Raman Study of Chain Deformation in Polypropylene

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Summary

Raman spectroscopy was used to study the transfer of energy that occurs among the internal vibrations of crystalline isotactic polypropylene as it is compressed. The C-C-C group was found to play a significant role in the sub- CH_3 sequent chain deformation.

Introduction

In a solid crystal a polymer can exist in straight chains with dimensions in the order of tens of nanometers. By using Raman spectroscopy we have studied conformational changes in the helical chains of crystalline isotactic polypropylene and concluded that kinks can be caused in the chains through the application of non-hydrostatic high pressures.[1] The unit cell of crystalline isotactic polypropylene (IPP) is monoclinic and each cell contains four chains. The chain has three monomers in an identity period and the symmetry of the line group is C_3. The vibrational spectra is well known.[2-4]

In this work we use Raman spectroscopy to study the onset of deformation in the chain as the sample is compressed.

Experimental

The experimental technique has been described elsewhere.[1] Cylindrical rods of crystalline isotactic polypropylene, measuring 3.0 mm length and 3.18 mm diameter, were inserted into a high pressure cell with sodium chloride windows. The Raman spectra were taken at room temperature with the signal analyzed by a Spex 1401 monochromator and excitation provided by the 5145 Å Ar^+ laser line.

Results and Discussion

Figure 1 is a partial Raman spectrum of crystalline isotactic polypropylene at different pressures. The normal vibration which gives rise to the band at 1104 cm^{-1} is a mixture of different internal coordinates consisting of the C-CH$_3$ stretch, CH$_3$ rock and CH bend.[3,4] The band at 1153 cm^{-1} is made up of

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FIGURE 1
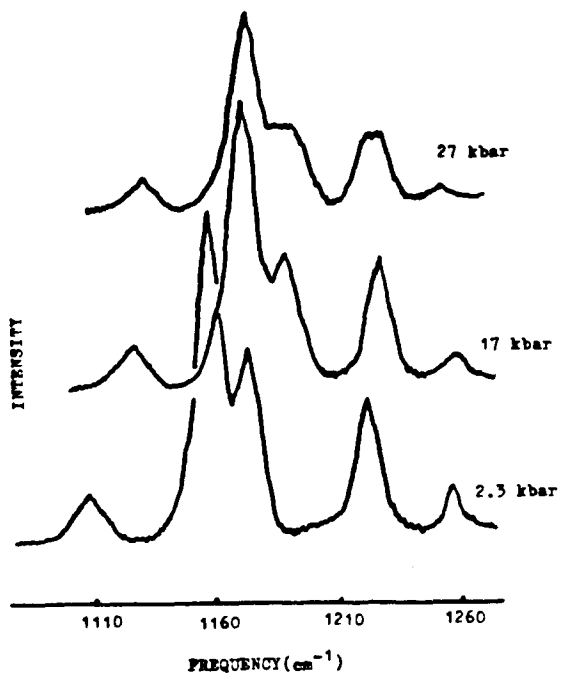
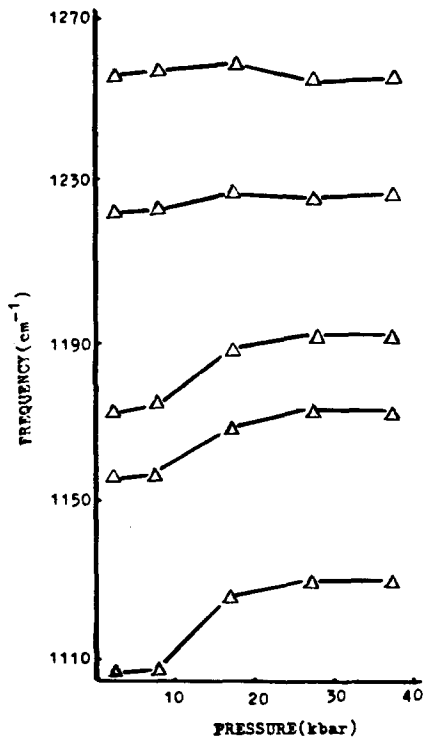Partial Raman spectrum of isotactic polypropylene at 295 K and at different pressures

INTENSITY

27 kbar

17 kbar

2.3 kbar

1110   1160   1210   1260

FREQUENCY(cm^{-1})

FREQUENCY(cm^{-1})

1270

1230

1190

1150

1110

10   20   30   40

PRESSURE(kbar)

FIGURE 2

Frequency shift as a function of pressure.

C-C stretch, C-CH$_3$ stretch, CH$_3$ rock and CH bend.[3,4] The mode at 1170 cm^{-1} is a hybrid of the C-C stretching, CH$_3$ rocking and CH bending vibrations.(3,4) The trio of bands at 1104, 1153 and 1170 cm^{-1} have the C-CH$_3$ vibrations coupled to the C-C stretch and therefore can be considered to be derived from the vibrations of the C-C-C group.
CH$_3$

The vibration at 1220 cm^{-1} is a mixture of the CH$_2$ twist, CH bend and C-C stretch while the normal mode at 1256 cm^{-1} consists of the CH bend, CH$_2$ twist and CH$_3$ rock.[3,4] The two bands at 1220 and 1256 cm^{-1} are thus seen to couple the motions of the CH$_2$ and CH groups and hence to be more indicative of the C-C-C vibrations than of the C-C-C vibrations.
CH_3

Figure 1 shows the Raman spectra of these bands at different pressures, and Figure 2 plots the progression of the frequencies with increasing pressure. It is at once seen that the normal vibrations (1104, 1153 and 1170 cm^{-1}) associated with the C-C-C group show a relatively greater jump (20 cm^{-1}) in frequency,
CH$_3$
under compression, than those modes associated with the C-C-C vibration. This difference in frequency shifts can be interpreted in terms of redistributions of energy among the internal coordinates. As the chains are brought together, the magnitude, number and direction of the force lines of interaction between non-bonded atoms on neighbouring chain units change.[5] Consider the C-C-C group,
CH_3
for instance, and limit the interactions to those of the nearest neighbor. Then the group will have a specific number of non-bonded repulsion force lines connected to it through the nearest neighbor non-bonded interactions. As the sample is compressed, the number, magnitude and direction of these lines will change to give a different equilibrium state. The net result is that when the group undergoes the motions corresponding to the normal vibrations, the constraint on, and therefore the frequency of some internal coordinate will increase while another may decrease. Specifically then, for the C-C-C group
CH_3
that is in a deformed state in which there is a net increase in the constraint along the C-CH$_3$ axis, the frequency of the C-CH$_3$ stretch will be higher than in a state with less constraint. Also, the frequency difference between the C-CH$_3$ stretching frequencies in the two states above will be higher than the difference between the C-C stretching frequencies in them. This accounts for the differences in the frequency versus pressure plots for the C-C-C and the C-C-C groups in Figure 2. It has been shown that compression can cause kinking
CH$_3$
in the chains of solid crystalline isotactic polypropylene.[1] The Raman spectra obtained in this experiment demonstrates how this may occur. As the chains are brought together under compression, non-bonded atom-atom repulsion on the methyl groups cause a net increased constraint that is greater along the C-CH$_3$ axis than in the directions perpendicular to it. This perturbation is transmitted through C-C bonds so as to cause a change in the C-C-C internal equilibrium angles. Such a change will contain at least one trans-gauche transformation. The net result is that the chain slips or becomes kinked. The increase in chain kinks is equivalent to the formation of more rotational isomers of the chain unit and the spectral lines will become broader.

490

Acknowledgement

References

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