

Effect of quenching on the polymorphic crystallization of poly(oxetane)

E. Pérez, A. Bello, and J.G. Fatou*

Instituto de Plásticos y Caucho, Juan de la Cierva 3, E-28006 Madrid, Spain

Summary

The crystallization from the glassy state of poly(oxetane) or poly(trimethylene oxide), after quenching the molten polymer in liquid nitrogen, has been studied by differential scanning calorimetry and X-ray diffraction analysis. The results indicate that two crystalline modifications are obtained, depending on the crystallization temperature: the orthorhombic modification is produced when the temperature is higher than $-30\text{ }^{\circ}\text{C}$, while the trigonal form is found below $-45\text{ }^{\circ}\text{C}$, both forms coexisting at intermediate temperatures.

Introduction

It is well known that symmetrical polyoxetanes, with general formula $(-\text{CH}_2-\text{CR}_2-\text{CH}_2-\text{O}-)_n$ can exhibit polymorphism. While the C-O bonds, due to sterical impediments, are always in trans configuration, the other two C-C bonds in the main chain can be found under any possibility in such a way that three crystal structures with conformations $(\text{T}_2\text{G}_2)_2$, $\text{T}_3\text{GT}_3\bar{\text{G}}$ or all-trans, were identified for unsubstituted poly(oxetane), PTO (1,2), or poly(3,3-dimethyl oxetane), PDMO (3), although some of the crystalline forms were obtained under stretching (another all-trans structure can be obtained for PTO in the presence of water (1,4)).

However, not all of these modifications can be produced by crystallization from the melt (5), due to the influence of thermodynamic and kinetic factors. This influence has been studied on PDMO (6) and, although the monoclinic form, with $\text{T}_3\text{GT}_3\bar{\text{G}}$ conformation, is thermodynamically the most stable at any temperature, the orthorhombic, $(\text{T}_2\text{G}_2)_2$ modification can also be obtained at the lower temperatures and, once formed, it is stable at any temperature below its melting point.

* To whom offprint requests should be sent

In a previous work (5), only the orthorhombic modification of PTO was found in the crystallization from the melt of this polymer, and the influence of temperature and molecular weight on its crystallization was studied (7,8).

In this work, we analyze the crystallization of PTO, showing that the trigonal $T_3GT_3\bar{G}$ crystal modification is favored by crystallization from the glassy state, after quenching the molten polymer below its glass transition temperature, and can be obtained in a certain interval of crystallization temperatures.

Experimental

The monomer was prepared from 1,3-propanediol and polymerized in methylcyclohexane, at 0 °C, using triethyloxonium tetrafluorborate as catalyst. The polymer was fractionated with acetone-water as the solvent-non solvent system, at 30 °C, and a fraction with number-average molecular weight of 79000, determined in toluene at 25 °C in a Mechrolab 502 membrane osmometer, was selected for this work.

The crystallization was studied by calorimetry in a Mettler TA 3000 calorimeter with a DSC-30 head. The samples were previously melted for 15 minutes at 80 °C and then, rapidly quenched to -150 °C. After that, a specified isothermal temperature was set, in the range from -55 to -20 °C, and the crystallization endotherm was followed. After completion, the melting was registered at a heating rate of 8 °C/min.

The X-ray diagrams were obtained at room temperature with a Geiger counter X-ray diffractometer made by Philips Co, using nickel-filtered K_α radiation.

Results and Discussion

Previous results for PTO crystallized from the melt at relatively low undercoolings show only a melting peak corresponding to the orthorhombic modification of this polymer (5). However, if the crystallization is carried out from the glassy state, after quenching the sample below the glass transition temperature, -70 °C (8), two peaks are found, as it can be seen in Fig. 1. So, one melting peak at 14 °C appears at crystallization temperatures, T_c , below -45 °C and other, at 20 °C, when T_c is higher than -30 °C. Both peaks are found at the intermediate T_c of -36 °C. This behavior is parallel to the crystallization of PDMO from

Fig. 1. DSC curves of PTO after quenching in liquid nitrogen and crystallized at: a) -20°C ; b) -30°C ; c) -36°C ; d) -45°C ; e) -55°C .

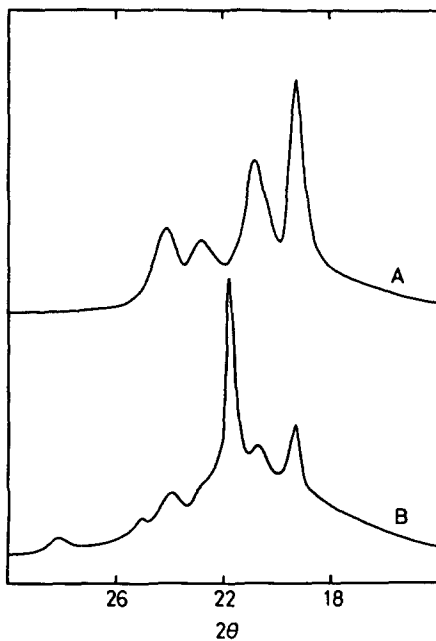
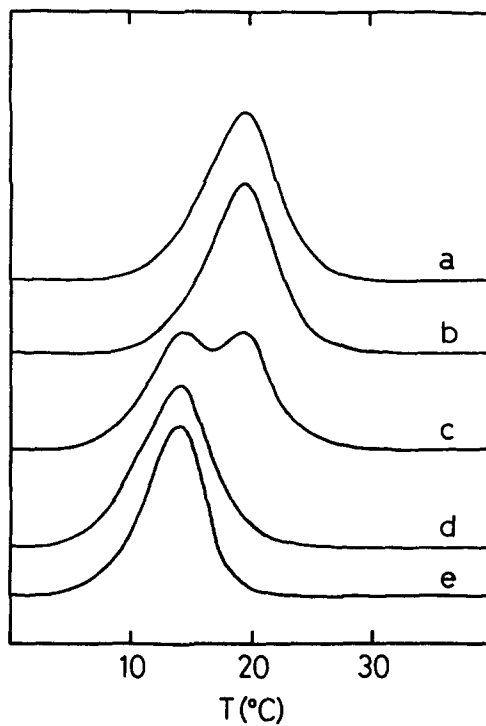


Fig. 2. X-ray diffraction diagrams of PTO after quenching in liquid nitrogen and crystallized at -20°C (A) and -50°C (B).

the molten state, although the relative interval, over the total crystallization range, where the low temperature form of PTO is obtained, is much smaller than in PDMO.

X-ray diffraction was used to determine that the two melting peaks in Fig. 1 really correspond to different crystalline modifications. An important problem was the fact that the actual melting temperatures are lower than room temperature. It was solved by the annealing of the samples at 0 °C before the diffraction diagrams were recorded at room temperature. Thus, Fig. 2 shows the diffractograms of two samples of PTO prepared at different crystallization temperatures. It can be deduced that only the orthorhombic modification is produced at -20 °C, with a characteristic maximum at the Bragg angle $2\theta = 19.3^\circ$, corresponding to the 200 plane (1). However, a different diffraction pattern was obtained when crystallizing at -50 °C, appearing a maximum at 21.8° assigned to the 300 and 211 reflections of the trigonal modification of PTO (1). A minor proportion of orthorhombic form is also observed for that preparation but, judging from Fig. 1, it is supposed that it was formed during the annealing process.

Another elegant method to distinguish between the $(T_2G_2)_2$ and $T_3GT_3\bar{G}$ crystal conformations in these polyoxetanes has been shown very recently by using solid-state ^{13}C NMR techniques (9). In that work, it is found that magnetic inequivalence, explained in terms of the γ -gauche effect, is present inside the same monomer unit only in the $T_3GT_3\bar{G}$ conformation for the two methylene carbons adjacent to the oxygen (and also for the two methyl substituents in the case of PDMO). Thus, the crystalline resonances due to the mentioned carbons appear as a doublet for the $T_3GT_3\bar{G}$ conformations of PTO and PDMO while all of them are singlets in the case of $(T_2G_2)_2$ conformations.

In conclusion, the two melting peaks in Fig. 1 correspond to different crystalline forms of PTO: a low-temperature form, trigonal, with $T_3GT_3\bar{G}$ conformation and an apparent melting point of 14 °C, and an orthorhombic $(T_2G_2)_2$ modification that can be obtained in a wide range of higher temperatures, what allowed to determine an equilibrium melting point of 50 °C (10), although its actual melting is at 20 °C in the range here studied.

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