Infrared Spectra and Steric Structure

of Head-to-Tail Polypropylenes

Kurzmitteilung

by

Mario Peraldo, Giulio Natta, and Adolfo Zambelli

From the Istituto di Chimica Industriale del Politecnico, Milano, and the Istituto di Ricerca "G. Donegani", Soc. Montecatini, Milano, Italy

Kurzmitteilung

Infrared Spectra and Steric Structure of Head-to-Tail Polypropylenes

By Mario Peraldo, Giulio Natta, and Adolfo Zambelli

Different opinions are reported in the literature about the band observed at 970 cm^{-1} in all head-to-tail polypropylenes. For example, some authors suggest that the broadening shown by such a band in the more soluble fractions of the isotactic-type polypropylenes might depend on the length of the isotactic blocks[1]; other authors have concluded that this band, like that at ~1155 cm^{-1} is not characteristic of particular helix conformations or of any specific stereoregularity[2].

In syndiotactic polypropylene in solution, short chain segments of variable length alternate with zig-zag and helix conformations[3]. In its spectrum two bands are observed: at 975 and at 962 cm^{-1} which are very near to those presented by syndiotactic polypropylene in the two-fold helix and in the zig-zag phases (977 and 963 cm^{-1} respectively)[4,5]. This suggests to correlate the band at 975 cm^{-1} with the short helix chain segments and the band at 962 cm^{-1} with the zig-zag ones. These bands being very sharp, too, their positions do not seem to depend considerably on the length of the segments with one of the two conformations.

A third band, at 968 cm^{-1}, is observed in the spectrum of some predominantly syndiotactic polypropylenes, as for example in that of Fig. 1c. Owing to the almost complete absence of the band at 1253 cm^{-1} we shall speak of hereinafter, and of considerable variations in the spectrum around 972 cm^{-1}, *i.e.* owing to the almost complete absence of isotactic methyl groups, this band must be connected with the heterotactic methyl groups or with short chain segments they belong to[5]. In syndiotactic

polypropylene in solution, the CH(CH₃) groups are either between a *trans* and a *gauche* bond (syndio TG) or between two *trans* bonds (syndio TT); in the solutions of isotactic polypropylene, they are predominantly between a *trans* and a *gauche* bond (iso TG)[6]; and the two bonds adjacent to a heterotactic CH(CH₃) group are predominantly TT or TG (hetero TT or TG)[7]. Therefore we are led to correlate each peak of Fig. 1 with one
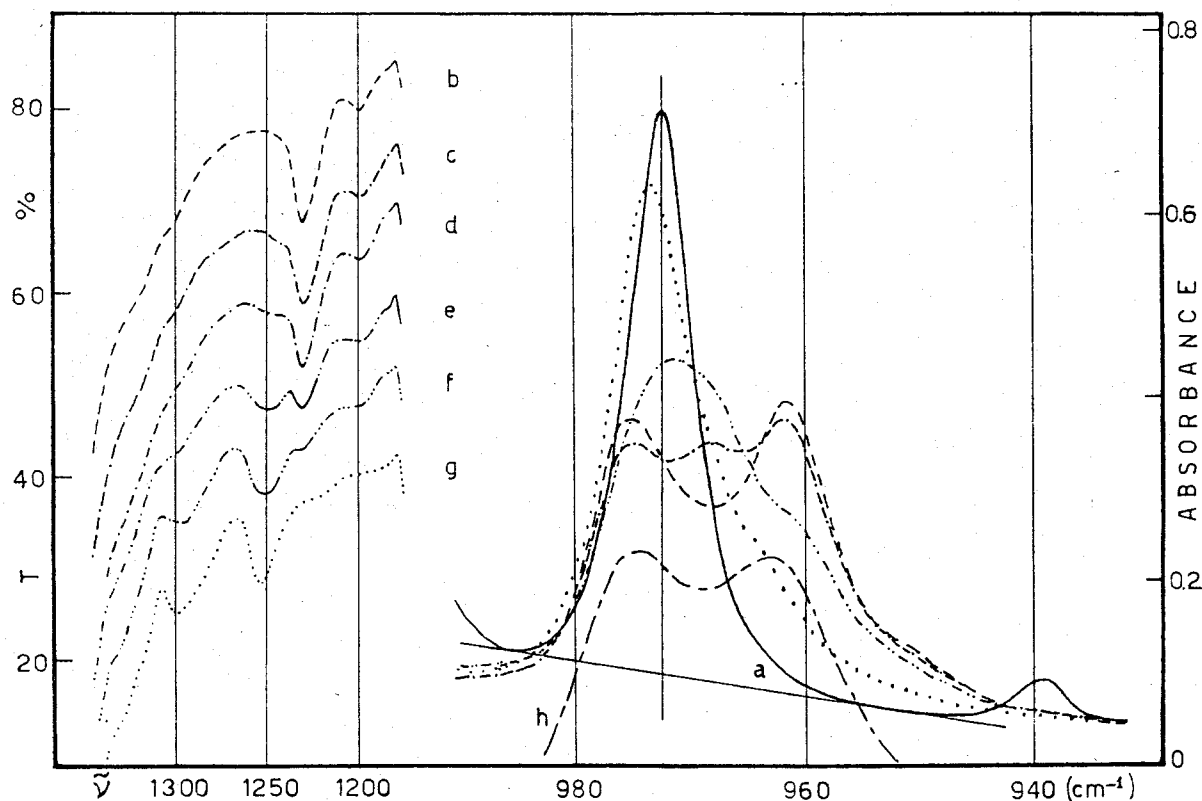

Fig. 1. IR spectra of samples of head-to-tail polypropylenes with different steric structures. The transmission scale refers to b), all the others are displaced
  a) Isotactic in the crystalline state
b) to g) In CS₂ solution, 40 mg./cm³ 1 mm [in particular: b) syndiotactic nearly pure; c) impure mostly for heterotactic, very little crystallizable; d) practically uncrystallizable, prevailingly syndiotactic; e) atactic with a fair distribution of steric elements; f) practically uncrystallizable, prevailingly isotactic; g) low-molecular-weight isotactic]
  h) Syndiotactic just melted

or at most two of these different combinations of configurations and conformations around each CH(CH₃) group, *i.e.* 975 syndio TG, 972—973 iso TG, 968 hetero, 962 syndio TT, and, the different conformations being in equilibrium, directly with the local, iso, hetero or syndiotactic configurations. In isotactic polypropylene in solution, in correspondence with

each inversion of hand of the helix, there is a methyl group between a *trans* and an eclipsed bond (iso TE)[6]; therefore at least a part of the absorption observed around 963 cm^{-1} in its spectrum might correspond to the TE isotactic methyl groups. When crystallized or in the smectic phase[8], these groups are present exclusively in the disordered part of the sample and the absorption mentioned above, together with other possible absorptions of the amorphous isotactic polypropylene in that range, is almost undetectable. The additional absorption observed around 962 and 968 cm^{-1} in the spectra of sterically impure isotactic polypropylene solid samples is therefore mainly connected respectively with the presence of syndiotactic and heterotactic methyl groups and not to the length of the isotactic blocks.

It cannot be quite excluded that all the bands considered above are related in a somewhat more complex way to the local configuration and conformation of the chain. The overall surface of these bands is fairly constant, in agreement with a single origin for all.

The R ratio between the right and left sides of the line at 972 cm^{-1} [1] (with respect to a straight base line between 895 and 950 cm^{-1}) is $\sim$0.95 for crystalline isotactic polypropylene, and $\sim$1.1 for isotactic polypropylene (necessarily with a very low molecular weight) in solution. In head-to-tail uncrystallizable (atactic) polypropylenes in solution, the R ratio is as low as $\sim$1.4, if the polymers are very rich in permanences; it is $\sim$2 for the polymers that are very rich in inversions, and can exceed 2.2 if most permanences are adjacent to inversions. Head-to-tail polypropylenes with permanences and inversions in different ratios and distributed in a completely different manner can show, and actually show, equal values of R. If a syndiotactic polypropylene in solution is pure, R is $\sim$1.9, while it increases with the content of heterotactic methyl groups, and for the sample of Fig. 1c R is $\sim$2.3. These data seem to suggest that the heterotactic methyl groups contribute to R to a far greater extent than the syndiotactic ones. In the heterotactic sequences, two heterotactic methyl groups are present per inversion, and less than one for each syndiotactic block. For this reason, R might approach a relationship with the concentration in permanences and inversions. Generally, however, no relationship is attained even to a first approximation, R being a function of more than one variable. Approximately linear relationships might be foreseen for the polymers in which the predominant steric impurities are either only syndiotactic or only heterotactic methyl groups.

Usually, one parameter is not enough to characterize the steric microstructure although, in some cases, it may be preferable to a mere crystallinity or helix content measurement. R and the ratio between the

absorbance at 961 (read on the base line considered above) and the total surface of the band or compensation with a pure isotactic sample, could perhaps be very effective in order to evaluate prevailingly isotactic polypropylenes. For a rapid evaluation of the steric purity of these polymers, the absorptions at 960 and 966 cm^{-1} and the depth and shape of the window at 1240 cm^{-1} are very useful. For an evaluation of a syndiotactic polypropylene, it can be observed that the ratio between the intensities of the bands at ∼975 and 962 cm^{-1} is markedly influenced by the presence of isotactic methyl groups and the depth of the window at 967 cm^{-1} is much influenced by the presence of heterotactic groups (and perhaps also by head-to-head impurity).

The band at ∼1154 cm^{-1} for samples in the amorphous state is almost independent of the configuration of the chain and, in agreement with the well-known correlation, it corresponds to the $CH(CH_3)$ groups linked to one or more CH_2 groups at each side[9]; therefore it is practically not characteristic of the alternate sequences of the (CH_2) and $CH(CH_3)$ groups[2,10]; in fact it is always present, even when the $CH(CH_3)$ groups are more distant than in head-to-tail polypropylene.

Two weak bands of similar intensity can be detected at 1253 and 1230 cm^{-1} in the spectra of isotactic and syndiotactic polypropylenes respectively, when examined in the amorphous state (Fig. 1). In prevailingly syndiotactic polymers, which show the band at 968 cm^{-1}, a third, partially resolved band can be observed (at ∼1245 cm^{-1}), clearly connected with the presence of adjacent permanences and inversions. All of them are present in the atactic and block polymers in variable intensity ratios, and the bands at 1253 and 1245 cm^{-1}, usually unresolved, form the band at ∼1250 of the atactic polymers. Probably, these three (or more) bands have a similar origin to that of the bands observed, almost in the same position, in the zig-zag syndiotactic polypropylene and in the helix isotactic one. These last bands have been attributed to the rocking of the CH and CH_3 groups and to the twisting of the CH_2 groups[11,12] or, in isotactic polypropylene, substantially to the twisting of the CH_2 groups[13]. At least to a first approximation, the bands at 1253, 1245, and 1230 cm^{-1} of head-to-tail polypropylenes in the amorphous state are to be correlated with very short isotactic, heterotactic, and syndiotactic elements respectively, each having a particular local conformation[7], e.g. zig-zag in the syndiotactic one, or even with isotactic, heterotactic, and syndiotactic triades.

At first sight, the weak band at ∼1295 cm^{-1} seems rather proportional to isotactic than to heterotactic triad amounts and the weak one at ∼1200

cm^{-1} to inversions. Isotactic and syndiotactic polypropylenes in solution and in the melted state show partially resolved, very low intensity bands at 460 cm^{-1} and at 485 cm^{-1} respectively. Other differences are observed between 1140 and 990 and between 600 and 500 cm^{-1}. The bands at 10.38 μ (963 cm^{-1}) and at 8.13 μ (1230 cm^{-1}) had been at first correlated generically to the frequency of occurrence of steric inversions in the chain[14]. A better approach has been attained by now. In order to improve the correlations observed, to obtain quantitative relationships and a good characterization of the polypropylenes, a comparison of IR and NMR spectra[15] as well as of the local conformations[7] is being made. The topic dealt with in this communication will be the subject of a next more detailed paper.

[1] J. L. KOENIG and A. VAN ROGGEN, J. appl. Polymer Sci. 9 (1965) 359.

[2] T. MIYAZAWA, Polymer Letters 2 (1964) 847.

[3] P. CORRADINI, P. GANIS, and P. OLIVERIO, Rend. Accad. Naz. Lincei 33 (1962) 420.

[4] G. NATTA, M. PERALDO, and G. ALLEGRA, Makromolekulare Chem. 75 (1964) 215.

[5] M. PERALDO and M. CAMBINI, Spectrochim. Acta [Oxford] 21 (1965) 1509.

[6] P. CORRADINI and G. ALLEGRA, Rend. Accad. Naz. Lincei 30 (1961) 516.

[7] Unpublished data.

[8] G. NATTA, M. PERALDO, and P. CORRADINI, Rend. Accad. Naz. Lincei 26 (1959) 14; R. L. MILLER, Polymer [London] 1 (1960) 135.

[9] A. L. McMURRY and V. THORNTON, Analytic. Chem. 24 (1952) 318; D. C. SMITH, Naval Research Laboratory Report C-3274-1948.

[10] V. L. FOLT, J. T. SHIPMAN, and S. KRIMM, J. Polymer Sci. 61 (1962) 517; J. M. LOMONTE, J. Polymer Sci. B 1 (1963) 645.

[11] R. G. SNYDER and J. H. SCHACHTSCHNEIDER, Spectrochim. Acta [Oxford] 20 (1964) 853.

[12] J. H. SCHACHTSCHNEIDER and R. G. SNYDER, Spectrochim. Acta [Oxford], in press.

[13] T. MIYAZAWA, Y. IDEGUCHI, and K. FUKUSHIMA, J. chem. Physics 38 (1963) 2709.

[14] G. NATTA, I. PASQUON, P. CORRADINI, M. PERALDO, M. PEGORARO, and A. ZAMBELLI, Rend. Accad. Naz. Lincei 28 (1960) 540.

[15] E. LOMBARDI, A. SEGRE, A. ZAMBELLI, A. MARINANGELI, and G. NATTA, Paper presented at the International Symposium on Macromolecular Chemistry, I.U.P.A.C., Prague 1965.