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Abstract: From the alternating copolymerization of carbon monoxide and styrene with a soluble palladium containing catalytic system a product fraction insoluble in boiling 2-butanone was isolated which is highly crystalline. The polymer has been identified mainly by ¹H- and ¹³C-NMR spectroscopy and by X-ray diffraction as syndiotactic poly(1-oxo-2-phenyltrimethylene). This polymer completely epimerizes to atactic poly(1oxo-2-phenyltrimethylene) in the presence of sodium 2-chlorophenolate.

The preparation of linear CO/styrene alternating copolymers has been described in 1986 by Drent^[1]. However, under some of the experimental conditions indicated in the patent a mixture of polymers is actually obtained. After extracting such a mixture with boiling ethyl methyl ketone the polymer which is not dissolved shows an X-ray powder spectrum with many sharp lines (Fig. 1) indicative of a fairly high degree of crystallinity. This is rather unexpected as the polymer is obtained using a soluble organometallic Pd catalyst.

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The polymer fraction investigated by us has a sharp melting point at 290°C, $M_{\rm n} = 6700$ (vapour pressure osmometry in o-chlorophenol at 80 °C). The density measured at 24°C by flotation on a film cast from hexafluoroisopropanol solution is 1.252 g/cm³. UV spectrum: $\lambda_{max} = 287$ nm, $\varepsilon = 570 \text{ L/(mol \cdot cm)}$ (in hexafluoroisopropanol at room temperature). Elemental analysis: C 81.26%, H 6.14% (calc. 81.79, 6.10).

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^{*} Correspondence: Prof. Dr. P. Corradini Dipartimento di Chimica, Università di Napoli Via Mezzocannone 4, I-80134 Napoli (Italia)

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the above assumptions the recovered polymer does not crystallize, is soluble in chloroform, and shows a glass transition (DSC determined) at about 100 °C. For the stereoregular chain of poly(1-oxo-2-phenyltrimethylene) the most simple conceivable steric structures are the isotactic 3 and the syndiotactic 4 ones.



Fig. 1. X-ray powder diffraction pattern of poly(1-oxo-2-phenyltrimethylene) as a function of 2θ (Cu_{κ_2}).



Fig. 2. ¹³C-NMR spectrum of a solution of poly(1-oxo-2-phenyltrimethylene) in hexa-fluoroisopropanol (• solvent).



Fig. 3. a) Expanded ¹³C-NMR spectrum of the solution of the polymer in hexafluoroisopropanol in the region of 136-139 ppm; b) same as in a) for the solution of the polymer in o-chlorophenol in the presence of sodium o-chlorophenolate heated at 60° C under nitrogen for 24 h.

The NMR spectrum of Fig. 3a appears to be consistent with a prevailingly isotactic *or* with a prevailingly syndiotactic structure with less than 10% steric irregularities, most probably of the kind expected for a chain-end^[2] sterically controlled polymerization.



Though oriented material was not available to us to get X-ray fiber spectra, we could arrive at a reasonable interpretation of the X-ray powder spectra indicating a syndiotactic structure for the polymer. In analogy with the case of the crystalline alternating copolymer CO/ethylene, i.e. poly(1-oxotrimethylene)^[3], let us make the hypothesis that the identity period c is near to 7.5-7.6 Å. With this assumption the observed X-ray Bragg distances and intensities of the reflections may be interpreted with a unit cell having $a = 15.5 \pm 0.1 \text{ Å}^{(5)}$, $b = 6.15 \pm 0.06$ Å, $\beta = 105 \pm 2^{\circ}$; space group P2₁/c and containing two chains $(\rho_{\text{calc.}} = 1.27 \text{ g/cm}^3, \rho_{\text{obs.}} = 1.252 \text{ g/cm}^3).$



Fig. 4. 'H-NMR spectrum of a solution of the poly(1-oxo-2-phenyltrimethylene) in dimethylsulfoxide before (above) and after (below) the epimerization treatment.

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Further consideration of the intensities gives compelling indications for a trial structure in which the chain is crossed by the crystallographic glide-plane of symmetry and successive benzene rings along the chains are on the same side of the backbone.

Trial syndiotactic chain models were built with bond lengths and bond angles as in the published structure of poly(1-oxotrimethylene)^[3]. We varied the internal rotation angles of the chain 5 under the



simplifying assumption that $\theta_2 = -\theta_1$; moreover $\theta_3 = f(\theta_1, \theta_2)$ as required by a glide-plane tc repetition^[4]. A preliminary model of the structure, which provided good accordance between observed and calculated intensities (taking B = 8 Å² and the atomic scattering factors as in Ref.^[5]), is shown in Fig. 5. The baricenter of the carbon chain atoms A is x/a = 0.11, while the relative height for the facing benzene rings B and C is $\Delta z = 1.9$ Å. The as yet optimized internal rotation angles of the chain assumed for this preliminary accordance (Fig. 6) are: $\theta_1 = 167.5^\circ$, $\theta_2 = -167.5^\circ$, $\theta_3 = -153.9^\circ$, giving a unit height^[4] h = 3.78 Å, c = 2h = 7.56 Å.

In conclusion, the X-ray data show that the fraction insoluble in ethyl methyl ketone of the polymer obtained with homogenous Pd catalysts consists of an alternated crystalline head-to-tail copolymer of CO and styrene, poly(1-oxo-2-phenyltrimethylene), which has a substantially syndiotactic structure. Furthermore, the NMR data indicate that stereoregularity is prevailingly chain-end controlled, as it is in the case of the new syndiotactic polystyrene^[2].

Received: November 1, 1989 [FC 183]

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Fig. 5. Model of packing in the crystalline state of syndiotactic poly(1-oxo-2-phenyltrimethylene).



Fig. 6. Chain conformation in the crystalline state of poly(1-oxo-2-phenyltrimethylene); the hydrogen atoms are indicated only for the methine groups in order to show the syndiotacticity.