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# Temperature Dependence of the 720 $cm^{-1}$ IR Band of Poly(Octadecyl Ethylene) and Poly(Octadecyl Ethylene Oxide) Studies on Comb-Like Polymers III.*

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## Summary

The dependence of the 720 $cm^{-1}$ I.R. band upon the temperature has been investigated for isotactic and atactic samples of poly(octadecyl ethylene oxide) and poly(octadecyl ethylene). It is known in fact that a splitting of the band associated with the rocking vibration of methylene sequences can be correlated with orthorhombic packing of these latter.The results indicate that,besides isotactic poly(octadecyl ethylene),also the atactic polyolefin and the isotactic and atactic polyethers have orthorhombic packed chains provided that the temperature is sufficiently low. The orthorhombic to hexagonal transition takes place on a wide temperature range.

## Introduction

Besides X-ray diffraction, I.R.- spectroscopy can be usefully employed to investigate the type of packing of linear paraffinic chains in crystalline organic materials. In fact,as shown by CHAPMAN(1957),a doublet in the 720 $cm^{-1}$ region of the infrared spectrum of long chain compounds can be correlated with orthorhombic packing of the hydrocarbon chains,whilst a single band in this region can be correlated with hexagonal or triclinic packed chains. Since the extent of splitting depends on the nature and magnitude of the interactions between chains,it is possible that a long-chain molecule may be packed in an orthorhombic manner without causing the appearance of a doublet,e.g. when distortions occur in the cell.However,where two components are observed,it is plausible to predict that the hydrocarbon chains have orthorhombic packing.

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Usually, as shown by MÜLLER(1932), the orthorhombic subcell observed at low temperature in long-chain compounds, is transformed on heating to a hexagonal subcell. This transformation takes place discontinuously at a phase transition temperature, as it has been observed for linear paraffins (HOFFMAN and DECKER, 1953) or gradually over a relatively wide temperature range.

The 720 $cm^{-1}$ infrared band has been used also to determine the type of packing of the side-chains of comb-like polymers (PLATE and SHIBAEV, 1974). In the early works on these materials, it was assumed without sufficient ground that this packing was perfectly similar to that displayed by linear paraffins and polyethylene, i.e. orthorhombic. Subsequent studies carried out with a variety of techniques showed that the side-chain packing was in fact hexagonal for most comb-like polymers (PLATE and SHIBAEV, 1974). For example, poly(vinyl stearate) has been shown to display a hexagonal packing of the paraffinic side-groups even at -196 °C (SHIBAEV et al., 1968). Furthermore, it has been demonstrated (MOROSOFF et al., 1965) that even the solid state polymerization of a single crystal of vinyl stearate causes the transformation of the orthorhombic subcell of the monomer to the hexagonal subcell of the polymer. The same result has been obtained by solid state polymerization of ordered vinyl stearate multilayers (ENKELMANN and LANDO, 1977). The only known example of comb-like polymers with the side-chains packed in an orthorhombic lattice is that of isotactic polyolefins with the Type II structure (i.e., crystallized by slow cooling from the melt) (TURNER JONES, 1964). These latter polymers have been shown to lose the orthorhombic structure at temperatures close to the melting temperature (HOLLAND-MORITZ et al., 1976). The atactic-rich fraction of the polyolefins, obtainable by solvent extraction of the crude products of the stereospecific polymerization has been found to possess a hexagonal structure at room temperature, independent of the thermal history (MAGAGNINI et al., 1980). A hexagonal subcell has also been proposed for isotactic polyolefins with the Type I structure (FRASER et al., 1973) as well as for isotactic polyolefins quenched from the melt (MAGAGNINI et al., 1980).

In the present note we describe the results of a study of the temperature dependence of the 720 $cm^{-1}$ infrared band for different samples of poly(octadecyl ethylene oxide) (ANDRUZZI et al., 1980) and of poly(octadecyl ethylene) (MAGAGNINI et al.,1980).

## Experimental

The synthesis of the samples has already been described (MAGAGNINI et al.,1980;ANDRUZZI et al.,1980). The atactic-rich samples of both poly(octadecyl ethylene) and poly(octadecyl ethylene oxide) were obtained by solvent extraction of the polymers prepared by stereospecific polymerization.A sample of atactic poly(octadecyl ethylene oxide) was also prepared by cationic polymerization and was found to have structure and properties very similar to those of that obtained by extraction (ANDRUZZI et al.,1980).

The I.R. spectra were performed on a Perkin-Ellmer 180 spectrophotometer using a conventional cell for high and low temperatures. The abscissa scale was ten times expanded.All the specimens were examined as films obtained by slightly pressing a weighed amount of powdered polymer brought to a temperature very close to that of melting.

## Results

The dependence of the 720 cm$^{-1}$ infrared band on the temperature for the atactic- and isotactic-rich fractions of poly(octadecyl ethylene) is illustrated by Fig.1 (inserts A and B). At room temperature (25 °C) the band is single and almost symmetric for the atactic-rich polyolefin whereas,as already found for homologous polyolefins(FRASER et al.,1973), it is splitted for the isotactic-rich one. This agrees with the X-ray data(MAGAGNINI et al.,198o) and confirms that at room temperature the side-chains are packed in an orthorhombic subcell for the isotactic-rich fraction of the polyolefin (cooled slowly from the melt) and in an hexagonal one for the atactic-rich fraction.

On lowering the temperature the extent of the splitting becomes more evident for isotactic poly(octadecyl ethylene).For the atactic-rich sample, the 720 cm$^{-1}$ band becomes progressively more asymmetric,and,at -180 °C,a pronounced shoulder is present at about 730 cm$^{-1}$. Although the splitting of the band is not very marked, the evidence accumulated for low molecular weight long-chain molecules indicates that the side-chains of atactic poly(octadecyl eyhylene) undergo a transition from hexagonal to rhombic packing when the temperature is lowered. This transition seems to take place progressively on a wide temperature range.

Fig.1 (inserts C and D) shows the temperature dependence of the 720 cm$^{-1}$ band for atactic and isotactic poly(octadecyl ethylene oxide). Both polymers display a single almost symmetric band at room temperature. However, in decreasing the temperature, a tendency towards the splitting of the band is noticed and, at -180 °C, the shape of the absorption band is similar to that of the isotactic polyolefin at room temperature. It may be concluded therefore that for both atactic and isotactic poly (octadecyl ethylene oxide) the hexagonal subcell prevailing at room temperature is steadily transformed to an orthorhombic one as the temperature is lowered.

The percent transmittance measured at the spectral position corresponding to the maximum absorption near 730 cm$^{-1}$ observed at - 180 °C for each of the samples investigated is reported in Fig. 2 as a function of the temperature. The transmittance increases gradually with temperature for all polymers studied following S-shaped curves. The data for cationic poly(octadecyl ethylene oxide) fit the same curve obtained for the atactic sample of the polymer recovered by extraction. The same Fig. 2 shows similar plots obtained for a commercial film of polyethylene and for pure octacosane. For polyethylene the transmittance at 731 cm$^{-1}$ is found to increase much more steeply. For pure octacosane a discontinuous transmittance variation is observed at ca. 56 °C. This temperature corresponds closely to that determined with different techniques (HOFFMAN and DECKER, 1953) for the $\alpha$-$\beta$ transition of this material.

The data of Fig. 2 lead to the conclusion that the hexagonal-orthorhombic transition takes place in poly (octadecyl ethylene) and poly(octadecyl ethylene oxide) samples over a very wide temperature range. Thus, whereas the transition occuring in linear paraffins with a number of carbon atoms above ca. 22 is readily determined by calorimetric techniques, any eventual heat effect associated with the transformation taking place in poly (octadecyl ethylene) and poly(octadecyl ethylene oxide) cannot be appreciated through differential calorimetry. In fact DSC failed to show endotermic phenomena which could be associated with the orthorhombic to hexagonal transition of these materials: the heat effects found at considerably higher temperatures are as already discussed due to the melting of the crystalline phases originated by the atactic and the stereoregular materials

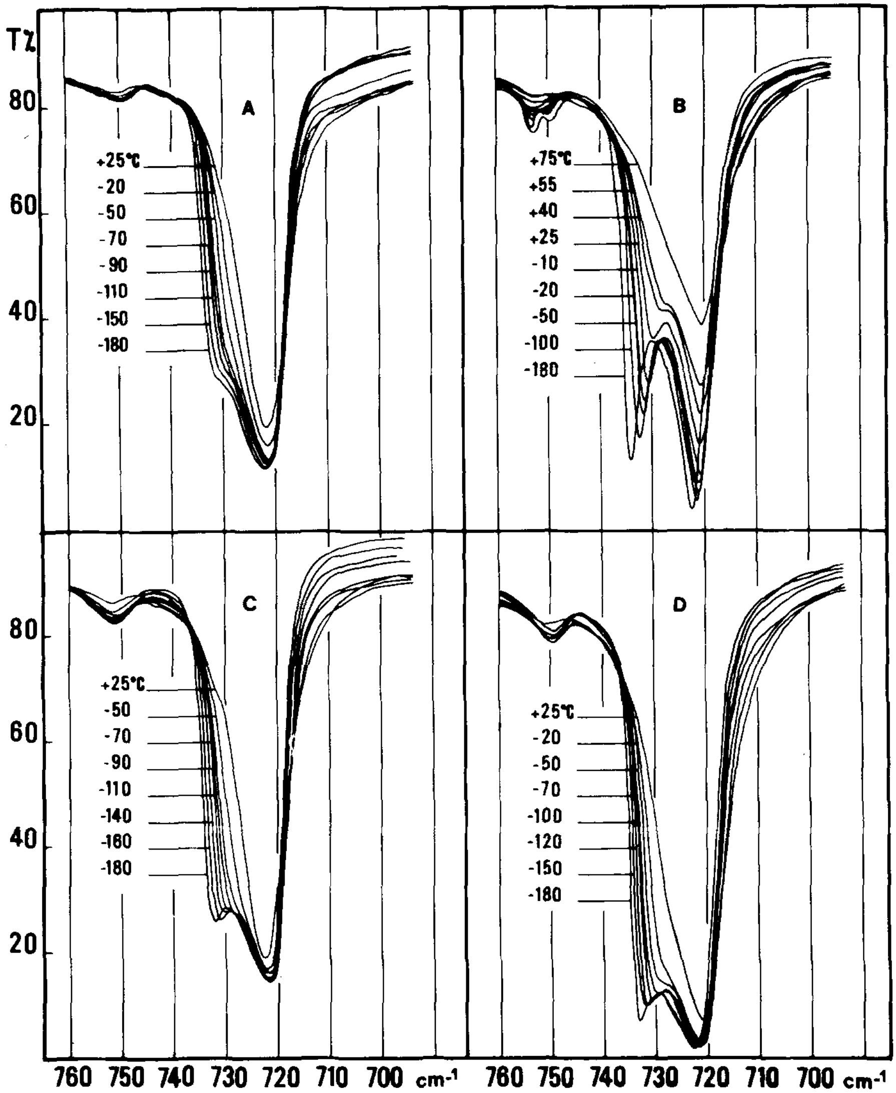

Fig.1- The 720 $cm^{-1}$ band at different temperatures for:
A- atactic poly(octadecyl ethylene)
B- isotactic poly(octadecyl ethylene)
C- atactic poly(octadecyl ethylene oxide)
D- isotactic poly(octadecyl ethylene oxide)

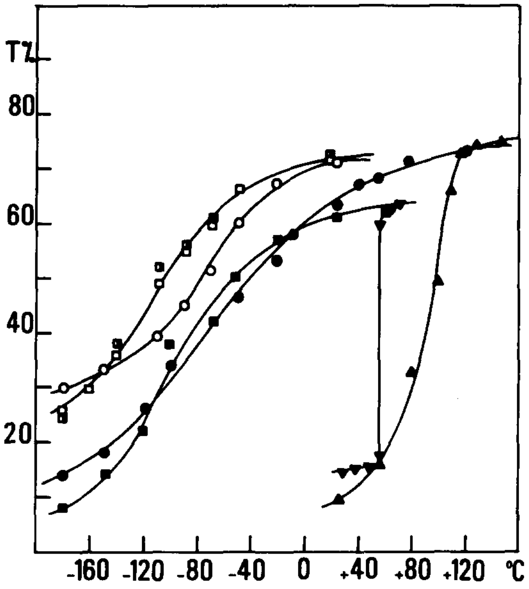

Fig.2-Temperature dependence of the percent transmittance measured at the indicated frequencies for:
o - atactic poly(octadecyl ethylene)(731 $cm^{-1}$),
● - isotactic poly(octadecyl ethylene)(734 $cm^{-1}$)
□ - atactic poly(octadecyl ethylene oxide)(732 $cm^{-1}$)
▣ - cationic poly(octadecyl ethylene oxide(732 $cm^{-1}$),
■ - isotactic poly(octadecyl ethylene oxide)(733 $cm^{-1}$)
▲ - commercial polyethylene(731 $cm^{-1}$)
▼ - octacosane(730 $cm^{-1}$)

(MAGAGNINI et al.,1980; ANDRUZZI et al.,1980).

It is evident from Fig.1 that for all the samples studied the two components of the 720 $cm^{-1}$ band are far from having equal or nearly equal intensity as it happens for high density polyethylene and linear paraffins. This may be explained on the basis of the structure of comb-like polymers. The diffractometric data of TURNER JONES(1964),in fact,indicate that even for isotactic polyolefins the first portion of the side-chains leaving the backbone cannot be packed in an orthorhombic subcell. The work of JORDAN et al. (1971) on the other hand has proved that for other comb-like polymers the first sequence of 8-10 methylene groups of the paraffinic side-chains has a disordered conformation and, therefore, cannot contribute to the splitting of the 720 $cm^{-1}$ band.

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