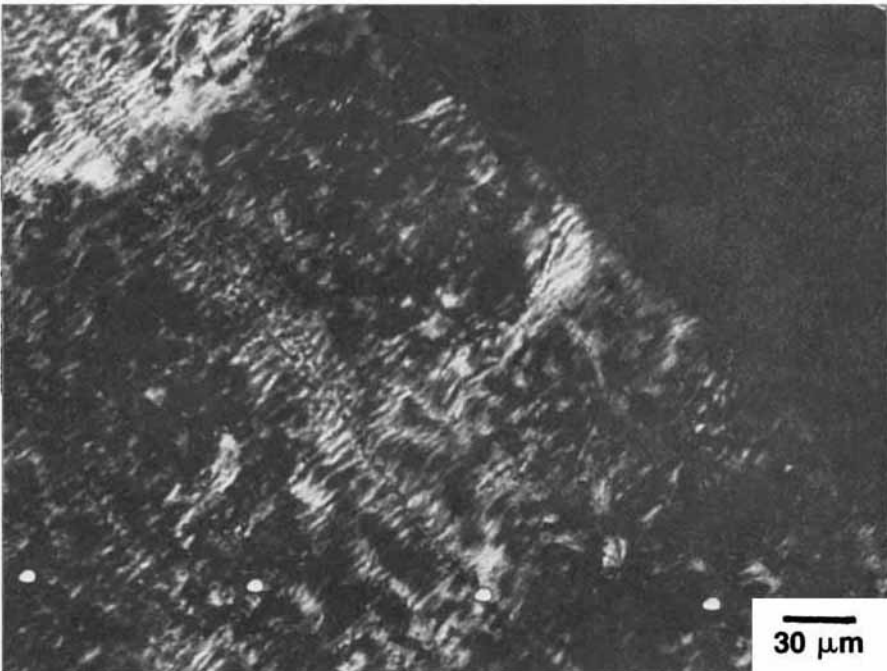

10 µm

Fig. 4.   (*Continued from the previous page.*)

PE Film–Unstretched (Sample #2)

PE Film–300% Stretched (Sample #2)

Fig. 5.   Optical micrographs of polyethylene films isothermally crystallized in the DSC for 1 h at 123°C.
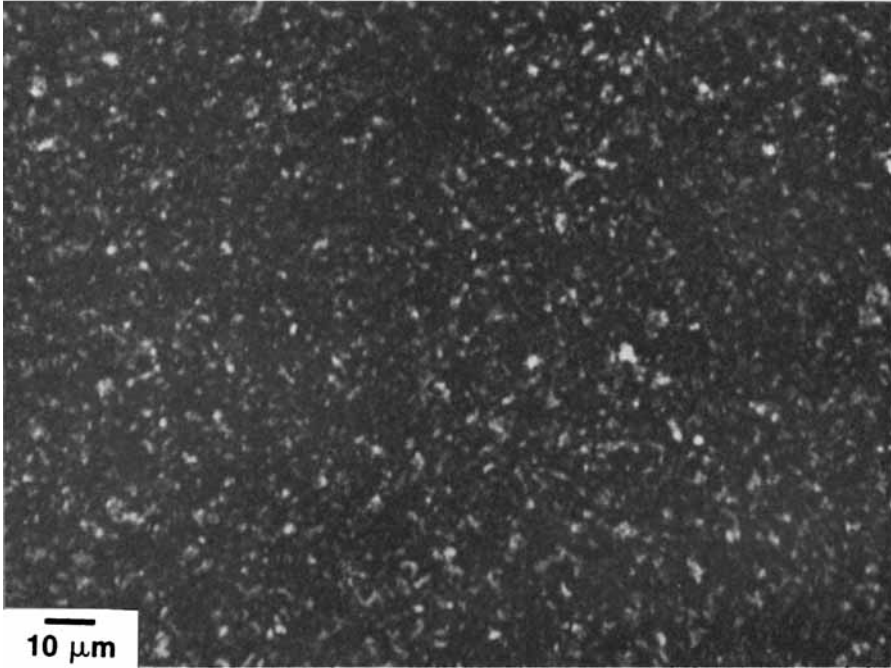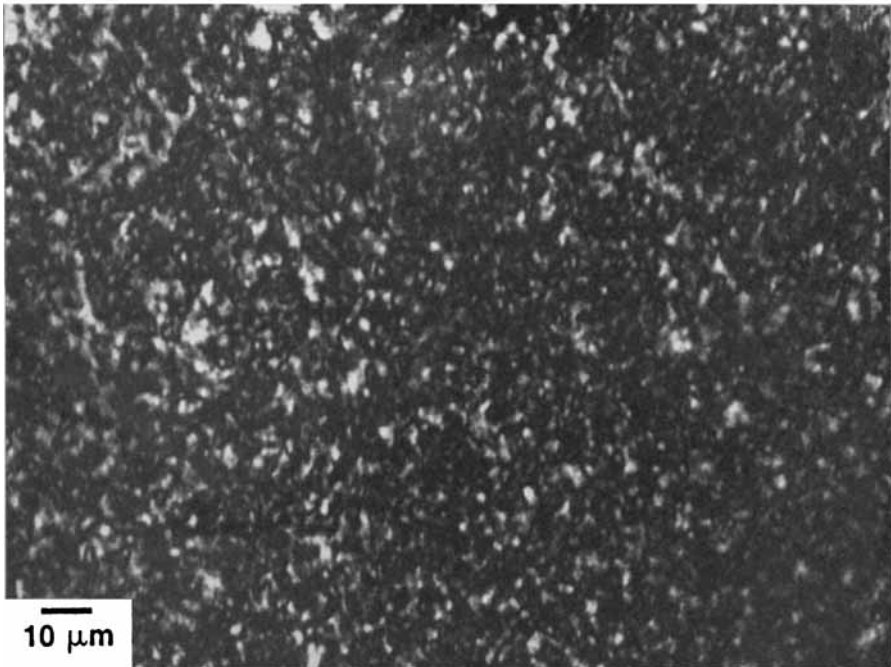
PE Film–Unstretched (Sample #4)

PE Film–900% Stretched (Sample #4)

Fig. 5.   (*Continued from the previous page.*)

interactions, being much less pronounced in E/CTFE, PTFE, and PET, have no major effect on the melt-crystallization behavior. In the case of polyethylene there are no polar interactions and, therefore, the recrystallization rate of the molten polymer tends to be similar for the stretched and unstretched films.

CONCLUSIONS

The crystallization behavior of polymers from the molten state is influenced by the orientational history. The orientational memory is not erased within the time scale of our experiments, for example, 5 min at a temperature well above the equilibrium melting temperature of the polymer. Moreover, the manner in which orientational memory affects the crystallization rate depends upon the polymer structure.

References

1. E. Turska and S. Gogolewski, *J. Appl. Polym. Sci.*, **19**, 637 (1975).
2. A. Keller and M. J. Machin, *J. Macromol. Sci. (Phys.)* **B1**, 41 (1967).
3. Y. P. Khanna, Unpublished Data, Allied-Signal, Inc. (1985).