

## Stereospecific Polymerization of $\beta$ -Methyl- $\beta$ -propiolactone<sup>1</sup>

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(Received September 3, 1971)

**KEY WORDS** Stereospecific Polymerization / DL- $\beta$ -Methyl- $\beta$ -propiolactone / Isotactic Poly ( $\beta$ -hydroxybutyrate) / X-ray Fiber Diagram / Polarized IR Spectrum /

Only a few papers have reported the polymerization of the substituted  $\beta$ -propiolactone.<sup>2,3</sup> Very recently, Shelton, Lando, and Agostini<sup>4</sup> polymerized D(+)- $\beta$ -methyl- $\beta$ -propiolactone to give poly( $\beta$ -hydroxybutyrate), identified as the naturally occurring substance. We would like to report the stereospecific polymerization of DL- $\beta$ -methyl- $\beta$ -propiolactone to give isotactic poly( $\beta$ -hydroxybutyrate).

DL- $\beta$ -Methyl- $\beta$ -propiolactone (I) was synthesized by the reaction of acetaldehyde with ketene. The product was dried over calcium hydride for 7 days and then distilled, bp 46—47°C (7 mm). (Yield, 70% based on acetaldehyde). It was further dried over calcium chloride (previously heated to 450°C) for 24 hr and then distilled just before use.

Polymerization of (I) using  $\text{BF}_3 \cdot \text{OR}_2$ , a typical cationic catalyst, proceeded very rapidly to give only oily products. With  $n\text{BuLi}$ , a typical anionic catalyst, no polymer was obtained. Using a coordinate catalyst such as trialkylaluminum or its derivatives gave mixtures of isotactic and atactic polymers. A typical example of the latter case is as follows: A solution of (I) (2.05 g 27 mmol) in toluene (2.0 ml) containing  $[\text{Et}_2\text{AlOCPPhNPh}]_2$ <sup>5,6</sup> (0.0758 g 0.135 mmol) was sealed in an ampoule under dry nitrogen atmosphere and was kept at 60°C for 7 days. The polymerization was terminated by adding petroleum ether—water (20:1, v/v) mixture. The insoluble product obtained was dissolved in chloroform and the solution was filtered, and the raw polymer was obtained by adding diethyl ether to the filtrate (yield 1.72 g

84%). The raw polymer was fractionated with acetone to give an insoluble fraction (0.38 g, 19% yield) of crystalline polymer, and a soluble fraction (1.34 g, 65% yield) of amorphous polymer. The two fractions were shown to be poly( $\beta$ -hydroxybutyrate) by elemental analyses. The mp of the crystalline fraction (167—169°C) was slightly lower than that of the natural polymer (174—177°C).

The NMR spectra of chloroform solutions of the crystalline, the amorphous, and the natural polymers all show a multiplet assigned to methine proton at 5.28 ppm, a doublet to methylene protons at 2.25 ppm, and a doublet to methyl protons at 1.30 ppm, in intensity ratios of 1:2:3.

The IR spectra of unoriented films of the synthetic crystalline and the natural polymers, prepared by casting from chloroform solution have characteristic bands at 1735, 1680, 1293, 1280, 1230, 915, 900, 670, 620, 515, and 460  $\text{cm}^{-1}$ . These were absent in films of the synthetic amorphous polymer. These absorption bands are crystalline bands, because IR spectra for the three polymers were identical for the liquid state. Polarized IR spectra of the oriented film of the synthetic crystalline and the natural polymers<sup>7</sup> were identical (see Figure 1).

The X-ray fiber photograph of the oriented synthetic crystalline polymer is shown in Figure 2. The fiber period is 5.94 Å, and the interplanar spacings and intensities agree satisfactorily with those of natural polymer.<sup>7</sup> These facts, combined with the observation that the chain conformation of natural polymer is a  $2_1$ -helix<sup>7</sup>, suggest that in the crystalline part of the

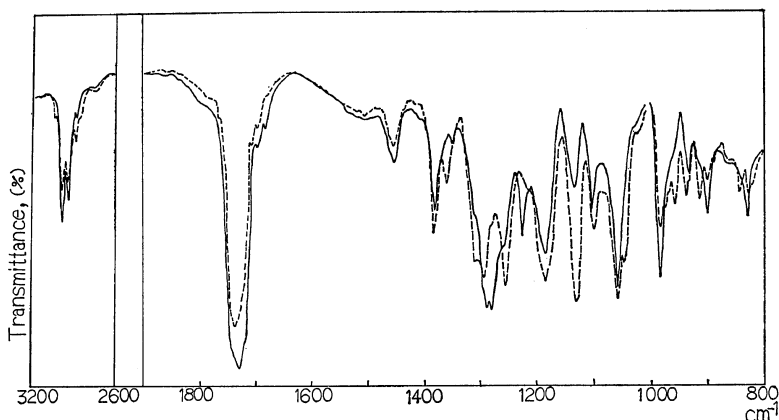


Figure 1. Polarized infrared absorption spectrum of the crystalline poly(DL- $\beta$ -methyl- $\beta$ -propiolactone): —, electric vector perpendicular to elongation; ----, electric vector parallel to elongation.

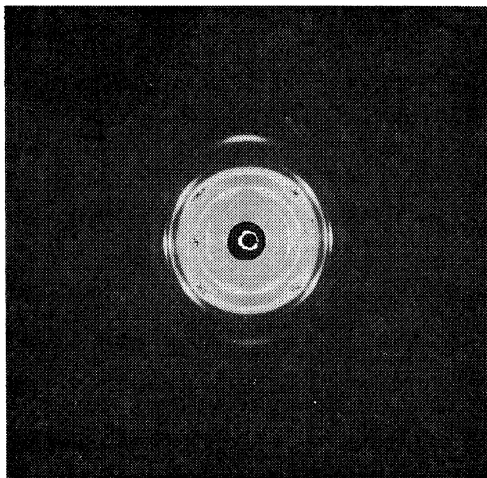


Figure 2. X-ray fiber photograph of the crystalline Poly(DL- $\beta$ -methyl- $\beta$ -propiolactone).

synthetic crystalline polymer D- and L-chain aggregate independently to build the crystallite.

All the experimental results given above indicate that the crystalline polymer obtained by the polymerization of  $\beta$ -methyl- $\beta$ -propiolactone using organoaluminum catalyst is highly isotactic.

*Acknowledgement.* The authors are grateful

to Prof. S. Fukui of Kyoto University for a gift of natural poly( $\beta$ -hydroxybutyrate), to Dr. K. Okamura of Kyoto University for the information on the structure of natural poly( $\beta$ -hydroxybutyrate), and to Prof. H. Tadokoro, Dr. Y. Chatani and Dr. M. Kobayashi of this Department for interpreting X-ray and IR data.

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