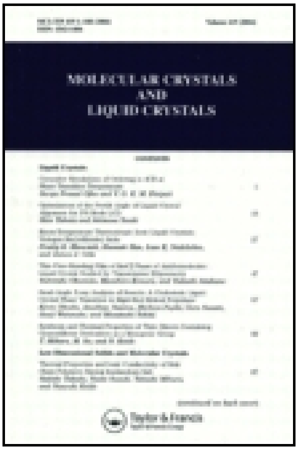

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SYNTHESIS, POLYMERIZATION AND X-RAY STRUCTURE (MONOMER AND POLYMER) OF THE UNSYMMETRICAL DIACETYLENE pTS-pFBS

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Abstract Some preliminary results on the new unsymmetrical diacetylene pTS-pFBS are presented. pTS-pFBS is the disubstituted molecule R-C≡C-C≡C-R' where R is CH_3-Ph-SO_2-CH_2O and R' is F-Ph-SO_2-CH_2O, R and R' being respectively the side groups of the well known symmetrical diacetylenes pTS and pFBS. Synthesis, crystallization and thermal polymerization data are described. The X-ray crystal structures of monomer and polymer pTS-pFBS had been determined at 143 K and are discussed in terms of particular reflections.

INTRODUCTION

Some diacetylenes, R-C≡C-C≡C-R', where the side groups R and R' are identical or different, can be converted via topochemical solid state reactions into macroscopic crystals of conjugated polymer chains extended along crystallographic directions[1,2]. The mechanism and kinetics of solid state polymerization of symmetrical diacetylenes like pTS (CH_3-Ph-SO_2-CH_2O) and pFBS (R=R'=F-Ph-SO_2-CH_2O) have been intensively studied[1-3].

The structures of pTS and pFBS monomer and polymer crystals are isomorphous at room temperature, and down to 220 K ($P\,2_1/c$, $Z = 2$)[10,11]. pTS monomer exhibits an incommensurate phase in the range 155 to 195 K[4,5]. Its low temperature structure, as well as that of the polymer (which shows a phase transition at 190 K), remains $P\,2_1/c$ with a doubling of the unit cell ($Z = 4$) and two inequivalent sites. In contrast pFBS monomer does not display any phase transition. The structure and reactivity differences between pTS and pFBS have recently been investigated in detail [6].

There are only a few data on the solid-state properties of unsymmetrical diacetylenes, $R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}R'$. As a part of a general study of chiral and/or dissymetrical diacetylenes, we report here some preliminary results on the properties of the new diacetylene pTS-pFBS which combines the side group of pTS with that of pFBS. This compound was independently and simultaneously synthesized in Paris[7] and in Bayreuth[8].

SYNTHESIS

For the preparation of pTS-pFBS (6-(p-toluenesulfonyloxy)-2,4-hexadiynyl p-fluorobenzenesulfonate), 2,4-hexadiyne-1,6- diol (HDD) was first monoesterified in the presence of one equivalent of p-toluenesulfonyl chloride to give the monoester $CH_3\text{-}Ph\text{-}SO_2\text{-}OCH_2\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_2OH$. The latter was easily separated by chromatography from the residual diol HDD and the diester. Next, the monoester, on reaction with p-fluorobenzenesulfonyl chloride, afforded pTS-pFBS in good yield[7]. The purification was effected by chromatography over silica gel and recrystallization. Differential scanning calorimetry (DSC) gave m.p. = 71°C and enthalpy of fusion $\Delta H_f = 33{,}6$ kJ/mole (Figure 1).

POLYMERIZATION DATA

The isothermal polymerization of polycrystalline samples of pTS-pFBS was studied by using a differential microcalorimeter (Perkin-Elmer DSC-2) connected to a HP 86 computer for data acquisition and processing, as previously described for pTS[9] . The induction period was found to last ca. 4 times longer than that of pTS, about 60 H at 60°C and 28 H at 67°C (Figure 1). The polymerization was complete after ca. 50 H at 67°C, and the rate constant during the autocatalytic process was estimated to be ca. 1.4 10^{-4}s (about half the value found for pTS at the same temperature [9]). The polymerization enthalpy is ΔH_p = -36±2 kcal/mole (-150.6±8 kJ/mole), a value probably slightly underestimated due to the poor quality of the data gathered during the induction period.

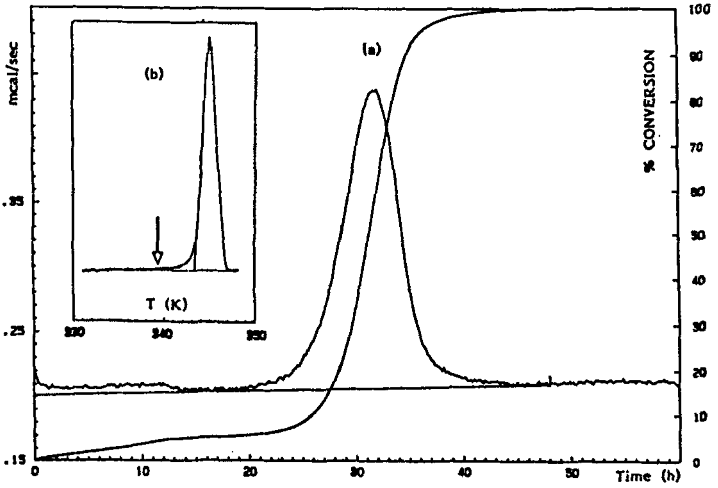

Figure 1. (a) Isothermal polymerization exotherm and % monomer conversion, for a 71-mg polycrystalline sample at 67°C; (b) melting endotherm of monomer at a scanning rate of 1.25 K/min (the arrow indicates the temperature at which the polymerization experiment shown in (a) was effected.

CRYSTAL STRUCTURE DETERMINATION OF MONOMER AND POLYMER pTS-pFBS

In a first stage crystals suitable for structural study were grown from acetone at 4°C and small plates of about (0.4 x 0.3 x 0.3) mm were used. After that (see discussion), other crystals (synthesized in Paris [7], and in Bayreuth by Strohriegl[8] by a slightly different method) were grown in ethylacetate-n-hexane (1/1) solutions and used for structural determination. The monomer was polymerized by annealing at ca. 335 K for at least 60 H. The structures were studied on a Enraf-Nonius CAD 4 automatical diffractometer and data were processed with a PDP8 computer.

The low-temperature structures of the monomer and polymer were studied at about 145 K (where the polymerization is sufficiently slow to allow the data collection for the monomer). Polymer structure was also recorded at room temperature. The unit cell parameters were determined from the angles of 25 strong reflections and the structures were solved by direct methods. As the case may be,the hydrogen atoms were refined (297 variables in the group Pc ; 155 variables in the group $P\,2_1/c$) or not (2 x 126 variables in the group Pc), after location by Fourier difference.

For pTS-pFBS crystals grown from acetone (origin 1), the best full-matrix refinements (alternative refinements of each half molecule) gave the following results when calculations are made in the monoclinic group Pc (Z=2) :

*Monomer at 143 K (1427 reflections with $I > 3\sigma(I)$ for 297 variables)

- hypothesis 1 (fig. 2-a and paper [7]) : $R = 0.039$ and $R_w = 0.038$
- hypothesis 2 (fig. 2-b) : $R = 0.045$ and $R_w = 0.043$

*Polymer at 293 K (1486 reflections with $I > 3\sigma(I)$ for 297 variables)

- hypothesis 1 : $R = 0.043$ and $R_w = 0.037$

*Polymer at 143 K (1653 reflections with $I > 3\sigma(I)$ for 297 variables)

- hypothesis 1 : $R = 0.044$ and $R_w = 0.042$;

For crystals grown from ethylacetate-n-hexane 1/1 (origin 2) whatever the synthesis [7,8], the best full-matrix refinements (alternative refinements of each half molecule) gave the following results when calculations are made in the group Pc ($Z = 2$) :

*Monomer at 146 K (1347 reflections with $I > 3\sigma(I)$ for 2 x 126 variables)

- hypothesis 1 : $R = 0.038$ and $R_w = 0.039$
- hypothesis 2 : $R = 0.037$ and $R_w = 0.035$

*Polymer at 293 K (1203 reflexions with $I > 3\sigma(I)$ for 2 x 126 variables)

- hypothesis 1 : $R = 0.049$ and $R_w = 0.047$
- hypothesis 2 : $R = 0.049$ and $R_w = 0.048$

When calculations are made in the monoclinic group $P\,2_1/c$ the best refinements give the following results :

*Monomer at 146 K (155 variables) : $R = 0.038$ and $R_w = 0.036$

*Polymer at 293 K (155 variables) : $R = 0.054$ and $R_w = 0.053$.

In all events, the R values for the monomer are slightly lower than for the polymer. It is possible that solid state polymerization, even if it is considered complete, is accompanied by the development of defects correlated with the presence of domains in the monomer crystals (see discussion).

The lattice parameters of pTS-pFBS monomer and polymer crystals from origins 1 and 2 are listed in table 1.

The comparison of these data with the corresponding best known values for pTS and pFBS monomer and polymer crystals [7] shows that the lattice parameters of pTS-pFBS

TABLE I Lattice parameters of crystals from monomer pTS-pFBS and polymer from corresponding monomer

pTS-pFBS grown from acetone (origin 1)

Pc Z=2	monomer 143 K	polymer 143 K	polymer 293 K
a/Å	14.246(9)	14.110(5)	14.228(6)
b/Å	5.115(2)	4.907(2)	4.902(2)
c/Å	14.356(7)	14.437(5)	14.521(9)
β/d°	116.48(6)	116.27(3)	116.02(5)
V/Å^3	936.3(7)	896.3(5)	911.4(8)
*μ/cm^{-1}	3.14	3.28	3.23

pTS-pFBS from ethylacetate-hexane (origin 2)

Pc Z = 2	monomer 145 K		polymer 293 K
a/Å	14.311(6)		14.223(6)
b/Å	5.116(3)		4.901(2)
c/Å	14.351(9)		14.520(7)
β/d°	116.67(4)		115.92(4)
V/Å^3	937.1(5)		910.4(7)
*μ/cm^{-1}	3.23		3.20

* linear absorption coefficient at $\theta = 0$.

are almost exactly the average of the corresponding values of pTS and pFBS. This seems to be consistent with polymerization kinetics, showing that pTS-pFBS is intermediate in reactivity between pTS and pFBS. The same remark holds for the angle between the diacetylene axis and the b direction (the stacking axis) in pTS-pFBS monomer (44.5°) and polymer (14°).

DISCUSSION

Preliminary studies made on pTS-pFBS crystals of the origins 1 and 2 (on a diffractometer for monomer and polymer, on Weissenberg photographs for polymer) showed the presence of (0k0) reflections (k = 2n + 1) without diffusion (030 in the monomer, 010 and 030 in the polymer), slightly weaker for crystals from origin 2 but with $F_0 \sim F_c$ when refinement calculations are made in the group Pc. This observation and the fact that the scattering pattern is asymmetric lead us to conclude that the structures belong to the non-centrosymmetric monoclinic group Pc.

The structures can be solved in the group Pc and the preliminary refinements can be performed without difficulty. However it is difficult to accurately interprete the Fourier Difference maps around methyl groups and fluor atoms. In addition, the anisotropic refinements lead to local deformations of the molecule, probably on account of the correlations due to the pseudosymmetry of the pattern. It is possible to reduce partially these deformations with alternative refinements of each half molecule.

As we noticed previously for the crystals from origin 1, the best full-matrix refinements give a significant preference for the hypothesis 1 [7] (Fig. 2-a) rather than 2 where methyl groups and fluor atoms are inverted (Fig. 2-b). On the other hand, in the case of crystals from origin 2 (whathever the synthesis [7,8]) it is not possible to make a warrantable choice between the two hypotheses. So it is possible to refine in the monoclinic group P 2_1/c (where the pattern is half a molecule and methyl group and fluor atom are taken superimposed with multiplicity of 0.7 for the fluor). In this case, there are no more local geometrical deformations of the molecule because there is no more reason to have correlations.

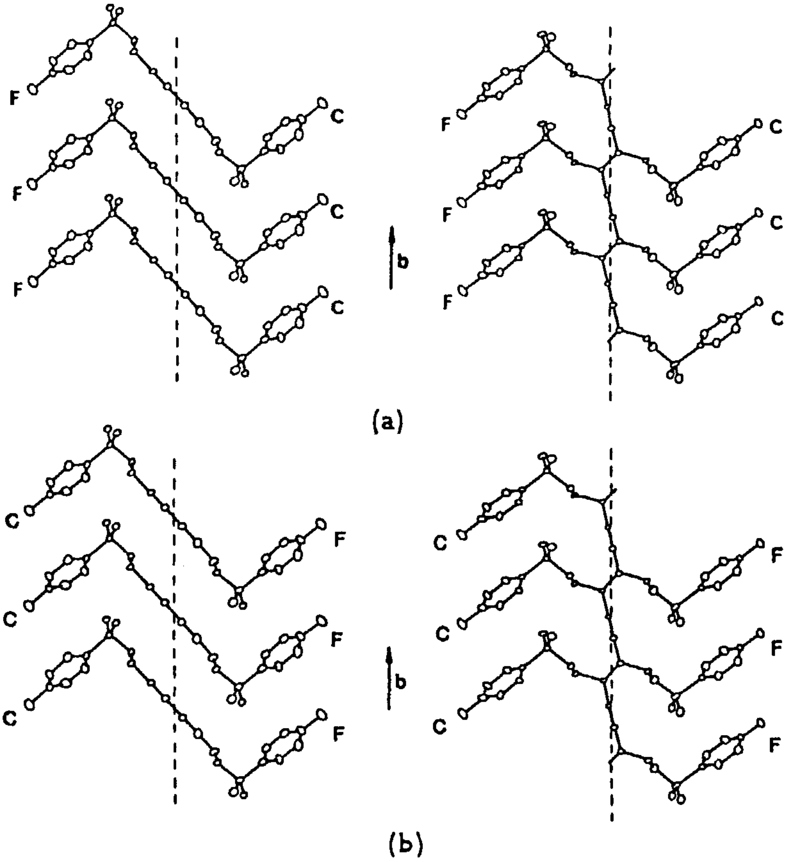

FIGURE 2. Crystal packing of pTS-pFBS monomer and polymer crystals in :

- hypothesis 1 (a) : fluor atoms on the left side
- hypothesis 2 (b) : fluor atoms on the right side.

As a preliminary conclusion, it may be considered that pTS-pFBS monomer and polymer structures belong to the non-centrosymmetric monoclinic group Pc (Z = 2) but it seems possible that crystals are formed with two types of domains with the molecular packings shown on Fig. 2-a and Fig. 2-b. One possibility would be sheet-shaped domains lying parallel to plane (b,c), which corresponds to the natural and easiest cleavage faces[1,2]. Another possibility would be domains placed side by side in the crystal. In connection with that, it is interesting to note that monomer crystals from origin 1 are often almost entirely slightly orange with in color remaining part, even though crystals from origin 2 show juxtaposition of orange and pink zones (spectroscopic studies are in progress in Bayreuth [12]). Each type of domain should not be systematically present in the ratio one to one, as it seems to be the case of the crystals from origin 1.

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