

## On the crystalline nature of poly(di-isopropyl fumarate)

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### Summary

Molecular order of poly(di-isopropylfumarate) (PDIPF), obtained by free-radical initiation, is investigated by calorimetric measurements and X-ray diffraction analysis. It is found that the polymer decomposes without melting at temperatures above 200°C while displaying two endothermic transitions, probably of the solid-solid type, at 65 and 126°C respectively. Further evidence of crystalline order and orientability is provided by the X-ray experiments which show one equatorial (11.16 Å) and two meridional (4.81 and 2.40 Å) reflections respectively. The corresponding stereoselective nature of the polymerization reaction is interpreted as resulting from the steric influence of the bulky isopropyl substituents of the monomer.

### Introduction

It is a well-established fact that vinyl monomers easily undergo free-radical, chain reactions leading to high-molecular weight polymers. On the other hand, 1,2-disubstituted ethylene compounds were widely believed not to polymerize due to the steric hindrance originated by the 1,2-substituents. In the last few years, however, a series of reports have appeared (1) showing that alkyl fumarates do indeed polymerize, albeit at rates much lower than what is usual for normal vinyl monomers, leading, nevertheless, under special conditions, to high-molecular-weight compounds. Contrary to the expectations, however, the results also showed that the rates of polymerization increase with increasing volume of the alkyl substituents. Thus, fumaric acid as well as the corresponding methyl and ethyl esters polymerize at rates excindingly smaller than those of the bulky isopropyl and tert-butyl fumarates (2).

The special character of these polymers chain structure, which by means of adequate substitution reactions may lead to whole new families of polymers, and the surprising physicochemical aspects of the polymerization reactions have all prompted an investigation on such materials specially in regard to their structural and conformational characteristics. In particular it was of interest to study how the volume of the bulky substituents may affect the steric placement of the incoming monomer units during the propagation stage of the chain reaction. The present report will refer exclusively to the observations about poly(di-isopropyl fumarate) (PDIPF).

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### Sample preparation

High-molecular-weight PDIPF was prepared by free-radical polymerization with AIBN initiator, in bulk and in 30% toluene solution respectively. The experiments effectively led to the expected molecular weights ( $M_n = 185,000$  g/mol) as revealed by osmotic measurements (3). Also, GPC analysis indicated that the polymer prepared in bulk displays a broader distribution of molecular weight than the one in 30% toluene solution (4).

### Calorimetric and crystallographic analysis

The thermal properties of the solid PDIPF samples were investigated by differential scanning calorimetry (DSC) employing a DuPont 910-DSC instrument, whereby the measurements were put into a quantitative basis by means of indium calibration standards. For the structural investigations X-ray diffraction experiments were carried out employing  $\text{CuK}\alpha(\text{Ni})$  radiation at 30 KV and 35 mA, and a Weissenberg camera. Fiber-like specimens were spun from concentrated toluene solution. In order to impose molecular orientation on some of the fibers, they were subsequently drawn at around  $100^\circ\text{C}$  and at nominal draw ratios from 2 to 4. Two different types of X-ray geometries were applied for the study. First, the classical rotation set up with the fiber axis parallel to and coincident with the axis of rotation, and second an oscillation arrangement (5) with the fiber axis perpendicular to the rotation axis of the camera, and the oscillations taking place within the plane defined by the fiber axis and the axis of propagation of the primary X-ray beam. This geometry allowed the simultaneous registration of the meridional and equatorial reflections in the case of oriented fibers.

### Results and discussion

Differential scanning calorimetry shows that the polymer has a great thermal stability beginning to decompose, without melting, at temperatures above  $200^\circ\text{C}$ . Also, the DSC scan (Figure 1) displays two endothermic peaks at  $65^\circ$  and  $126^\circ\text{C}$  which, in view of the enthalpies involved, 1.20 and 0.41 Kcal/mole respec-

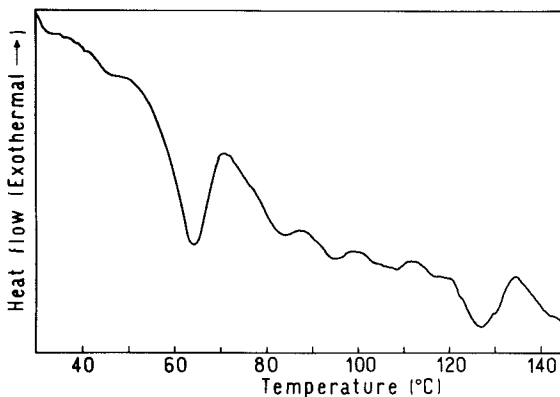
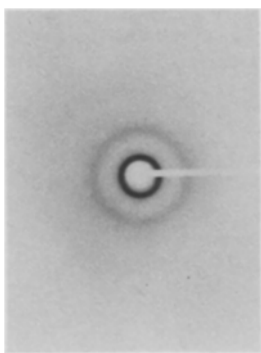


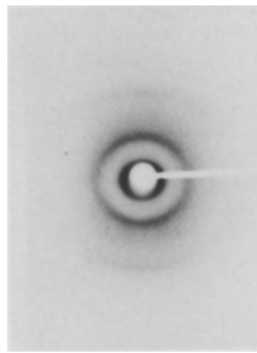
Figure 1 - DSC trace of PDIPF. Heating rate:  $10^\circ\text{C}/\text{min}$ .

tively, probably correspond to two different solid-solid transitions. The diffraction studies carried out on non-stretched material resulted in diagrams (Figure 2) displaying three concentric rings, typical of unoriented, crystalline substances. They are centered at 2.40, 4.81 and 11.16 Å respectively, whereby, the broadening of the diffraction domains points to the high paracrystalline character of the polymer lattice. Annealing of the samples at 70° for 16 hrs led to a slight improvement in crystalline order while, on the other hand, a treatment at 140°C for 18 hrs produced irreversible disappearance of all evidence of crystallinity.

The X-ray diagram corresponding to a drawn sample is shown in Fig. 3, where the uniform rings of Fig. 2 are now concentrated in one equatorial ( $d = 11.16$  Å) and two meridional (4.81 and



**Figure 2** - X-ray diffraction pattern of unoriented PDIPF.  $\text{CuK}\alpha(\text{Ni})$  radiation, cylindrical camera, exposure time: 14 hours.



**Figure 3** - X-ray diffraction pattern of oriented PDIPF. Meridional (fiber) axis vertical. Conditions as in figure 2.

2.40 Å) arcs respectively. The meridional ones, two subsequent orders of the same reflection, clearly evidence the crystalline regularity along the chain-axis direction of the polymer, while the equatorial reflection, related to regular packing in the lateral sense, displays the spacing expected from the cross section of the bulky PDIPF chain. In fact, from the molecular models of threodiisotactic PDIPF constructed by Otsu et al (2-6), the polymer chains would be expected to behave as cylinders 13 Å in diameter, packed in a hexagonal lattice and giving rise, therefore, to the observed 11.16 Å equatorial reflection.

In conclusion, the crystalline nature of the PDIPF clearly demonstrates the stereo selective character of the polymerization reaction since a random placement of configurations would otherwise lead to chain molecules with an irregular sequence of tacticities wholly incompatible with the crystalline state. This is a remarkable accomplishment in view of the fact that the stereoregularity does not arise from any kind of special catalyst but simply from the molecular structure of the reacting monomer.

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