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Characterization of the conformers in poly(3,3-diethyl oxetane) by vibrational spectroscopy

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SUMMARY

The monoclinic and orthorhombic conformers of Poly(3,3-Diethyl oxetane) can be obtained depending on crystallization temperature. However, if the crystallization of a given modification is unaccomplished, the other modification can be crystallized from the amorphous phase. The molecular vibrations in the region 700-800 cm^{-1}, which are associated with the "breathing" mode, are highly dependent on the conformation of the polymer chain. This band is used to study the influence of the temperatures and times of crystallization on the structural modifications of this polymer.

INTRODUCTION

Polyoxetanes belong to a type of polyethers with the general form $(-O-CH_2-CR_1R_2-CH_2-)_n$. The properties of this kind of polymers are related to the substitution of R_1 and R_2 by alkyl groups. The branched polyethers with symmetrical side groups are semicrystalline and have a variety of conformational forms, closely related to its physical properties.

The crystalline modifications of these branched polyethers depend on the undercooling. Thus, three crystalline modifications of Poly(3,3-Dimethyl oxetane)($R_1,R_2=CH_3$), and two of Poly(3,3-Diethyl oxetane)($R_1,R_2=C_2H_5$) are described (1,2). Poly(3,3-Diethyl oxetane) itself is obtained in a monoclinic (I) conformation when crystallization temperature is higher than 45°C, and orthorhombic (II) form appears with a crystallization temperature below 20°C. X-Ray analysis (3) show a planar zig-zag conformation in modification I and $(T_2G_2)_2$ conformation for the modification II.

In previous work (4-6) we have presented for the Poly(3,3-Dimethyl oxetane) (PDMO) the strong dependence on the conformations with external physical variables (temperature, stretch, pressure). Following this research we extend these studies to the Poly(3,3-Diethyl oxetane) (PDEO).

For analyzing the chain conformation of these polymers, detailed studies on the model compounds $(-O-CH_2-CR_1R_2-CH_2-)_n$ by vibrational spectroscopic method are important, since the conformations of polymorphic PDMO have been previously investigated (4-7). On this study a normal coordinate analysis is thoroughly realized for the two stable modifications (7). Vibrational spectroscopy is used on this paper to study the influence of the crystallization temperature and time on the polymorphous behaviour of the Poly(3,3-Diethyl oxetane).

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EXPERIMENTAL

Preparation of samples

The samples are selected with a molecular weight Mn = 800.000. All the samples were melted by raising the temperature above the melting temperature (T = 346 K), after letting them to crystallize at different temperatures. The presence of the two polymorphic forms on the samples was obtained by hindering the crystallization process of a conformer, following with the crystallization of the other conformer. The samples studied were obtained with these processes:

a) Crystallization at 50°C during 24 hours.
b) Crystallization at 50°C during 120 min., forthgoing at 9°C during 24 hours.
c) Crystallization at 50°C during 90 min., forthgoing at 9°C during 24 hours.
d) Crystallization at 50°C during 40 min., forthgoing at 9°C during 24 hours.
e) Crystallization at 9°C during 24 hours, previously quenched at 0°C.

On samples a and e only a conformer is present and the two conformers are on samples b, c and d.

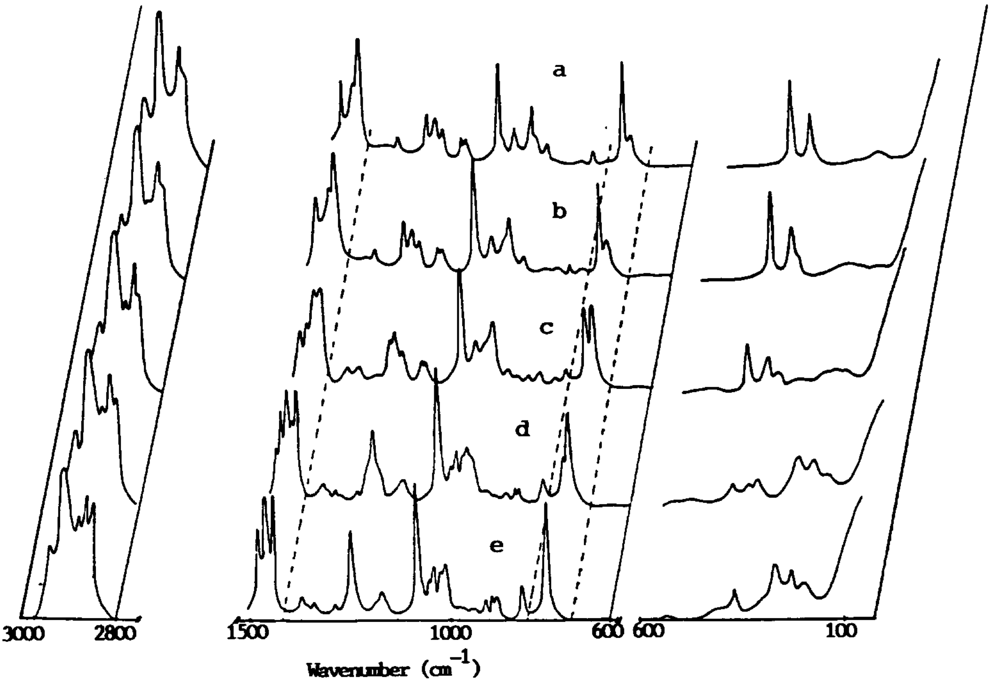

Figure 1. Raman spectra of semicrystalline Poly(3,3-Diethyl oxetane). a: monoclinic conformation; b,c and d: monoclinic and orthorhombic conformation; e: orthorhombic conformation.

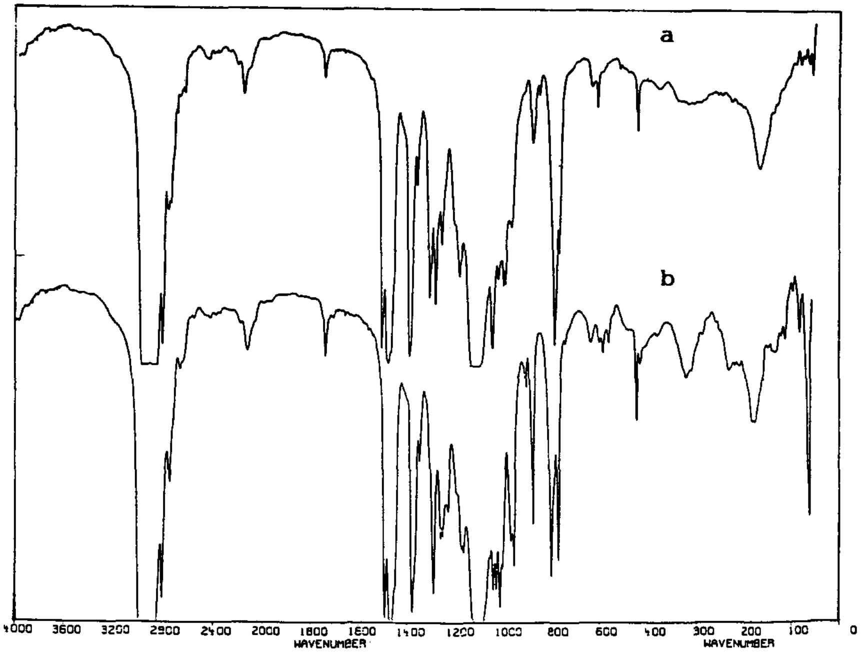

Figure 2. Infrared spectra of semicrystalline Poly(3,3-Diethyl oxetane). a: Monoclinic conformation; b: orthorhombic conformation.

Apparatus

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 source of illumination. The laser power was approximately 150 mw at the sample. Spectral slit widths were ca. 1.5 cm^{-1} at 19.430 cm^{-1} for all measurements.

Infrared spectra were recorded using a Mattson FTIR CYGNUS 100 with a resolution of 1 cm^{-1} and 50 scans.

RESULTS AND DISCUSSION

According to the kinetics crystallization studies (2) the samples a and e are completely crystallized on monoclinic and orthorhombic conformation respectively. However, an unfinished crystallization process of the monoclinic modification is produced on samples b, c and d. These samples are later completely crystallized on the orthorhombic conformation obtaining a different amount of both conformers depending on time of crystallization at high temperature.

The Raman spectra of the five samples studied are presented in Figure 1. Figures 1 a and e correspond to the spectra of semicrystalline PDEO with the presence of only one conformer, while the other spectra show the contribution of both conformers. In Figure 2 the infrared spectra of the PDEO crystallized with the presence of each conformer (samples a and e) can be observed.

Similarly to the vibrational analysis of the PDMO (7), the most important differences are situated in three regions of the Raman spectra (700-800 cm^{-1}, 1400-1500 cm^{-1} and 2800-3000 cm^{-1}). In the Infrared spectra are also obtained differences in the 750-1350 cm^{-1} region for the two conformers. The results of this normal coordinate treatments indicate that the "breathing" mode situated at frequencies about 800 cm^{-1} is sensitive to the skeletal conformation of the molecule.

For the comparison of the Raman spectra of $(T_2G_2)_2$ conformers of PDMO and PDEO a similar evolution of the band situated between 700-830 cm^{-1} can be noticed. The presence of heavier side groups leads to a lower frequency. The other two regions correspond to the bending (1400-1500 cm^{-1}) and stretching (2800-3000 cm^{-1}) CH_2 and CH_3 modes, and similarly to the PDMO are also sensitive to the molecular conformation, but is complicate to characterize each conformer.

With reference to the results of the normal coordinate calculations (7) in conjunction with the above spectral observations, it is clearly shown that the "breathing" band is a good key band for analyzing the Raman spectra and is of use in identifying the conformers existing on the sample. However, the superposition of the bands on the vibrational spectra makes painful the assignment of an accurate value to the amount of each conformer on the sample and, therefore, the crystallinity values cannot be simply evaluated.

In summary, the results show that, depending on crystallization temperature, the two stable molecular conformations of Poly(3,3-Diethyl oxetane) can be separately obtained and, samples with both conformers can be also crystallized. The vibrational results allow to conclude that the vibrational spectroscopy is a very sensitive technique to detect the evolution of the structural conformations of this kind of branched polyethers.

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