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Analysis of the longitudinal acoustic mode (LAM) of poly(3,3-dipropyl oxetane)

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SUMMARY

The analysis of the Raman low frequencies region of the Poly(3,3-Dipropyl oxetane) allows to separate the torsional motions from the Longitudinal Acoustic Mode (LAM). Shift frequencies of this last band are observed with different annealing temperatures, which result in an increase of the crystallinity.

INTRODUCTION

The polymers derived from oxetane and its 3,3-dialkyl derivatives with the general structure $\text{+} O - CH_2 - CR_1R_2 - CH_2 \text{+}_n$ are semicrystalline polymers when the pendant side groups (R_1 and R_2) are identical. The main interest in the analysis of this series corresponds to the study of the effect of side groups on the thermal properties, crystallization mechanism, crystalline modifications and morphology, and recent studies have been concerned with these aspects (1-4).

The first term, polyoxacyclobutane or polyoxetane, presents four crystal modifications (5), Poly(3,3- Dimethyl oxetane) (PDMO) presents three modifications (6) and Poly(3,3- Diethyl oxetane) (PDEO) presents two crystalline modifications depending on crystallization conditions (7).

Vibrational analysis has been recently used for the study of polymorphism in this series and it was shown that Raman scattering is a powerful technique to characterize the conformation of chain molecules and, therefore, the behaviour of the polymorphic phases. Thus, the influence of the crystallization conditions in the two stable configurations of PDMO and PDEO was analyzed (8-10). Previous work on Poly(3,3-Dipropyl oxetane) (PDPO) demostrated the existence of only one stable configuration (11).

Moreover, it was demostrated that low frequency Raman spectroscopy can be very useful in the analysis of crystals (12-14). The Raman band associated with the Longitudinal Acoustic Mode (LAM) was used to measure the ordered segments of the lamellae in crystalline polymers.

The spectroscopic values compare quite well with those obtained by other techniques as SAXD and Electron Microscopy. However, a limitation for the use of Raman LAM in the study of lamellar structures is related, first

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*To whom offprint requests should be sent with the proximity to the Rayleigh line and fluorescence effects; and second with the proper value of the Young´s modulus in the chain direction of the polymer.

Previous work on the first terms of the polyalkyl oxetane series showed that the Raman band in the low frequency region is not observed. Contrary to this result, the PDPO shows such a band which corresponds to the LAM, allowing its analysis in function of the thermal treatments of this polymer (11).

Therefore, the aim of this work is to analyze the Raman low frequencies region of PDPO that will allow to separate the torsional motions from the LAM and to correlate the frequency shift and shape of this band as the crystallinity is increases due to the annealing procedures.

EXPERIMENTAL

Sample preparation

The polymerization of the monomer 3,3-Dipropyl oxetane was carried out by using triethyl oxonium hexafluorantimoniate as catalyst by the method previously described (11,15). The obtained polymer was fractionated and the molecular weight of the fraction selected for this work is Mn=45.000.

The samples were crystallized by undercooling from 15ºC above the melting temperature to room temperature. After this process they were annealed during 24 hours at different temperatures (11).

Apparatus and procedures

Raman spectra were measured with a Jobin-Yvon Ramanor HG 2S double monochromator and a DILOR XY spectrometer with multichannel detection (512 intensified diodes). The 514.5 nm line of an Argon ion laser was used as the excitation source with a power at the sample of 250 mw. Spectral slit widths were ca. 0.5 cm^{-1} at 19.430 cm^{-1} for all measurements.

All the data obtained from the Ramanor were collected and processed with a Commodore microcomputer system (11).

RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra at low frequencies in the region 10-50 cm^{-1} for the samples of PDPO annealed at different temperatures. As we can observe two maxima appear in this region; one of them at a constant frequency for all the samples, whereas the other band shows a shift to the lower frequency with the annealing temperature. The frequencies corresponding to the samples of PDPO are shown in Table 1. The values were obtained through a deconvolution program which allows to get the two isolated bands.

A normal coordinate treatment was realized for the first element of the polyoxetanes series, the Poly(3,3-Dimethyl oxetane) (16) and the vibrational frequencies in this region were mainly assigned to the torsional motion of CC and CO. Therefore, we can assigne the band situated at 37 cm^{-1} to this movement for the PDPO.

The moving band is very sensitive to the annealing temperature and, this behaviour is similar to those obtained in Polyethylene (17), Polyoxymethylene (18) or Polyesters (19) when the lamellar thickness is

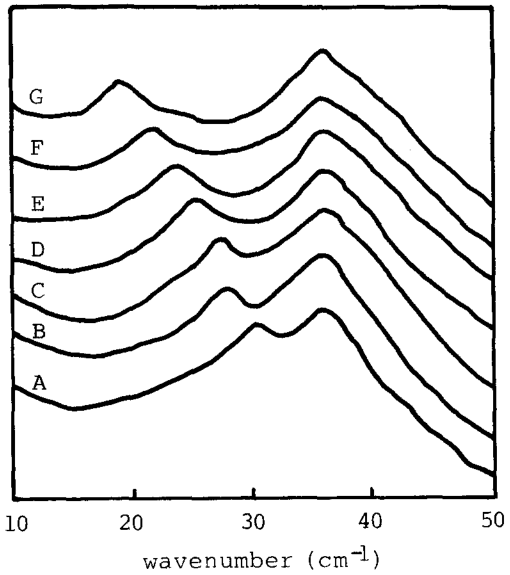

Figure 1. Low frequency spectra for samples of Poly(3,3-Dipropyl oxetane) with different annealing temperatures. (A):25°C, (B):54°C, (C):66°C, (D): 77°C, (E):89°C, (F):103°C, (G):115°C

Table 1

Frequencies of the LAM for Poly(3,3-Dipropyl oxetane)

Sample	$T_{annealing}$ (°C)	$\Delta\nu$ (cm^{-1})
A	25	31
B	54	30
C	66	28.5
D	77	25.5
E	89	24.5
F	103	22
G	115	19.5

increased. These bands correspond to the Longitudinal Acoustic Mode also obtained previously in other Polyethers (20-22). This frequency ($\Delta\nu$) is related to the lamellar thickness (L) by the well-known equation (23):

$$\Delta\nu = \frac{m}{2cL}\left(\frac{E_c}{\rho}\right)^{\frac{1}{2}}$$

with m the order mode, c the speed of light, E_c Young's modulus in the chain direction and ρ the density of the vibrating frequency.

The analysis of the LAM frequencies can be utilized to determine the length of ordered segments of the polymer chains that contains the lamellae

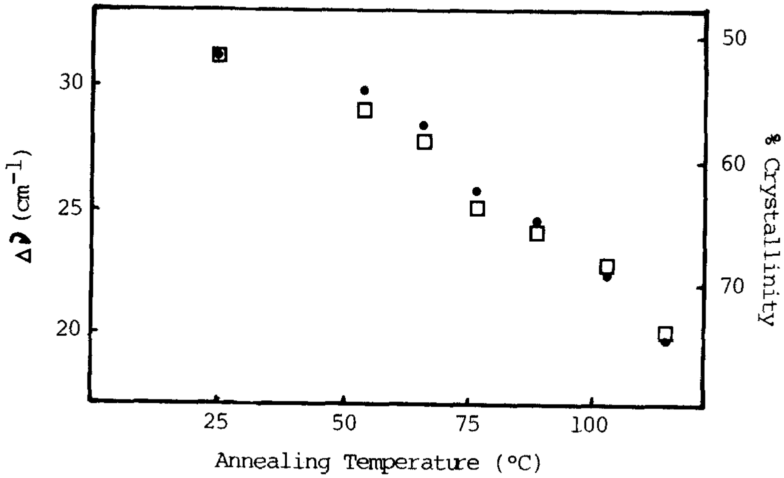

Figure 2. Crystallinity and LAM frequencies vs. the annealing temperatures for Poly(3,3-Dipropyl oxetane)

in semicrystalline polymers. Thus,in the PDPO the variation of the LAM is due to an increase in lammellar thickness. In fact, if we represent the crystallinity values obtained previously for these samples (11), we can observe in Figure 2 a good fitting between the relative variation of the crystallinity and the LAM frequencies and therefore, the lamellar thickness.

From this study it can be concluded that the lower frequency band obtained on the Raman spectrum for the Poly(3,3-Dipropyl oxetane) is assigned to the Longitudinal Acoustic Mode. Furthermore, the variation of the frequency of this LAM with the annealing process allows to say that the increase of the lamellar thickness is produced by an increase of the ordered part from the amorphous phase.

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