

NOTES

Determination of the Degree of Helical Structure and Related Isotacticity of Polypropylene by an Infrared Method

In the past no adequate method has been available specifically for the determination of isotacticity in polypropylene resins. An infrared method has been developed in this laboratory which measures that portion of the isotactic chains existing in a helical configuration. This method has been found superior to the presently accepted extraction procedure.¹ The study of a number of polypropylene films suggested that the "normalized intensity" of the 8.57 μ band was an intrinsic measure of the isotacticity of each base resin, although previous investigators^{2,3} have not reported this relationship (cf. Fig. 1). This band, for example, was appreciably diminished upon quenching (from the melt) potentially high crystalline films to a medium crystallinity. Simultaneously the 8.67 μ band and the broad medium band in the 11.5–12.8 μ region increased in intensity. These absorptions had been previously identified with both the molten isotactic form and the atactic species.⁴ The quenched films yielded an x-ray pattern qualitatively identical to either the monoclinic⁵ or the monoclinic plus the hexagonal⁶ crystalline modifications. However, the "smectic" form⁷ associated with the uncrystallized helices was absent.⁸

Peraldo⁹ has assigned this 8.57 μ band to a helical methyl rocking or wagging vibration with the major component parallel to the helical axis.

[Since this band exhibited parallel dichroism for oriented specimens^{4, 10} and the energy of vibration (1167 cm^{-1}) is much too large for the methyl wagging mode, it can be tentatively assigned to the helical methyl rock $[\text{R}(\text{CH}_2)\text{A}]$.

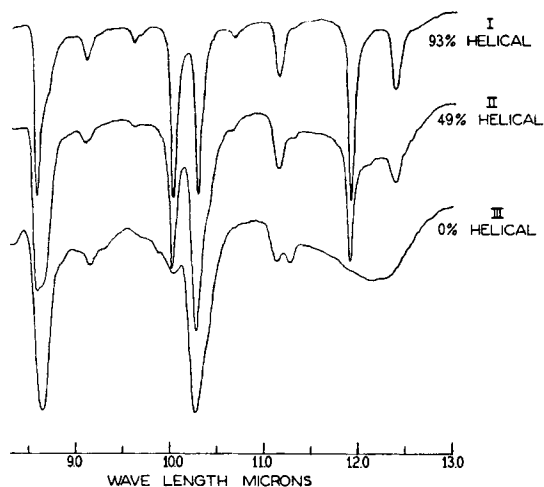


Fig. 1. The infrared spectra of highly isotactic (I), partially isotactic (II), and atactic (III) polypropylene.

The 8.67 μ band in the atactic spectrum has nearly the same peak intensity (identical integrated intensity), and is slightly broader than the 8.57 μ band of the crystalline isotactic form. Its proximity to the helical $\text{R}(\text{CH}_2)\text{A}$ at 8.57 μ , and the transition from this position observed upon quenching indicates that the 8.67 μ peak is also a methyl rocking mode. The intensity of this band is not susceptible to polarization effects, signifying a random distribution of the amorphous chains. It appears that the nonhelical methyl rock is degenerate with that of the atactic species.

Assuming, then, that the absorbance ratio $A_{8.57 \mu}/A_{10.27 \mu}$ is directly related to the degree of helical structure (the 10.27 μ band having been found to be a true measure of the density-thickness product to a maximum thickness of 0.05 mm.), we have examined the infrared spectra of 66 films representing 30 base resins and synthetic mixtures. These films were selected on the basis of their wide range of crystallinities and thermal histories. The density of the infrared-irradiated portion of the films was determined by the density gradient method at 23°C. The results of these analyses are embodied in Figure 2. The data were subjected to a Least Squares treatment, and the standard deviation from the resultant regression line in Figure 2 was $\pm 2.4\%$. The large intercept is primarily due to the contribution from the 8.67 μ band shoulder.

If it is assumed that the intensity of this shoulder obeys Beer's Law, then:

$$A_{8.57 \mu}/A_{10.27 \mu} = [K_1 H_I/100] + [K_2(100 - H_I)/100] \quad (1)$$

where H_I is the weight percentage helical content, and K_1 and K_2 are the extinction coefficients of the 8.57 μ helical band and the 8.67 μ amorphous band shoulder, respectively. Since all the chains exist in a helical configuration at 100% crystallinity, then extrapolation of the regression line in Figure 2 to the theoretical specific volume ($= 1.069$) of the

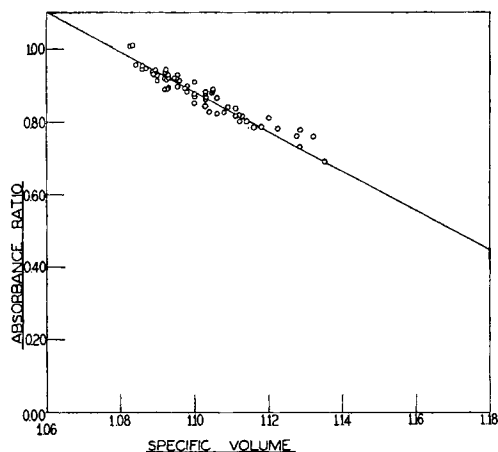


Fig. 2. Correlation of absorbance ratio $A_{8.57 \mu}/A_{10.27 \mu}$ with specific volume for polypropylene films.

TABLE I
The Helical Contents of Soxhlet-Extracted Polypropylene Fractions

Sample no.	Fraction	Fraction weight-%	Helical content	
			Weight-%	Wt., g./100 g. of whole polymer
TMA 147	Unextracted whole polymer	100.0	75.0	— 75.0
	Ether-soluble extract	8.9	0	0
	Heptane-soluble extract	10.8	55.5	6.0
	Extraction residue	80.3	83.0	67.0
TMA 220	Unextracted whole polymer	100.0	78.0	— 78.0
	Ether-soluble extract	7.7	0	0
	Heptane-soluble extract	9.0	58.5	5.5
	Extraction residue	83.3	86.0	71.5
TMA 232	Unextracted whole polymer	100.0	80.5	— 80.5
	Ether-soluble extract	1.7	0	0
	Heptane-soluble extract	6.0	66.5	4.0
	Extraction residue	92.3	82.5	76.0

monoclinic or hexagonal unit cell gives $K_1 = 1.055$. The value of 0.347 was obtained for K_2 by calculating the absorbance ratio $A_{8.57 \mu} / A_{10.27 \mu}$ of the 8.67μ band shoulder at 8.57μ from the spectrum of the pure atactic species. Substitution of these values in eq. (1) yields:

$$H_I = 141.2(A_{8.57 \mu} / A_{10.27 \mu}) - 49.0 \quad (2)$$

for the particular infrared spectrometer employed in this study (Perkin-Elmer Model 21).

The helical content as calculated from eq. (2) appears to approach a maximum for films which have been annealed at 160°C . for 15 minutes in Carbowax 600, with subsequent slow cooling to room temperature. However, the helical content was found to be far less sensitive to thermal history than was the degree of crystallinity (a mean difference between the annealed and unannealed films of 2.6% in helical content vs. 11.0% in the degree of crystallinity). Since it appears that the maximum helical configuration was achieved by the forementioned annealing process, then the application of this method to annealed films provides a measure of the "effective isotacticity" of the film resin.

The validity of eq. (2) was confirmed by comparing the total of the helical contents of variously extracted fractions with that of the whole polymer. The results for three typical polypropylene resins are summarized in Table I. The whole polymers and the heptane-insoluble fractions were annealed at 160°C to permit maximum conversion to the helical conformation. Similar results were obtained for an annealed synthetic mixture.

In each case the material balance is maintained within the limits of experimental error. However, the total isotacticities as measured by the infrared method are lower than those reported for the extraction procedure (the extraction residue). This result is to be expected since the extraction method measures only the bulk solubility properties of the polymer, and cannot sharply differentiate between the various isomeric forms present due to their variation in molecular weight. The heptane-soluble portion of these three resins were presumed to contain the bulk of the stereoblock material, and this was evidenced by a positive departure from the regression line in Figure 2. Continuing x-ray studies

indicate that these deviations can be quantitatively correlated to the uncrystallized helices associated with the stereoblock material.

It is generally accepted that the strong tendency for polypropylene to exist in the helical state, even upon severe quenching, is responsible for many of its unique physical properties such as stiffness, tensile strength, and surface hardness. Thus the present infrared method facilitates the determination of the maximum helical content, or "effective isotacticity," which is a highly significant characteristic of the polymer, and is believed to closely approximate the actual isotacticity.

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