Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1963

SovietRxiv

Fig. 1. Fulfillment of the linear dependence between D_{1380}/D_{976} and D_{1460}/D_{976} (see equation (2))

Figure 1: Fig. 1. Fulfillment of the linear dependence between D_{1380}/D_{976} and D_{1460}/D_{976} (see equation (2))

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1963. Volume 152, No. 5

PHYSICAL CHEMISTRY

Yu. V. KISSIN, V. I. TSVETKOVA, N. M. CHIRKOV

DETERMINATION OF THE DEGREE OF ISOTACTICITY OF POLYPROPYLENE FROM ITS INFRARED SPECTRA

(Presented by Academician N. N. Semenov, 12 VI 1963)

All bands in the IR spectra of crystalline stereoregular polymers can be divided into three groups. The first group comprises bands corresponding to vibrations of the functional groups of the polymer. The specific integral intensity of such bands does not change when the aggregate state of the polymer changes. The second group comprises bands corresponding to vibrations that appear only in ordered helical chains (tacticity bands) (^{1}). As a rule, the specific integral intensities of such bands also do not depend on the aggregate state of the polymer, owing to preservation of the short-range one-dimensional order of the chain upon dissolution or melting of the polymer (^{2}). The third group comprises bands formed as a result of intermolecular order (crystallinity bands). These bands disappear upon melting or dissolution of a crystalline polymer.

Fig. 1. Fulfillment of the linear dependence between D_{1380}/D_{976} and D_{1460}/D_{976} (see equation (2))

In the spectrum of isotactic polypropylene all three indicated types of bands are present. The 1460 cm^{-1} band, corresponding to scissoring vibrations of CH_2 groups, has the same specific intensity in all types of polypropylene. The 1154 and 976 cm^{-1} bands are tacticity bands; they are absent from the IR spectra of atactic polymer (^{3}). The 1380 cm^{-1} band, assigned to symmetric deformation vibrations of CH_3 groups, is present in the spectra of all types of polypropylene and may be assigned to the bands of the first group. However, its intensity, as shown in the present work and in (^{3}), changes strongly on going from isotactic to atactic polypropylene. Consequently, the 1380 cm^{-1} band may be regarded as an isotacticity band.

Finally, the bands 1170, 997, 900, 843, and 809 cm^{-1} are crystallinity bands (^{4}).

When comparing different catalysts, the magnitude of the degree of isotacticity of the polypropylene obtained on them is of great importance. However, the methods described up to the present for determining the degree of isotacticity of polypropylene ($^{5-7}$) were, in essence, only methods for estimating its crystallinity, since the intensities of various crystallinity bands were taken as the measure of the degree of isotacticity. At the same time, one cannot expect a linear dependence between the degree of crystallinity and the degree of isotacticity. Moreover, with different cooling regimes of the molten polymer one can obtain films of different degrees of crystallinity (quenching of the polymer).

According to the method we propose, the intensity of the 1154 or 976 cm^{-1} bands may be taken as a measure of the degree of isotacticity of polypropylene. The intensity of the 1460 cm^{-1} band is taken as an internal standard for film thickness.

However, it should be taken into account that the considerable overlap of the 1154 and 1170 cm^{-1} bands makes it inconvenient to use the 1154 cm^{-1} band as a quantitative measure of the degree of isotacticity. For this reason, in what follows the intensity of the 976 cm^{-1} band is taken as the measure of the degree of isotacticity.

We assume that there is a linear relationship between the ratio D_{976}/D_{1460} and the degree of isotacticity of polypropylene. For a completely atactic polymer, $D_{976}/D_{1460} = 0$. The maximum value of this ratio, which is observed for polymer fractions insoluble in hot n-heptane, corresponds to 100% isotacticity, i.e., the degree of isotacticity is equal to

$$\frac{D_{976}/D_{1460}}{(D_{976}/D_{1460})_{\max}}.$$

In some cases the 1460 cm^{-1} band cannot be used as an internal thickness standard. Thus, for example, in the case of ethylene-propylene copolymers the optical density of this band is proportional to the total number of CH$_2$ groups in both the ethylene and the propylene units. In these cases the 1380 cm^{-1} band may be used as an internal thickness standard. However, as already indicated, the intensity of this band depends on the degree of isotacticity of the polymer.

In general form one may write:

$$D_{1460} = K_{1460} l$$

$$D_{976} = K_{976}^{\mathrm{i}} C_{\mathrm{i}}$$

$$D_{1380} = \left[K^{\mathrm{i}}_{1380} C_{\mathrm{i}} + K^{\mathrm{a}}_{1380}(1 - C_{\mathrm{i}})\right] l,$$

where D are the optical densities of the bands, K^{i} and K^{a} are the "isotactic" and "atactic" absorption coefficients of the corresponding bands, l is the layer thickness, and C_{i} is the degree of isotacticity of the polymer.

Hence

$$\frac{D_{976}}{D_{1460}} = \frac{K^{\mathrm{i}}_{976} C_{\mathrm{i}}}{K_{1460}} \tag{1}$$

and

$$\frac{D_{976}}{D_{1380}} = \frac{K^{\mathrm{i}}_{976} C_{\mathrm{i}}}{(K^{\mathrm{i}}_{1380} - K^{\mathrm{a}}_{1380}) C_{\mathrm{i}} + K^{\mathrm{a}}_{1380}},$$

i.e., the ratio D_{976}/D_{1380} depends nonlinearly on C_{i}.

The reciprocal quantity

$$\frac{D_{1380}}{D_{976}} = \frac{K^{\mathrm{i}}_{1380} - K^{\mathrm{a}}_{1380}}{K^{\mathrm{i}}_{976}} + \frac{K^{\mathrm{a}}_{1380}}{K^{\mathrm{i}}_{976}} \frac{1}{C_{\mathrm{i}}},$$

therefore, when equation (1) is satisfied, there must be a linear relationship between D_{1380}/D_{976} and D_{1460}/D_{976}

$$\frac{D_{1380}}{D_{976}} = \frac{K^{\mathrm{i}}_{1380} - K^{\mathrm{a}}_{1380}}{K^{\mathrm{i}}_{976}} + \frac{K^{\mathrm{a}}_{1380}}{K_{1460}} \frac{D_{1460}}{D_{976}}. \tag{2}$$

Finally, the ratio D_{1380}/D_{1460} may also be used as a measure of isotacticity, since the 1380 cm^{-1} band is sensitive to the tacticity of the polymer. For this band ratio we obtain the equation

$$\frac{D_{1380}}{D_{1460}} = \frac{K^{\mathrm{i}}_{1380} - K^{\mathrm{a}}_{1380}}{K_{1460}} C_{\mathrm{i}} + \frac{K^{\mathrm{a}}_{1380}}{K_{1460}}, \tag{3}$$

i.e., the ratio D_{1380}/D_{1460} depends linearly on C_{i} and, if equation (1) is valid, on D_{976}/D_{1460}.

To verify the fulfillment of dependences (2) and (3), the intensities of the bands 1460, 1380, and 976 cm^{-1} were measured in the IR spectra of 28 polypropylene samples obtained on the catalytic systems α-TiCl$_3$—AlEt$_3$; α-TiCl$_3$—AlEt$_2$Cl; α-TiCl$_3$—AlMe$_3$; α-TiCl$_3$—AlPr$_3$; α-TiCl$_3$—Al-u-Bu$_3$; TiCl$_4$—Al-u-Bu$_2$Cl; TiCl$_4$—AlEt$_2$Cl, and also on cationic systems of the type TiCl$_4$—AlEtCl$_2$ and AlEt$_2$Cl —dichloroethane.

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

Fig. 2. Fulfillment of the linear dependence between D_{1380}/D_{1460} and D_{976}/D_{1460} (see equation (3))

Fig. 3. Dependence of the ratios D_{976}/D_{1460} and D_{976}/D_{1380} on the degree of isotacticity of polypropylene

The spectra were recorded on H-800 and IKS-14 instruments. The table gives the spectral slit half-widths S for the H-800 and the approximately corresponding geometrical slit widths of the IKS-14 monochromator. The recalculation of slit widths was carried out according to the formula $S = \sqrt{(Dl)^2 + \Delta\nu_B^2}$; the quantities D and $\Delta\nu_B$ were taken from work (4).

ν, cm^{-1}	1500	1400	1300	1200	1100	1000	900
S for H-800, cm^{-1}	4.3	3.8	3.2	3.0	2.8	2.6	2.3
l for IKS-14, mm	0.072	0.084	0.092	0.108	0.130	0.162	0.208

Measurement of the intensities at the maxima of the bands on the IKS-14 was carried out point by point or at a recording speed of 2 cm^{-1}/min. The work was performed with films 5-10 μ thick. The background lines in the spectra were drawn through the minima 1510 and 1310 cm^{-1} for the 1460 and 1380 cm^{-1} bands, and 1025 cm^{-1} for the 976 cm^{-1} band.

The limiting value of the ratio D_{976}/D_{1460} for all the polypropylene samples studied is 0.30. We assume that this value corresponds to 100% isotacticity (see Fig. 3). Thus, the degree of isotacticity of polypropylene can be determined by the formula:

$$C_i \cdot 100 = (D_{976}/D_{1460})/0.30(\%)$$

In the coordinates D_{1380}/D_{976} and D_{1460}/D_{976} (see equation (2)), the data for all polymers fall on a straight line

$$D_{1380}/D_{976} = 2.45 + 0.716(D_{1460}/D_{976}) \tag{4}$$

(see Fig. 1). Further, in the coordinates D_{1380}/D_{1460}—D_{976}/D_{1460} (see equation (3)), the data obtained fall on a straight line

$$D_{1380}/D_{1460} = 0.727 + 2.36(D_{976}/D_{1460}) \qquad (5)$$

(see Fig. 2).

The experimental confirmation of the linear dependences between the parameters of equations (2) and (3) is proof that the assumption of a linear dependence between D_{976}/D_{1460} and C_i is correct.

On the basis of equation (4), the form of the curve in the coordinates D_{976}/D_{1380} —degree of isotacticity was determined (see Fig. 3). This curve can

can be used not only for determining the degree of isotacticity of polypropylene, but also for determining the degree of isotacticity of propylene units in the copolymer of ethylene and propylene. The limiting value of D_{976}/D_{1380} is 0.208 for 100% isotactic polypropylene. The error of determination for high values of the degree of isotacticity does not exceed 3-4%.

Equation (5) can be transformed into the coordinates D_{1380}/D_{1460}—degree of isotacticity. The resulting equation

$$C_{\mathrm{i}} \cdot 100 = 1.413\,(D_{1380}/D_{1460}) - 1.026(\%)$$

can also be used to determine the degree of isotacticity of polypropylene; however, in this case the measurement error increases to 8-10%. It should be noted that in isotactic polypropylene $D_{1380}/D_{1460} = 1.45$, while in atactic polypropylene it is $\approx$ 0.7-0.8.

It is of interest to estimate the degree of isotacticity for the polypropylene samples studied. Most fractions of the polymer insoluble in hot *n*-heptane have a degree of isotacticity of 0-100%. Fractions soluble in cold heptane have a degree of isotacticity of 65-80%. Liquid polymers obtained on the catalytic systems $TiCl_4$—Al-*n*-Bu_2Cl and $TiCl_4$—$AlEt_2Cl$ have a degree of isotacticity of 50-60%, whereas polymers obtained on cationic catalysts are completely atactic.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
12 VI 1963

REFERENCES CITED

1. V. N. Nikitin, N. V. Mikhailova, DAN, **148**, No. 3, 624 (1963).

2. T. M. Birnshtein, Yu. Ya. Gotlib, O. B. Ptitsyn, *J. Polym. Sci.*, **52**, 77, 1961.
3. V. L. Folt, J. J. Shipman, S. Krimm, *J. Polym. Sci.*, **61**, No. 171, S17, 1962.
4. K. Abe, K. Yanagisawa, *J. Polym. Sci.*, **36**, 536, 1959.
5. J. P. Lyongo, *J. Appl. Polym. Sci.*, **3**, No. 9, 302, 1960.
6. J. J. Brader, *J. Appl. Polym. Sci.*, **3**, No. 9, 370, 1960.
7. J. P. Sibilia, R. C. Winklhofer, *J. Appl. Pol. Sci.*, **6**, No. 26, S56, 1962.
8. A. N. Aleksandrov, V. N. Nikitin, *Uspekhi fiz. nauk*, **56**, No. 1, 3 (1955).

Note: Figure translations are in progress. See original paper for figures.