The Structure of Poly(1-oxo-2-phenyltrimethylene): A Crystalline Alternating Styrene-Carbon Monoxide Copolymer

Paolo Corradini*, Claudio De Rosa, Achille Panunzi, Giorgio Petrucci*, and Piero Pino**

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

The crystallinity should be associated with a regular sequence of constitutional and configurational units at least for sufficiently long stretches of the polymer chain.

The $^{13}$C-NMR spectrum in hexafluoroisopropanol at room temperature (Fig. 2) shows substantially a single line at $\delta = 210.96$ indicating the presence of a single type of keto groups. Therefore it is consistent with the presence of one single type of constitutional repeating unit 1 and excludes substantial amounts of head-to-head tail-to-tail units 2. The existence of largely prevailing single resonances at $\delta = 42.4$ (CH$_3$ groups), 54.0 (CH groups), and 136.9 (phenyl-C1); cf. Fig. 3a) indicate that the polymer is substantially stereoregular.

The NMR spectrum of the polymer heated at 60°C under nitrogen for 24 h in o-chlorophenol in the presence of sodium o-chlorophenolate (0.022 M) shows remarkable changes in the region of 136–139 ppm (Fig. 3b), as well as in other regions. New resonances appear in fact also in the CO, CH$_3$, and CH regions.

However, the $^1$H-NMR spectrum (Fig. 4) still shows the ratios 1:2:5 among the signals of the methine, methylene, and methyl groups, which is in agreement with the presence of a single type of carbonyl group.

The polymer fraction investigated by us has a sharp melting point at 290°C, $M_T = 6700$ (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/cm$^3$. UV spectrum: $\lambda_{max} = 287$ nm, $e = 570$ L/(mol·cm) (in hexafluoroisopropanol at room temperature). Elemental analysis: C 81.26%, H 6.14% (calc: 81.79, 6.10).
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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-butanol was isolated which is highly crystalline. The polymer has been identified mainly by \(^1\)H- and \(^{13}\)C-NMR spectroscopy and by X-ray diffraction as syndiotactic poly(1-oxo-2-phenyltrimethylene). This polymer completely epimerizes to atactic poly(1-oxo-2-phenyltrimethylene) in the presence of sodium 2-chlorophenolate.

The preparation of linear CO/styrene alternating copolymers has been described in 1986 by Drexl[10]. 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.

The crystallinity should be associated with a regular sequence of constitutional and configurational units at least for sufficiently long stretches of the polymer chain.

The \(^{13}\)C-NMR spectrum in hexafluoroisopropanol at room temperature (Fig. 2) shows substantially a single line at \(\delta = 210.96\) indicating the presence of a single type of keto groups. Therefore it is consistent with the presence of one single type of constitutional repeating unit and excludes substantial amounts of head-to-head tail-to-tail units. The existence of largely prevailing single resonances at \(\delta = 42.4\) (CH groups), 54.0 (CH groups), and 136.9 (phenyl-C); cf. Fig. 3a) indicate that the polymer is substantially stereoregular.

The NMR spectrum of the polymer heated at 60°C under nitrogen for 24 h in o-chlorophenol in the presence of sodium o-chlorophenolate (0.022 M) shows remarkable changes in the region of 136-139 ppm (Fig. 3b), as well as in other regions. New resonances appear in fact also in the CO, CH\(_3\), and CH regions.

However, the \(^1\)H-NMR spectrum (Fig. 4) still shows the ratios 1:2:5 among the signals of the methine, methylene, and methyl protons. Therefore it is consistent with the presence of one single type of constitutional repeating unit and excludes substantial amounts of head-to-head tail-to-tail units. The existence of largely prevailing single resonances at \(\delta = 42.4\) (CH groups), 54.0 (CH groups), and 136.9 (phenyl-C); cf. Fig. 3a) indicate that the polymer is substantially stereoregular.

The crystal phase of the copolymer is formed as crystallites upon cooling of melts at 30°C. The polymer fraction investigated by us has a sharp melting point at 290°C, \(T_m = 6700\) (vapour pressure osmometry in o-chlorophenol at 80°C). The density measured at 24°C by flotation on a film cast o-chlorophenol in the presence of sodium o-chlorophenolate (0.022 M) shows re-
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 20 (CuKα).

The NMR spectrum of Fig. 3a appears to be consistent with a prevalingly isotactic or with a prevalingly syndiotactic structure with less than 10% steric irregularities, most probably of the kind expected for a chain-end 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), 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 ± 0.1 Å, b = 6.15 ± 0.06 Å, β = 105 ± 2°; space group P21/c and containing two chains (ρrel. = 1.27 g/cm³, ρtheo. = 1.252 g/cm³).

Fig. 2. 13C-NMR spectrum of a solution of poly(1-oxo-2-phenyltrimethylene) in hexafluoroisopropanol (· 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.

Fig. 4. 1H-NMR spectrum of a solution of the poly(1-oxo-2-phenyltrimethylene) in dimethylsulfoxide before (above) and after (below) the epimerization treatment.
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-oxo-trimethylene)\textsuperscript{13}. We varied the internal rotation angles of the chain under the simplifying assumption that $\theta_1 = -\theta_2$; moreover $\theta_3 = f(\theta_1, \theta_2)$ as required by a glide-plane \textit{hc} repetition\textsuperscript{14}. A preliminary model of the structure, which provided good accordance between observed and calculated intensities (taking $B = 8 \text{Å}^2$ and the atomic scattering factors as in Ref.\textsuperscript{15}), 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 $d_2 = 1.9 \text{Å}$. 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\textsuperscript{16} $h = 3.78 \text{Å}$, $c = 2h = 7.56 \text{Å}$.

In conclusion, the X-ray data show that the fraction insoluble in ethyl methyl ketone of the polymer obtained with homogeneous 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\textsuperscript{21}.

Received: November 1, 1989 [FC 183]

\[\text{Fig. 5. Model of packing in the crystalline state of syndiotactic poly(1-oxo-2-phenyltrimethylene).}\]

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

\[\text{References:}\]
\[\text{[4]}\ IUPAC Commission on Macromolecular Nomenclature, Pure Appl. Chem. 51 (1979) 1101.