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Crystalline Structure of Some Alternate Copolymers between Carbon Monoxide and Styrene Derivatives

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ABSTRACT: The crystal structure of some alternate copolymers of styrene and styrene derivatives with carbon monoxide is presented. We start from the crystal structure previously solved in the case of poly(1-oxo-2-phenyltrimethylene) (STCO), which gave clear evidences of the syndiotactic nature of this copolymer. The very close analogies between the X-ray powder diffraction spectra of copolymers of CO with *p*-fluorostyrene (pFSTCO), *m*-methylstyrene (mMSTCO), and *p*-methylstyrene (pMSTCO) with the spectrum of STCO allow us to postulate an analogous syndiotactic structure and a very similar chain conformation and packing model for them. The structural models have been refined for all four copolymers through the Rietveld method, giving the following results. (a) For STCO: space group $P2_1/c$, $a = 15.20$ Å, $b = 6.166$ Å, $c = 7.59$ Å, $\beta = 102.5°$. (b) For pFSTCO: space group $P2_1/c$, $a = 15.59$ Å, $b = 6.168$ Å, $c = 7.551$ Å, $\beta = 98.8°$. (c) For mMSTCO: space group $P2_1/c$, $a = 16.14$ Å, $b = 6.816$ Å, $c = 7.580$ Å, $\beta = 100.3°$. (d) For pMSTCO: space group $C2/c$, $a = 35.54$ Å, $b = 6.262$ Å, $c = 7.536$ Å, $\beta = 96.0°$. All the studied copolymers crystallize with the chain backbone in a nearly extended conformation, with very similar values of the dihedral angles. Roughly speaking, also the packing models are very similar. In all crystal structures the chains are arranged to form layers parallel to the *bc* plane piled along *a*. The packing models for the various copolymers present the most relevant differences in the stacking along *a* of these *bc* layers.

Introduction

The copolymers of carbon monoxide with olefins are interesting not only for their potential practical application but also for the low cost of monomeric constitutive units.[1] Recently Drent et al.[2] have shown that soluble organometallic palladium catalysts are able to promote the synthesis of a linear alternating copolymer of styrene and carbon monoxide [poly(1-oxo-2-phenyltrimethylene)], here in the following STCO.

De Rosa, Corradini, et al., on the basis of ^{1}H- and ^{13}C-NMR spectroscopy and X-ray diffraction data, proposed a syndiotactic structure[3] and resolved the crystalline structure for STCO.[4]

We have recently used the same catalytic system used by Drent et al., in ref 2 to synthesize alternating copolymers between carbon monoxide and some derivatives of styrene (i.e., *m*-methyl- and *p*-methylstyrene).[5]

The resulting copolymers (here in the following indicated as mMSTCO and pMSTCO, respectively), together with an additional copolymer between carbon monoxide and *p*-fluorostyrene (pFSTCO), are semicrystalline but of low molecular weight. Hence, it has not been possible to prepare oriented fibers nor single crystals.

X-ray powder diffraction spectra, however, present a fairly high number of reflections, indicating a high degree of constitutional and configurational regularity.

^{13}C-NMR data indicate not only the presence of only one kind of "head-to-tail" repetition unit, but also a substantial stereoregularity (whether syndiotactic or isotactic cannot be established on the basis of ^{13}C-NMR data alone).

It is possible, however, to establish on the basis of X-ray diffraction spectra that the asymmetric carbon atoms belonging to repeating units $-(CO-{}^{*}CH(Ar)-CH_2-)-$ (Ar = arene) follow each other along the chain with alternating opposite chirality.

Indeed, in the case of STCO, we recall that in refs 3 and 4 it has been possible to interpret the whole X-ray diffraction spectrum through a monoclinic unit cell and to index the very strong reflection at $d \approx 15$ Å as (100). Such a long *a* axis is compatible only with a trial chain structure in which the benzene rings along a given chain are on the same side of the backbone and almost projecting one above the other, giving clear evidences of the syndiotactic nature of the copolymer in question. Hence, a *tc* chain symmetry, with the dihedral angles in the backbone in a nearly *trans* conformation (compatible with an identity period $c \approx 7.5$–7.6 Å) was postulated. The assumption that the glide plane as a chain symmetry element is also preserved as a crystallographic symmetry element, besides packing considerations, led the authors of ref 3 to propose the space group $P2_1/c$, which was successfully confirmed by structure factor calculations.[4]

The very close analogies between the X-ray diffraction spectra of the copolymers of carbon monoxide and the derivatives of styrene under study with the spectrum of STCO (and in particular the presence of a sharp and strong reflection at spacing in the range $d \approx 15 \div 17$ Å, common to all the series) allow us to postulate an analogous syndiotactic structure and a very similar chain conformation and packing model for them.[5]

In this paper we shall deal with the crystalline structures of STCO, pFSTCO, mMSTCO, and pMSTCO. The proposed structural models have been refined through the Rietveld method using the same approach employed in the case of the crystalline structure refinement of isotactic polypropylene in the α-,[6] β-,[7] and γ-modifications.[8]

In our refinement procedure special attention has been paid to the evaluation of the background contribution to the diffraction spectra of the studied semicrystalline

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polymers: the background intensity has been accurately evaluated, recording the X-ray powder diffraction profile of amorphous samples suitably prepared.

Experimental Part

Alternate copolymers of carbon monoxide and styrene or styrene derivatives were obtained with the homogeneous catalytic system[1] $Pd(CH_3COO)_2$/1,10-phenanthroline/*p*-toluenesulfonic acid/1,4-benzoquinone, in methanol at 65 °C.[5]

The samples obtained, insoluble in the reaction media, after several washings with methanol, were separated from a lower molecular weight and less stereoregular fraction by Kumagawa extraction with 2-butanone.

An increase in crystallinity was obtained by quick thermal treatment (less than 4 min at a temperature ≈40 °C below the melting point of each crystalline copolymer).

Samples of amorphous copolymers were prepared by epimerization[3] of the crystalline samples in an *o*-chlorophenol/sodium *o*-chlorophenate solution (24 h at 60 °C) and reprecipitation in methanol.

X-ray powder diffraction spectra were recorded at room temperature with a Philips diffractometer, provided with a step scan attachment and a proportional counter, using Ni-filtered Cu Kα radiation. The range of 2θ diffraction angle examined was 3–55°, the count time for each step was equal to 60 s/step, and the step width was 0.05° (2θ).

We have checked that the preferred orientation of the crystallites in the samples was reduced to a minimum. Indeed, X-ray powder diffraction photographic spectra of our copolymers (obtained in the transmission geometry, by rotating the sample) give diffraction rings, in the same intensity ratio as the integrated intensities, deduced through the automatic collection.

The refinement procedure was done through the use of the program DEBVIN, first developed by Immirzi[6] and hence revised and implemented by Bruckner.[9]

Results and Discussion

Crystalline Structure and Refinement Procedure. One of the most interesting improvements which the introduction of a full profile X-ray powder diffraction refinement procedure for the crystalline structure of the polymers has given is the possibility to refine all together the chain conformation, the packing parameters, the cell constant, and nonstructural parameters.

The minimized function is:

$$\Omega^2 = \sum_i W_i(Y_{ci} - Y_{oi})^2 + \sum_j u_j(G_{oj} - G_j)^2 \qquad (1)$$

with Y_{oi} and Y_{ci} the observed and the calculated values of the intensity profile at $2\theta_i$ diffraction angle and W_i the weight factor, placed equal to $W_i = 1/Y_{oi}$ for $2\theta > 6.50°$ and equal to $W_i = 0.1/Y_i$ for $2\theta \leq 6.50°$; G_{oj} and G_j are the values which a given geometrical variable (i.e., bond lengths, bond angles, dihedral angles, distances between nonbonded atoms, etc.) is desired to assume and the corresponding value assumed by that variable at the given point of the refinement procedure, respectively; u_i is a suitable scaling factor.

In carrying out the structural refinement with the present approach, the agreement factor R_2' is defined as:

$$R_2' = \sum_i |Y_{oi} - Y_{ci}| / \sum_i Y_{ni} \qquad (2)$$

where Y_{oi} and Y_{ci} are the observed and calculated diffraction intensities, respectively, and $Y_{ni} = Y_{oi} - Y_{bi}$ where Y_{bi} includes the amorphous contribution.

The X-ray diffraction profiles of STCO, pFSTCO, mMSTCO, and pMSTCO are reported in Figure 1. Close analogies between the diffraction spectra of the latter three copolymers with the spectrum of STCO are apparent. We have hence postulated, in the case of the crystalline structure of copolymers of carbon monoxide with styrene derivatives, chain conformations and packing models very similar to those of STCO.

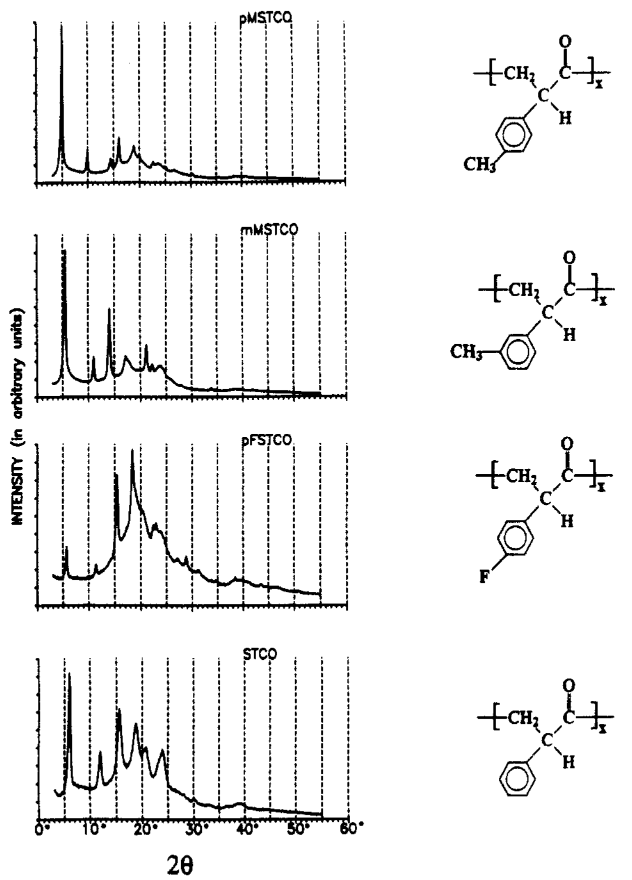

Figure 1. X-ray powder diffraction spectra of polymers taken into consideration.

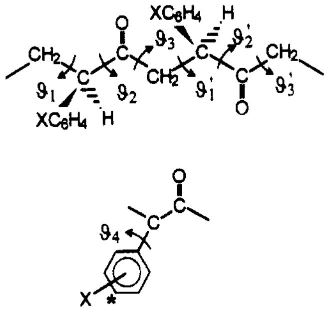

Figure 2. Definition of dihedral angles in the studied polymers.

Figure 2 sketches a portion of the chain of the copolymers under study and also defines the torsion angles. Observe that in a *tc* symmetry the asymmetric unit corresponds to half of the repetition unit, and ϑ_i' angles in a second half are related to the corresponding torsion angles of the first half of the repeating unit by the relationship $\vartheta_i' = -\vartheta_i$.

In ref 4 the chain symmetry for STCO was assumed to be *tc*, and, for the sake of simplicity, only the conformations with $\vartheta_2 = -\vartheta_1$ and ϑ_4 in a gauche state were taken into consideration. The value of ϑ_3 was regulated as a function of ϑ_1 (and hence ϑ_2) in order to get the experimental identity period. Only three parameters were left variable in the structure factor calculation, i.e., the value of ϑ_1, the *x* fractional coordinate of the chain axis, and the relative height of facing benzene rings.

In this paper we have preferred to treat all the dihedral angles as dependent variables, being a function of the position and of the orientation of the asymmetric unit

Table 1. Bond Lenghts and Bond Angles Used To Build the Model Chain of the Copolymers under Study and Kept Constant in the Refinement Procedure

lengths (Å)		angles (deg)	
C_{sp3}–C_{sp3}	1.54	C–C–C	111.0
C_{sp3}–C_{sp2}	1.51	C–(CO)–C	117.0
C_{sp2}–C_{sp2}	1.39	O–C–C	121.5
C_{sp2}–O	1.21	C–C–C_{ar}	111.0
C_{sp2}–F	1.35	C–C_{ar}–C_{ar}	120.0
		F–C_{ar}–C_{ar}	120.0

with respect to the axes of the unit cell. In brief, the coordinates of all atoms in the asymmetric units were first generated with respect to a frame with origin located at the center of the CH–CO bond, the z axes bisecting the consecutive CH_2–CH bond, the y axis setting in such a way that C* (see Figure 2) lies in the $+z$–y quarter plane, and x completing a right-handed orthogonal frame. Rotations Ω_x, Ω_y, and Ω_z around the axes and translations X, Y, and Z along the axes of the orthogonal frame were hence introduced as independent variables to be optimized in the refinement procedure. It was necessary, owing to the poor number of independent reflections in the X-ray diffraction spectra of the studied copolymer, to introduce geometrical restraints at the boundary of the unit cells: i.e., the bond lengths and valence angles joining atoms belonging to the same chain but located into adjacent cells along c were kept constant at the values listed in Table 1. In order to eliminate undesirable values of distances between atoms of adjacent chains, it was necessary to introduce additional restraints, keeping a couple of the atoms in question within a distance compatible with the sum of the corresponding van der Waals radii. At the final stages of the refinement procedure, when the mean-square convergence was reached, the restraints on the distances for nonbonded atoms were relaxed.

Hydrogen atoms were not considered.

The cell constants were of course refined.

Some nonstructural parameters were refined. In particular, it was necessary to refine the scaling factor for the amorphous X-ray powder diffraction profile in order to put the latter profile on the same intensity scale of the spectra of the semicrystalline copolymers. An additional segmental line spanning the whole spectrum with nodes having abscissa $2\theta = 3°$ and $55°$ and the ordinate to be refined on the intensity scale was considered.

The peak shape was assumed to be a Cauchy function with half-height width H equal to:

$$H = (U \tan^2[\theta] + V \tan[\theta] + W)^{1/2} \tag{3}$$

with θ the diffraction angle, U and V two variables to be optimized, and W depending on the (hkl) values through an adjustable estimation of crystallite dimensions.[9-11] It is necessary to point out, here, that the refinement procedure allows for the optimization of three parameters La, Lb, and Lc (related to the mean dimensions of the crystallites along the directions of the axes a, b and c, respectively; see Table 4) which do not give immediately the real average crystallite dimensions since the instrumental broadening is present and affects the peak shape; therefore, further elaboration would be required to obtain physically meaningful data. However, since in crystalline polymers like these under investigation the diffraction peaks' broadening is much higher than that due to instrumental effects, we may consider La, Lb, and Lc to underestimate the real crystallite dimensions only by a relatively small amount of the order of 10–20%.

Table 2. Refined Values of the Structural Parameters

	STCO	pFSTCO	mMSTCO	pMSTCO
space groups	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
a (Å)	15.20 (3) [15.5]	15.59 (2)	16.14 (1)	35.54 (2)
b (Å)	6.166 (7) [6.15]	6.168 (6)	6.816 (4)	6.262 (2)
c (Å)	7.590 (4) [7.56]	7.551 (2)	7.580 (2)	7.536 (1)
β (deg)	102.5 (1) [105°]	98.8 (1)	100.3 (1)	96.0 (1)
$R2'$ (%)	9.6 [14]	12	12	12
ϑ_1 (deg)	170 [167.5]	175	169	160
ϑ_2 (deg)	−162 [−167.5]	−158	−169	−172
ϑ_3 (deg)	−150 [−153.9]	−154	−157	−149
ϑ_4 (deg)	68 [60]	65	62	71
Ω_z (deg)	−109.0 (1)	−111 (1)	−114.4 (1)	−109.7 (1)
Ω_x (deg)	−4.1 (5)	−1.5 (2)	−2.8 (2)	−4.63 (2)
Ω_y (deg)	2.0 (4)	3.4 (1)	0.33 (3)	−1.67 (4)
X (Å)	1.725 (7)	1.657 (6)	1.541 (6)	10.51 (1)
Y (Å)	1.588 (7)	1.555 (3)	1.743 (3)	3.162 (1)
Z (Å)	0.11 (2)	0.33 (1)	2.42 (2)	1.39 (3)
S_{xb}	0.111 [0.111]	0.102	0.0993	0.296
$S_{z\Phi}$	0.256 [0.264]	0.247	0.517	0.453
d_c (g/cm^3)	1.262	1.388	1.182	1.163
d_o (g/cm^3)	1.256	1.331	1.166	1.158
d_a (g/cm^3)	1.200	1.306	1.150	1.133

A zero-point correction on the experimental 2θ scale was evaluated and in some cases a (small) preferred orientation detected. The latter is evaluated by the equation

$$PO = \exp(-G\alpha_{hkl}) \tag{4}$$

where α_{hkl} is the angle between the scattering vector of the (hkl) reflection and the scattering vector of a fixed (preferred) reflection (with indices $(h'k'l')$ given in the input).[9] In some cases also a factor relative to the asymmetry of the diffraction peaks was introduced. This peak asymmetry was described by adopting two half-peak functions with different half-height widths H' and H'', with $H' - H'' = 2H(A/(2\theta)^2)$, with H the half-height width without asymmetry and A a parameter to be refined.

For the sake of simplicity, in order to not proliferate too much the number of parameters to be refined in the optimization procedure, the thermal parameters (assumed isotropic) of all the atoms were always kept constant at a value of 7 Å^2.

Refinement of the Crystalline Structure of STCO. The structural outcomes of the present investigation on STCO in the crystalline form are summarized in Tables 2 (for the refined structural parameters), 3 (for the refined fractional coordinates of the atoms in the asymmetric units), and 4 (for the refined nonstructural parameters). The symbols S_{xb} and $S_{z\Phi}$ in Table 2 represent the shift along x of the chain axis and along z of the center of the phenyl rings, in fractional coordinates, while d_c is the crystallographic density and d_o and d_a are the experimental densities of the crystalline portion and of the amorphous sample, respectively.

The results of the present analysis essentially confirm the data previously obtained in ref 4 and reported in Table 2 between squared parentheses for comparison. The most relevant difference is in the value of $S_{z\Phi}$, which is $\approx 1/4$ in the present treatment and $S_{z\Phi} = 0.263$ in ref 4.

In Figure 3 we show a comparison between the observed (curve e) and the calculated (curve c) X-ray powder diffraction profiles, while curve d is the difference profile. Curve a underlying curve c is the X-ray diffraction profile of the amorphous sample, suitably scaled.

In Figure 4 we plot the packing model of STCO, as refined in the present treatment. Also evidenced are the most relevant distances between nonbonded atoms. The values of these distances are all within the limits allowed

Table 3. Refined Fractional Coordinates of the Asymmetric Unit for STCO, pFSTCO, mMSTCO, and pMSTCO

	x/a	*y/b*	*z/c*
		STCO	
C1	0.100 (1)	0.172 (3)	0.303 (3)
C2	0.1268 (6)	0.314 (2)	0.156 (3)
C3	0.1057 (6)	0.201 (2)	−0.025 (3)
C4	0.2251 (6)	0.376 (2)	0.208 (3)
C5	0.2912 (7)	0.218 (3)	0.216 (5)
C6	0.3817 (7)	0.276 (3)	0.264 (6)
C7	0.4061 (8)	0.490 (3)	0.304 (5)
C8	0.3399 (9)	0.648 (3)	0.297 (6)
C9	0.2494 (8)	0.591 (2)	0.249 (5)
O1	0.094 (2)	0.007 (2)	−0.032 (3)
		pFSTCO	
C1	0.0898 (5)	0.179 (1)	0.320 (2)
C2	0.1157 (4)	0.3142 (7)	0.165 (2)
C3	0.0994 (4)	0.1901 (7)	−0.009 (2)
C4	0.2093 (4)	0.3859 (9)	0.207 (2)
C5	0.2755 (5)	0.233 (1)	0.223 (2)
C6	0.3615 (5)	0.299 (1)	0.261 (3)
C7	0.3814 (5)	0.518 (1)	0.283 (3)
C8	0.3152 (6)	0.671 (1)	0.266 (3)
C9	0.2291 (5)	0.605 (1)	0.228 (2)
O1	0.0942 (6)	−0.0056 (6)	−0.012 (2)
F1	0.4650 (6)	0.582 (2)	0.320 (4)
		mMSTCO	
C1	0.0875 (7)	0.182 (1)	0.599 (2)
C2	0.1057 (4)	0.3111 (2)	0.444 (2)
C3	0.0884 (4)	0.2005 (2)	0.269 (2)
C4	0.1949 (4)	0.3877 (7)	0.482 (2)
C5	0.2622 (4)	0.2573 (9)	0.503 (4)
C6	0.3444 (5)	0.328 (1)	0.538 (5)
C7	0.3592 (5)	0.529 (1)	0.551 (4)
C8	0.2919 (5)	0.659 (1)	0.530 (5)
C9	0.2097 (5)	0.5885 (8)	0.495 (4)
O1	0.076 (1)	0.0254 (6)	0.264 (2)
C10	0.4175 (5)	0.186 (2)	0.561 (8)
		pMSTCO	
C1	0.2938 (2)	0.4182 (3)	0.576 (5)
C2	0.3030 (2)	0.5595 (3)	0.418 (5)
C3	0.2917 (2)	0.4505 (3)	0.242 (5)
C4	0.3443 (2)	0.6203 (5)	0.436 (6)
C5	0.3716 (2)	0.467 (1)	0.412 (6)
C6	0.4097 (3)	0.523 (1)	0.428 (7)
C7	0.4204 (3)	0.732 (1)	0.469 (6)
C8	0.3931 (3)	0.885 (1)	0.494 (6)
C9	0.3551 (3)	0.8294 (8)	0.477 (6)
O1	0.2815 (2)	0.2661 (3)	0.235 (5)
C10	0.4617 (3)	0.793 (1)	0.487 (7)

Table 4. Refined Nonstructural Parameters

	STCO	pFSTCO	mMSTCO	pMSTCO
zero shift (deg)	−0.07 (1)	0.06 (1)	0.065 (7)	0.061 (5)
G (deg^{-1})	0.07 (1)	0.03 (1)		0.265 (9)
indices	(100)	(100)		(001)
profile function param				
U (deg^2)	6.3 (3)	12 (1)	9.4 (8)	0[a]
V (deg^2)	1.5 (4)	−1.9 (3)	−2.3 (1)	0[a]
dimens of the crystallites				
La (Å)	255 (21)	213 (8)	116 (4)	1.9×10^2 (1)
Lb (Å)	50 (2)	48 (1)	71 (2)	86 (3)
Lc (Å)	24 (2)	13.2 (3)	19.8 (6)	15.4 (4)
asym factor				
A (deg^2)	6 (2)		6 (1)	4.4 (9)

[a] This value is not refined.

by the sum of van der Waals radii of the atoms in question and are listed in Table 5.

Refinement of the Crystalline Structure of pFSTCO. The packing model for pFSTCO as determined in the present analysis is not too much different from the packing model proposed in the case of STCO. This is not surprising, since a fluorine atom is very small and the substitution of a hydrogen atom in the phenyl rings with a fluorine should not perturb too much the conformation of the chain, the packing of the chains in the crystalline form, and the dimension of the unit cell.

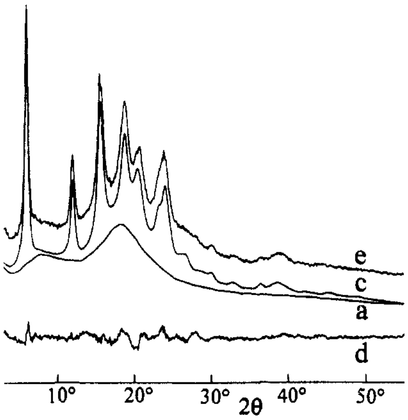

Figure 3. Comparison of the observed (curve e) and the calculated (curve c) powder diffraction profiles of STCO. Curve d is the difference profile. Curve a is the X-ray diffraction spectrum of an amorphous sample.

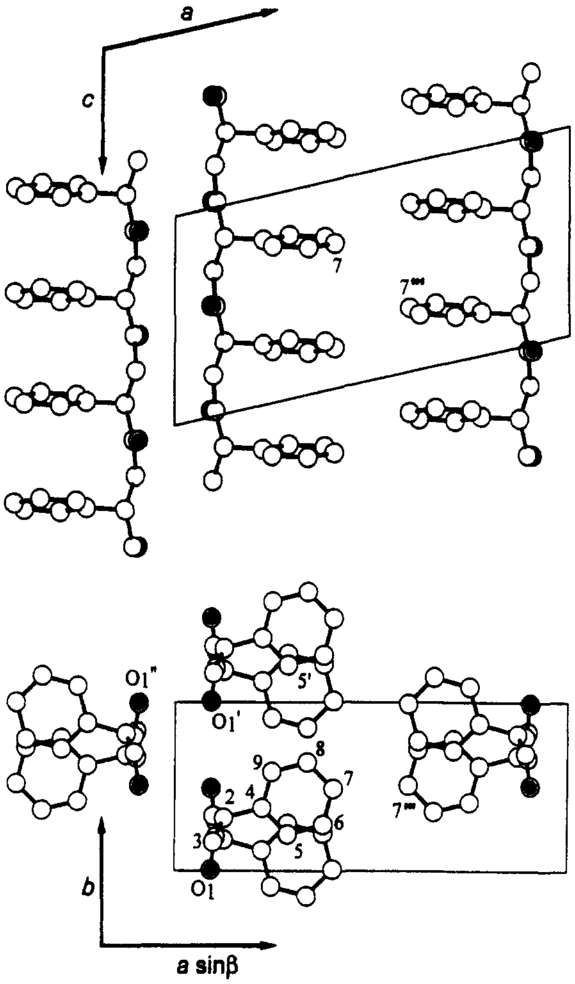

Figure 4. Refined packing model of STCO in the crystalline form, in *ab* and *ac* projections.

The results of these refinements are summarized in Tables 2 (for structural parameters), 3 (for the fractional coordinates of the atoms in the asymmetric unit), and 4 (for nonstructural parameters).

Figure 5 compares the calculated and the observed diffraction profiles and plots the difference profile. Figure 6 plots the packing model, while Table 5 lists the shortest distances between atoms belonging to adjacent chains.

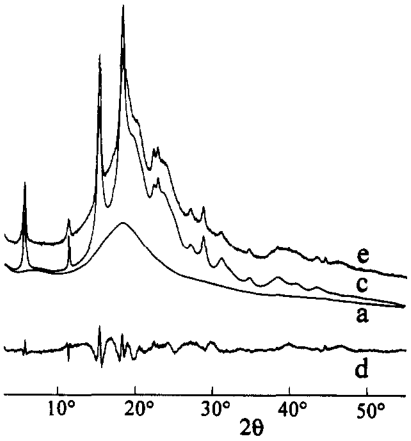

Figure 5. Comparison of the observed (curve e) and the calculated (curve c) powder diffraction profiles of pFSTCO. Curve d is the difference profile. Curve a is the X-ray diffraction spectrum of an amorphous sample.

Table 5. Distances between Atoms Belonging to Different Chains (See Figure 4 for STCO, Figure 6 for pFSTCO, Figure 8 for mMSTCO, and Figure 10 for pFSTCO)

STCO		pFSTCO	
bond	length (Å)	bond	length (Å)
$O1'$–$O1''$	3.0 [3.0]	O_1'–O_1''	3.0
$C8$–$C5'$	3.6 [3.9]	F_1–F_1'	3.0
C_7–C_7'''	3.7 [3.6]	$O1$–$C3''$	3.2
		$C8$–$C5'$	3.6
mMSTCO		**pMSTCO**	
bond	length (Å)	bond	length (Å)
O_1'–O_1''	4.2	O_1–O_1'	3.9
$C10'$–$C10'''$	3.9	$C10$–$C10'''$	4.6
$O1$–$C1''$	3.3	$O1$–$C1'$	3.4
$C8$–$C5'$	4.1	$C5'$–$C8''$	3.8

Refinement of the Crystalline Structure of mMSTCO. The first problem which such a polymer poses is the reciprocal position of methyl groups along the chain which are pendant from the phenylene rings in a meta position.

Under assumption that the glide symmetry is maintained, the refinements have been done in the space group $P2_1/c$, by placing the methyl groups in the meta outward positions, in both meta positions with occupation factor 0.5, and in the meta inward positions of the phenylene rings. The agreement factors obtained in the three cases were $R2' = 25\%$ when methyl groups are in the outward positions $R2' = 16\%$ when the methyl groups are present in both the meta positions (with occupation factors 0.5), and $R2' = 12\%$ when methyl groups are in meta inward positions. This clearly indicates that the latter model is the most probable for the mMSTCO polymer chain.

The chain conformation is very similar to that found for STCO and pFSTCO in the crystalline structure (see Table 2).

The most relevant difference in the packing model is in the different quotes along z of the phenylene rings, being in this latter case $S_{z\Phi} \approx {}^1/_2$, while in the case of STCO and pFSTCO it is $S_{z\Phi} \approx {}^1/_4$. Positioning phenylene rings at $S_{z\Phi} \approx {}^1/_4$ increases the calculated intensities of $\bar{1}11$ and 111 reflections (at $2\theta \approx 18°$ and 19°) which are not observed in the experimental spectrum. The calculated intensities of these two reflections are minima when $S_{z\Phi} \approx {}^1/_2$.

Table 3 lists the fractional coordinates of the asymmetric unit and Table 4 the refined nonstructural parameters. Figure 7 compares the calculated and the observed diffraction profiles and plots the difference profile. Figure 8 plots the packing model, while the shortest distances between atoms belonging to adjacent chains are listed in Table 5.

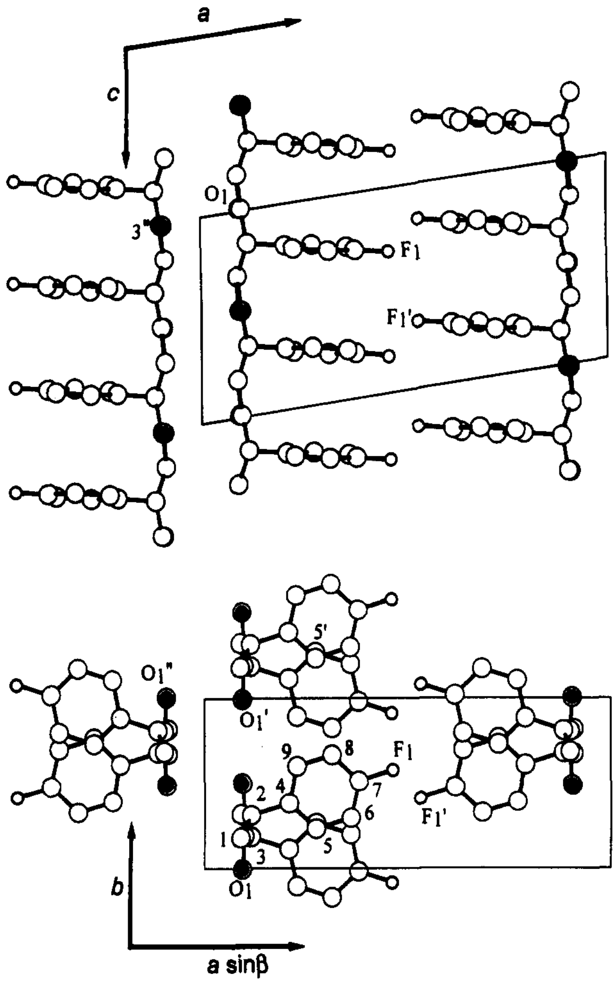

Figure 6. Refined packing model of pFSTCO in the crystalline form, in *ab* and *ac* projections.

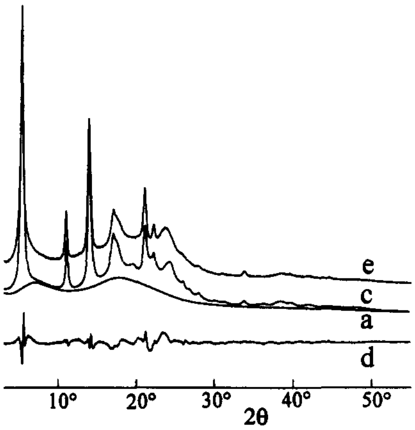

Figure 7. Comparison of the observed (curve e) and the calculated (curve c) powder diffraction profiles of mMSTCO. Curve d is the difference profile. Curve a is the X-ray diffraction spectrum of an amorphous sample.

Refinement of the Crystalline Structure of pMSTCO. The X-ray powder diffraction profile of pMSTCO presents a problem. If we consider the first five most intense diffraction peaks at $2\theta = 5°, 9.9°, 14.3°, 16°$, and 18.7°, it is found that they cannot be indexed with a monoclinic unit cell in the same way as STCO, pFSTCO, and mMSTCO (having Miller indices (100), (200), (110), (210) + (011) + ($\bar{1}$11) and (111), respectively). Many other different indexings have been attempted still using a monoclinic cell, indicating that it is possible to index the reflections all over the spectrum, with a monoclinic cell

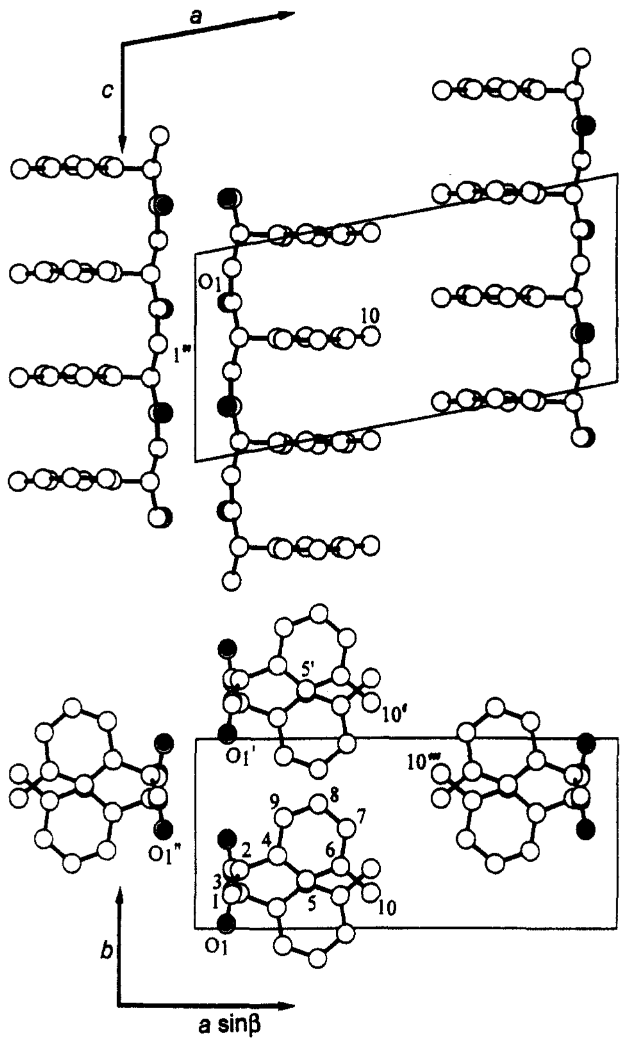

Figure 8. Refined packing model of mMSTCO in the crystalline form, in *ab* and *ac* projections.

having *a* in the range 18–20 Å and *c* in the range 7.50–7.60 Å, only in the hypothesis that a ($h0l$), with $l = 2n + 1$, reflection should be present and with strong intensity, possibly indicating a $P2_1$ space group symmetry. This leads to an inconsistency as far as the intensity, however: a syndiotactic chain like those of the polymers under study in a nearly *trans* planar form would not allow for strong ($h0l$) reflections with $l = 2n + 1$, even in the case that the glide symmetry is relaxed.

A different indexing is possible, however, still assuming a monoclinic symmetry if a doubled *a* axis and a C-centered unit cell are assumed. In the hypothesis that the glide symmetry of the chains is preserved, the space group $C2/c$ should be possible. These hypotheses have been confirmed in our calculations.

The refined parameters are reported in Tables 2 (structural parameters), 3 (fractional coordinates of the atoms in the asymmetric unit), and 4 (nonstructural parameters).

Figure 9 compares the calculated and the observed diffraction profiles and plots the difference profile, and Figure 10 plots the packing model, while the shortest distances between atoms belonging to adjacent chains are listed in Table 5.

It is worth noting that the packing model for this copolymer is quite different from those proposed for the other copolymers in this paper. Indeed the best agreement between calculated and experimental X-ray powder diffraction data is found for a model where the phenylene rings belonging to different chains at the *bc* interface are placed one in front to the other in the projection perpendicular to *c*, at variance with the preceding cases, where the symmetry implies for the phenyl/phenylene rings facing at the *bc* interface a shift of **b**/2 in the *ab* projection.

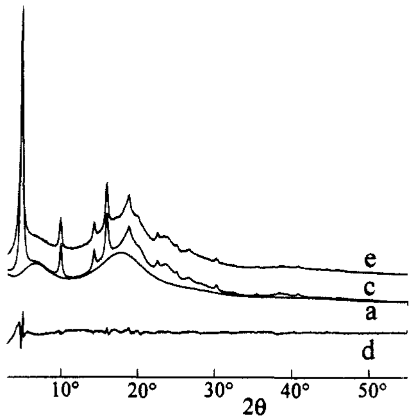

Figure 9. Comparison of the observed (curve e) and the calculated (curve c) powder diffraction profiles of pMSTCO. Curve d is the difference profile. Curve a is the X-ray diffraction spectrum of an amorphous sample.

Conclusions

The crystal structure solution and refinement (based on the X-ray powder diffraction profile) of a series of copolymers of styrene and styrene derivatives alternating with carbon monoxide gives clear evidences, not easily otherwise recognizable, of the syndiotactic nature of the studied copolymers.

All the studied copolymers crystallize with the chain backbone in the nearly extended conformation, with the dihedral angles ϑ_1 and ϑ_2 comprised in the range 160° ÷ 170°, $\vartheta_3 \approx 150°$, and ϑ_4 in the *gauche* state, giving a periodicity *c* in the range 7.50 ÷ 7.60 Å.

Roughly speaking also the packing models are very similar. We recall that STCO, pFSTCO, and mMSTCO crystallize in the space group $P2_1/c$, while pMSTCO crystallizes in the space group $C2/c$, with a doubled *a* axis. In all crystal structures the chains are arranged to form layers parallel to the *bc* plane piled along *a*. The packing models for the various copolymers present the most relevant differences in the stacking along *a* of these *bc* layers. These differences are only marginal between the crystal structure of STCO and pFSTCO. In the case of mMSTCO, the center of the phenylene rings is located very close to the quote along *c* of the inversion centers (at 0 and $^1/_2$), at variance with the crystal structures of STCO and pFSTCO, which show the center of the phenyl and phenylene rings in positions very close to the quote along *c* of 2_1 axes ($^1/_4$ and $-^1/_4$). The most relevant differences are found in the case of pMSTCO, showing the phenylene rings still at the same heights of inversion centers in $C2/c$ symmetry (0 and $^1/_2$), but a completely different way of facing the *bc* interface of the phenylene rings belonging to different *bc* layers (compare Figure 10 with Figures 4, 6, and 8).

It is worth noting (see Table 4) that the refined values of the crystallite dimensions along *a*, *b*, and *c* (*La*, *Lb*, *Lc*), although only indicative of the true mean dimensions (see before), suggest that the dimensions of the crystallites along *c* should be very short, while the crystallites should include about 10 cells along *a* and *b* directions.

A fairly good agreement between calculated and experimental profiles was obtained for all the copolymers. Discrepancies still present originate mostly because we

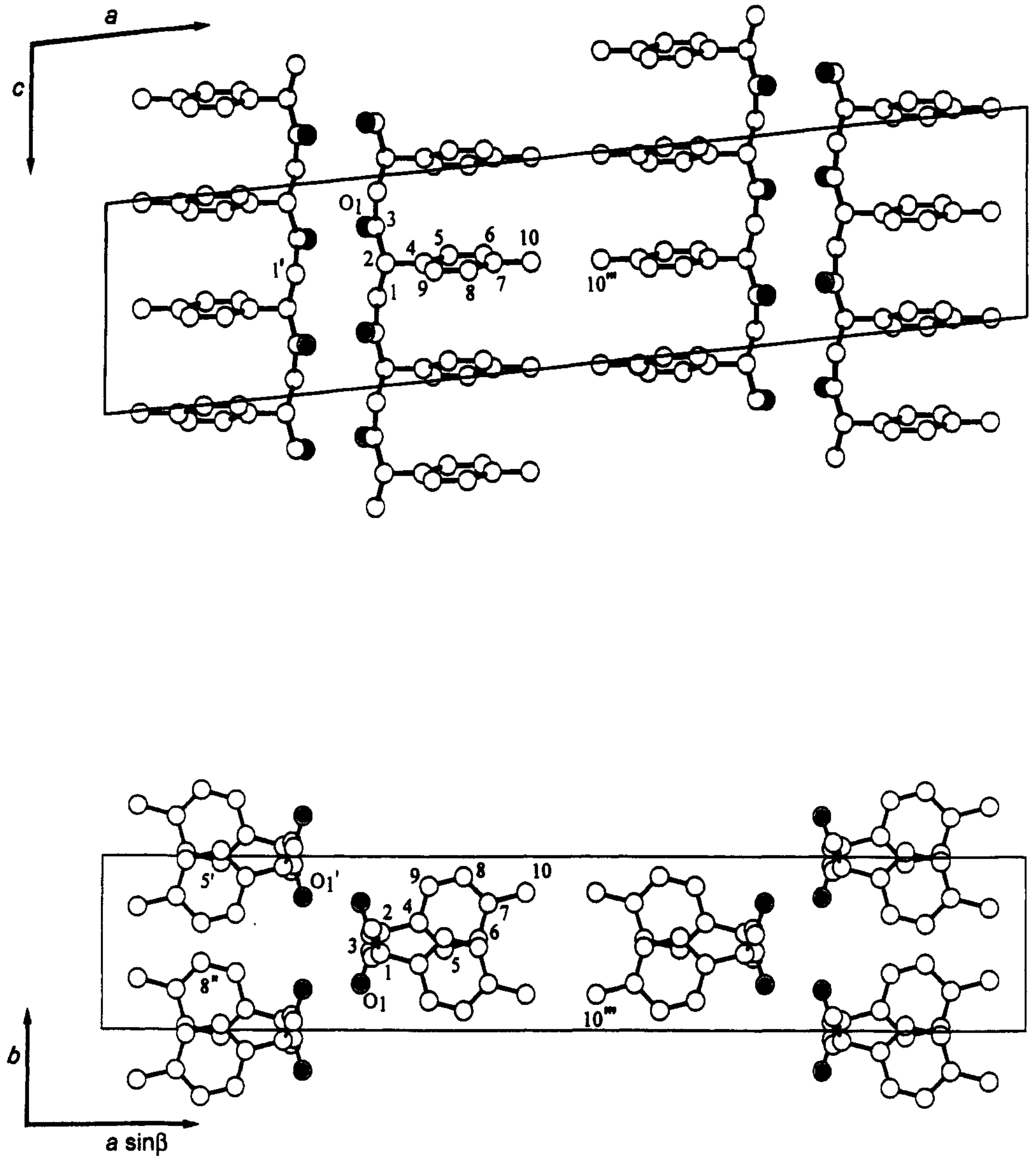

Figure 10. Refined packing model of pMSTCO in the crystalline form, in *ab* and *ac* projections.

refined a structural model under constraints. On the other hand, experimental data can allow only this kind of refinement approach, as just discussed in the original paper by Immirzi.[6]

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