

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 ste-

reoregular chain of poly(1-oxo-2-phenyltrimethylene) the most simple conceivable steric structures are the isotactic 3 and the syndiotactic 4 ones.

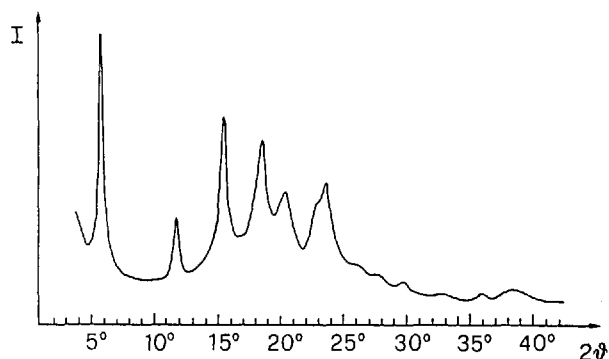
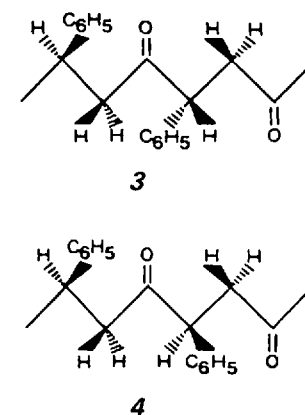


Fig. 1. X-ray powder diffraction pattern of poly(1-oxo-2-phenyltrimethylene) as a function of 2θ ($\text{CuK}\alpha$).

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)^[1], 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 $a = 15.5 \pm 0.1$ Å^[5], $b = 6.15 \pm 0.06$ Å, $\beta = 105 \pm 2^\circ$; space group $P2_1/c$ and containing two chains ($\rho_{\text{calc.}} = 1.27$ g/cm³, $\rho_{\text{obs.}} = 1.252$ g/cm³).

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^[2] sterically controlled polymerization.

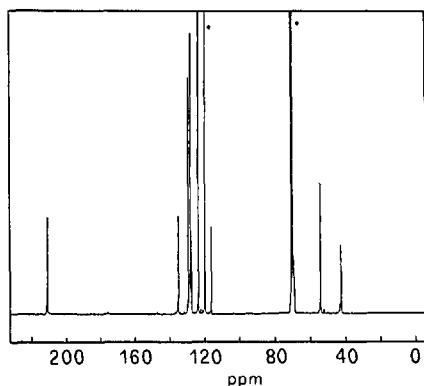


Fig. 2. ¹³C-NMR spectrum of a solution of poly(1-oxo-2-phenyltrimethylene) in hexafluoroisopropanol (• solvent).

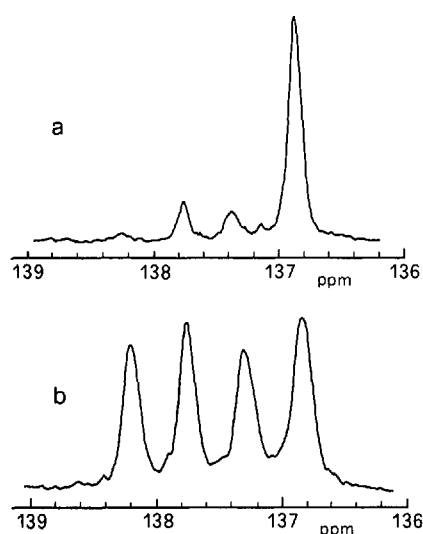


Fig. 3. a) Expanded ¹³C-NMR spectrum of the solution of the polymer in hexafluoroisopropanol in the region of 136–139 ppm; b) same as in a) for the solution of the polymer in *o*-chlorophenol in the presence of sodium *o*-chlorophenolate heated at 60°C under nitrogen for 24 h.

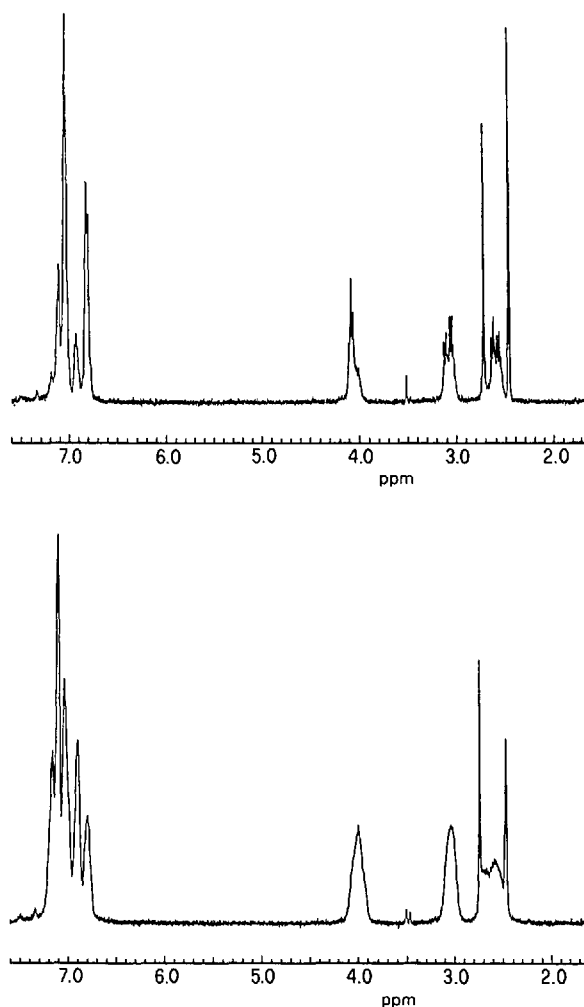
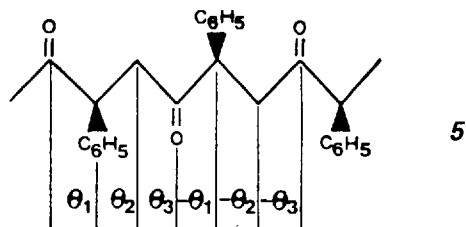


Fig. 4. ¹H-NMR spectrum of a solution of the poly(1-oxo-2-phenyltrimethylene) in dimethylsulfoxide before (above) and after (below) the epimerization treatment.

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)^[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 to repetition^[4]. A preliminary model of the structure, which provided good accordance between observed and calculated intensities (taking $B = 8 \text{ \AA}^2$ 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 $\Delta z = 1.9 \text{ \AA}$. 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] $h = 3.78 \text{ \AA}$, $c = 2h = 7.56 \text{ \AA}$.

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 prevalingly chain-end controlled, as it is in the case of the new syndiotactic polystyrene^[2].

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- [1] E. Drent, *Eur. Pat. Appl.* 0229408 (1986).
- [2] P. Corradini, V. Busico, G. Guerra, in W. Kaminsky, H.J. Sinn (Ed.): *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, Springer, Berlin (1988), p. 337.
- [3] Y. Chatani, T. Takizawa, S. Murahashi, Y. Sakata, Y. Nishimura, *J. Polym. Sci.* 55 (1961) 811.
- [4] IUPAC Commission on Macromolecular Nomenclature, *Pure Appl. Chem.* 51 (1979) 1101.
- [5] D.T. Cromer, J.B. Mann, *Acta Crystallogr.* A24 (1968) 321.

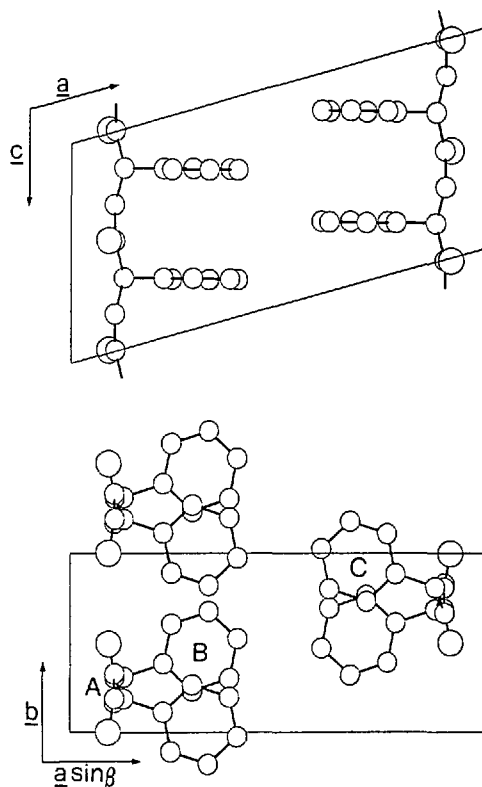


Fig. 5. Model of packing in the crystalline state of syndiotactic poly(1-oxo-2-phenyltrimethylene).

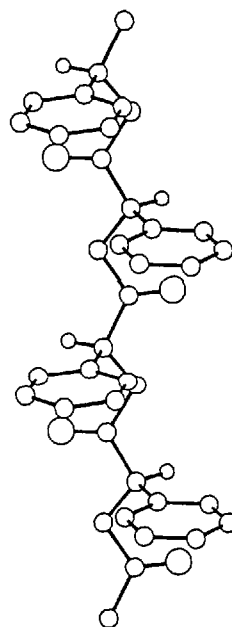


Fig. 6. Chain conformation in the crystalline state of poly(1-oxo-2-phenyltrimethylene); the hydrogen atoms are indicated only for the methine groups in order to show the syndiotacticity.