Orientation on Elongation at Rupture of Two Injection-Molded Isotatic Polypropylenes

INTRODUCTION

The infrared spectra of atactic and molten isotactic polypropylene are essentially identical.[1] When the isotactic polymer is cooled, the polymer molecules form helices.[2] This formation of helices is due to the chain ordering of some or all of the isotactic polymer molecules and not to any change in the amount of atactic molecules.[3]

The formation of helices results in interactions between closely spaced atoms in the polymer molecules. These interactions give rise to new characteristic infrared absorption bands in the spectrum of isotactic polypropylene at 809, 841, 899, and 999 cm^{-1}.[3] The assignments[4] of these bands as well as those at 975 and 1168 cm^{-1}, which are found in the spectra of both atactic and isotactic polypropylene, can be found in Table I.

TABLE I
Assignments of Polypropylene[a] Infrared Absorptions[b]

Band, cm^{-1}	Species[c]	Assignment
809	E	CH_2 rock + C—C chain stretch + C—CH_3 stretch
841	A	CH_2 rock + C—CH_3 stretch
899	E	CH_3 rock + CH_2 rock + CH bend
975	A	CH_3 rock + C—C chain stretch
999	A	CH_3 rock + CH_2 wag + CH bend
1168	A	C—C chain stretch + CH_3 rock + CH bend

[a]
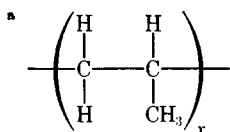
[b] See Zerbi and Piseri.[4]

[c] When three repeating monomer units are considered, the A species are vibrating in phase, and the phase difference between adjacent monomer units of the E species is 120°C.

X-Ray diffraction patterns indicate that isotactic polypropylene can exist in three different crystalline forms which can be attributed to different crystalline packing of the helices.[5] The infrared spectra of these forms are essentially identical with respect to absorption frequencies. Therefore, the characteristics of the infrared spectra depend on the molecular and not the crystalline symmetry of the polymer molecules.[6]

Therefore, it is concluded that the characteristic absorption bands of isotactic polypropylene at 809, 841, 899, and 999 cm^{-1} are not crystalline lattice vibrations, but rather they reflect chain ordering by being indicative of helical isotactic structure which exists only in the crystallites in the polymer.[6]

Texture, which is defined as the arrangement of crystallites with respect to each other and to amorphous regions, is significant in oriented polymers.[7] As far as the arrangement of crystallites is concerned, texture can be studied by X-ray diffraction. In some cases orientation of amorphous regions may be studied by infrared dichroism.

Our X-ray analyses of various samples of injection-molded isotactic polypropylene show patterns that differ in the intensities at the pertinent Bragg angles. This indicates
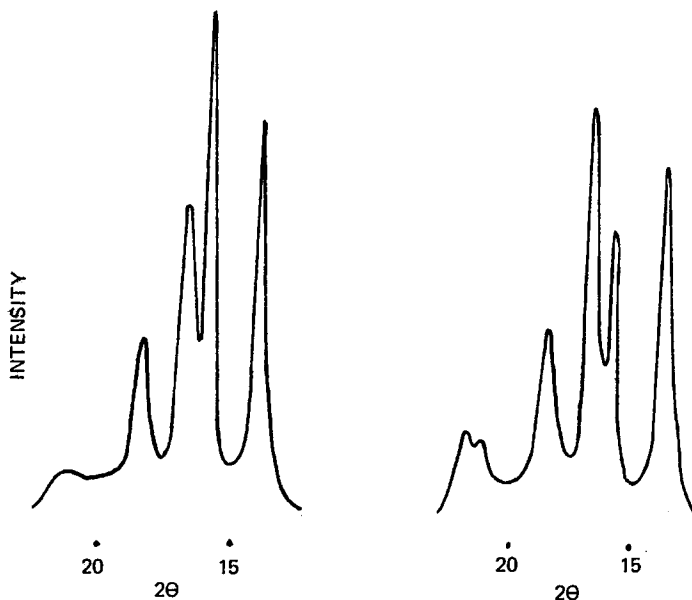
Fig. 1. X-Ray diffraction patterns of injection-molded polypropylene.

differences in the orientation of crystallites in the samples. Representative patterns showing extreme differences are shown in Figure 1. The infrared spectra of these samples are essentially identical with respect to absorption frequencies. However, the relative intensities of the absorption bands listed in Table I differ in the spectra. Therefore, an examination of the dichroism exhibited by these absorption bands may be rewarding.

Dichroism of an absorption band induced by strain in polymers is indicative of preferential orientation of the transition dipole moment of a given band vibration which is necessary for the absorption of radiation of a given frequency.[8] The transition moments, as reflected by the intensities of absorption bands, depend upon the orientation of the vibrations with respect to polymer chain skeleton. Also, as in the case of isotactic polypropylene, a given absorption may be dependent upon a particular backbone conformation.

The value of the dichroic ratio is dependent on the direction of the transition moment of a given vibration with respect to the conformation of a polymer. However, the magnitude of the ratio cannot, in most cases, be used alone to determine polymer conformation. Usually an analysis of the configuration statistics of the polymer chains as a whole is required to establish a given conformation.[9]

MATERIALS AND EXPERIMENTAL PROCEDURES

For the initial application of the above concepts to the study of chain orientation in polymers, we chose two isotactic polypropylene tensile bar samples designated 672 and 677, which were found to have respectively 100% and 35% elongation at rupture. Samples 672 and 677 were injection molded from commercial polymers having weight-average molecular weights of 390,000 and 290,000, respectively. Melt temperatures (375°F) and other molding conditions were similar for both samples. These samples were part of a study in which differences in elongation at rupture could not be explained by differences in molecular weight.

The samples were indexed with respect to a set of x, y, and z orthogonal axes. The x axes were taken as the direction of flow into the mold, with the y and z axes parallel and normal to the sample plane, respectively.

Dichroism of the infrared absorption bands listed in Table I was obtained with polarized infrared-attenuated total reflectance (IR-ATR) using a common beam wire grid polarizer and KRS-5 plates. In these studies the polarizer was set perpendicular to the spectrophotometer slits for maximum energy. Reflectivities along the x and y axes were measured by orienting a 10 mm $\times$ 10 mm sample, which was removed from the center of the tensile bar, first parallel and then perpendicular to the beam. Samples were then drawn along the x axes in an Instron tester at room temperature at an elongation just before rupture, and the spectra of the samples were again determined immediately after drawing as above.

Calculations of the dichroic ratios, dx/dy, were made as follows: It was found in both transmission and ATR studies of films that the 1462 cm^{-1} absorption did not show dichroism when isotactic polypropylene is drawn along the x axes. Therefore, in order to minimize errors in the measurement of absorption bands that may be due to differences in the contact area of the sample with the KRS-5 plate, the reflectivities of all bands studied were normalized to the reflectivities of the 1462 cm^{-1} bands for both the parallel and perpendicular orientations. These normalized reflectivities were then used to calculate the dx/dy values for each absorption band.

The dichroic ratios in the x and y directions were calculated by using the theory of Flournoy and Schaffers.[10] This theory presents formulas for the calculation of absorption indices (kx, ky, kz) when measuring spectra from surfaces of anisotropic, absorbing films by polarized infrared attenuated total reflection. Flournoy applied this theory to the study of oriented polypropylene films[11] and found that the approximate equality of the ky and kz ratios indicated radial symmetry about the x axis, i.e., the axis of drawing. In his[11] study, a draw ratio of $8x$ was used which produced a highly oriented sample. In our work, the tensile bars were not subjected to a high draw ratio during fabrication. As a result, orientation was studied by considering only the kx/ky ratios. The ratios were reproducible to 0.02 units.

The degree of crystallinity of both samples was determined by using a General Electric XRD3 X-ray diffraction instrument and the method of the Dow Chemical Company.[12]

RESULTS AND DISCUSSION

The degree of crystallinity of both nonelongated samples was 64%, and the infrared spectra of all samples were identical with respect to absorption frequencies. Dichroic ratios can be found in Table II.

Dichroic ratios reflect orientations of the transition dipole moments of bond vibrations. Although the band assignments (Table I) show complexity due to mixing of the vibra-

TABLE II
Dichroic Ratios kx/ky of Samples 672 and 677

Band, cm^{-1}	672 Ratios		677 Ratios	
	No elongation	Elongation $\sim$100%	No elongation	Elongation $\sim$35%
1168	0.73	1.36	1.31	0.85
999	0.67	1.04	1.43	0.93
975	0.61	1.07	1.44	0.94
899	0.68	0.57	1.06	0.69
841	0.72	1.41	1.05	1.00
809	0.97	0.79	1.09	0.61

tional modes, it can be said that dichroic ratios of these bands in isotactic polypropylene also indicate orientations of polymer chains. Therefore, the dichroic ratios (Table II) indicate that the orientation of the polymer chains in the 672 and 677 nonelongated samples must evidently be different.

The dichroic ratios of the 1168, 999, 975, and 841 cm^{-1} absorptions of the 672 elongated sample show parallel dichroism, whereas the 899 and 809 cm^{-1} absorptions show perpendicular dichroism (Table II). This is just what was expected from the work of Schmidt[6] and this laboratory in studies of uniaxially drawn isotactic polypropylene films in the x direction by transmission polarized infrared spectroscopy. This correlation is gratifying, because it means that bulk orientation of polymer chains in injection-molded parts might be correlated with surface orientation as measured by polarized attenuated total reflection.

The dichroic ratios of the 677 elongated sample also somewhat indicate orientation along the x axis. This is shown by the fact that the ratio of the 841 cm^{-1} band has the highest value and the 899 and 809 cm^{-1} bands are perpendicular bands. Although the ratios of the 1168, 999, and 975 cm^{-1} bands are low, the general pattern of all of the bands as a whole could indicate x axis orientation. However, other mechanisms may be involved in the orientation of this sample.

A comparison of the dichroic ratios of the 672 samples indicates that orientation is obtained by a uniaxial draw along the x axis. The drawing mechanism indicated by the dichroic ratios of the 677 samples is not as simple. In this case, the data indicate that possibly x axis orientation as well as biaxial orientation may be involved. Also the data indicate, as previously mentioned, that the 677 nonelongated sample has a different orientation pattern than the 672 nonelongated sample. This fact could account for the lower elongation at rupture of the 677 sample, which could be explained by an entropy effect that is related to the conformation of molecular chains.

In view of the fact that both samples were 64% crystalline and that the amorphous C—C chain stretch bands at 975 and 1168 cm^{-1} shown dichroism, it is interesting to note that possibly the amorphous portion of the polymer may exert a greater effect on the drawing mechanism or other physical properties than has been previously anticipated.

In any case, the data presented in this note do not explain how these polypropylenes acquired different orientation patterns during the injection-molding process. This, of course, is of significant importance and is the subject of our current studies.

CONCLUSION

We believe that the data presented in this report justify further investigations regarding the effect of orientation of polymer chains on various physical properties as measured by attenuated total reflection techniques. Work is continuing along these lines with the hope that this technique, as well as others, may contribute to an understanding of the differences found in the physical properties of plastic parts that are molded from both semicrystalline and amorphous polymers.

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