

Study of Reactive Diacetylenes: Structure of Monomer and Polymer pFBS Crystals

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Abstract

The crystal and molecular structures of the monomer diacetylene bis(*p*-fluorobenzenesulfonate) [2,4-hexadiynylene bis(*p*-fluorobenzenesulfonate), pFBS, C₁₈H₁₂F₂O₆S₂, *M_r* = 426.4], and of the corresponding polymer, were determined. Both crystals are monoclinic, *P*2₁/*c*, *Z* = 2. For the monomer, studied by neutron diffraction ($\lambda = 1.263 \text{ \AA}$) at 221 K, *a* = 13.932 (7), *b* = 5.147 (3), *c* = 14.062 (9) Å, $\beta = 114.32 (4)^\circ$, *V* = 919 (1) Å³, *D_x* = 1.54 g cm⁻³, final *R* = 0.056, *wR* = 0.061 for 1180 independent reflections with *I* ≥ 1.5σ(*I*). Unit-cell parameters and thermal expansion were measured between 200 and 300 K. Differences in packing and reactivity between pFBS and pTS [Aimé, Lefebvre, Bertault, Schott & Williams (1982). *J. Phys. (Paris)*, **43**, 307–321] monomers are discussed. For the polymer studied by X-rays at 295 K, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 3.4 \text{ cm}^{-1}$, *a* = 13.957 (6), *b* = 4.914 (2), *c* = 14.103 (6) Å, $\beta = 113.56 (4)^\circ$, *V* = 886.5 (6) Å³, *D_x* = 1.598 g cm⁻³, final *R* = 0.033 for 1928 unique reflections, *wR* = 0.031 for 1493 reflections. The polymer chain geometry is identical to that of poly-pTS, a typical enyne structure. Data taken on a partially reacted crystal containing ca 18% polymer show it to be a well ordered mixed monomer–polymer crystal.

Introduction

Diacetylenes are molecules of general formula *R*–C≡C–C≡C–*R'*, where *R* and *R'* – so-called side groups – may be a variety of molecular groups. The initial motivation, and still a major one, for the study of diacetylene crystals is that they are the only practical route to macroscopic polymer single crystals (Bässler, 1984; Bloor & Chance, 1985; Enkelmann, 1984; Sixl, 1984). Polydiacetylene crystals contain long, perfectly ordered, one-dimensional conjugated chains. High-quality polymer crystals are obtained *via* a topochemical reaction leading from a monomer single crystal to the polymer crystal continuously through

monomer–polymer solid solutions, in which the reaction proceeds homogeneously. The course of the reaction (that is, the kinetics and the polymer molecular-weight distribution) is determined by the crystal structure, the elastic constants, and their variation with polymer content. Molecular packing in the monomer crystal is mainly determined by the side groups, and a suitable choice ensures that, although the reacting C atoms move by more than 1 Å, most atoms in the unit cell are only slightly displaced, allowing the lattice constants to change smoothly from the monomer to the polymer values (Enkelmann, 1984), and the crystallinity to be preserved.

The most thoroughly investigated diacetylene is pTS, in which *R* and *R'* are CH₃–C₆H₄–SO₃–CH₂–. Its thermal polymerization rate increases dramatically when the polymer content exceeds about 10%. Several of the models proposed to explain the unusual kinetics, notably the ‘elastic strain’ theory of Baughman (Baughman, 1978; Baughman & Chance, 1980), are discussed in Bässler’s (1984) review. The reactivity of diacetylenes is, however, far from being well understood, and predicting reactivity and polymerization kinetics from crystal structure remains a challenge.

In the present paper, the crystal and molecular structure of monomer and polymer pFBS are studied (Yee, 1979). Here *R* and *R'* are F–C₆H₄–SO₃–CH₂–, so that pFBS differs from pTS solely by replacement of the terminal methyl groups by F atoms. We believe the study is of interest for three main reasons.

First, it is interesting to study the effect on reactivity of such small molecular changes. pFBS shows the same general reaction kinetics as pTS, but the actual rate is about one order of magnitude smaller. pTS and pFBS belong to the same space group, have similar unit-cell dimensions (Yee, 1979; Enkelmann, 1983), and a good knowledge of the monomer structure would help in understanding the reactivity differences.

Secondly, although pTS has been used as a standard material for detailed studies, phase changes below room temperature, in the monomer as well as the polymer,

greatly complicate low-temperature spectroscopic measurements (Bloor & Preston, 1977; Sebastian & Weiser, 1979). pFBS does not show these phase changes (Chance, Yee, Baughman, Eckhardt & Eckhardt, 1980). A comparison of the two materials might give some insight into the origin of pTS phase transitions. More important, poly-pFBS is now more often used as a standard polydiacetylene in spectroscopic studies (Sixl & Warta, 1985), so again an accurate structure determination would be useful.

Thirdly, this study is relevant to the determination of polydiacetylene chain geometry in the crystal. Two different (extreme) conjugated structures can be written for a polydiacetylene chain: an 'acetylenic' or enyne structure, and a butatriene one (Enkelmann, 1984; Schott & Wegner, 1987). Since polydiacetylene crystals are usually obtained from the corresponding monomer single crystal *via* continuous unit-cell change with only small atomic movements, that is, a very special reaction path, the polymer crystal structure obtained is a local minimum of crystal energy, not necessarily the lowest minimum. The side groups play a role in the total crystal energy, so that polymer chains may conceivably have different geometries in different polydiacetylene crystals. Poly-pTS (Kobelt & Paulus, 1974) and several other polydiacetylenes have an enyne geometry, that is a succession of double, single, triple bonds, but several published structures differ significantly from it (Enkelmann, 1984; Schott & Wegner, 1987). Among the latter is poly-pFBS (Enkelmann, 1983); this is surprising since the optical properties of poly-pTS and poly-pFBS are very similar, except for the site splitting (Bloor & Preston, 1977; Schott, Batallan & Bertault, 1978; Sebastian & Weiser, 1979) associated with the low-temperature phase transition in poly-pTS. One would have expected similar chain geometries; hence, reinvestigation of the poly-pFBS structure may be useful.

Experimental

The material

pFBS monomer was first synthesized and studied by Yee (1979). Together with pTS-pFBS mixed crystals, it was further studied by Enkelmann (1983) who reported the crystal and molecular structure of pFBS monomer at 110 K and of pFBS polymer at 295 K. A low temperature was used in the studies of the monomer – as was done before on pTS (Enkelmann & Wegner, 1977) – to slow down the polymerization induced by the X-ray beam.

In the present work, pFBS was prepared from *p*-fluorobenzene sulfonyl chloride and hexadienediol by the method of Yee (1979), and purified by recrystallization and chromatography. The resulting white powder was used as starting material for crystal growth, by slow evaporation of an acetone solution

under argon gas in the dark at 277 K. The resulting platelets were colorless or faintly pink colored, thus they contained almost no polymer – much less than nominal 'pTS monomer' – and they did not contain pale orange spots, which are often seen in pFBS crystals. The origin of this orange color, which is not observed in pTS, is unknown.

pFBS polymer was prepared by thermal polymerization in the dark at 333 K. An isothermal polymerization run at 336.7 K in a Perkin-Elmer DSC2 microcalorimeter confirmed that the polymerization kinetics of our product are identical to those observed by Yee (1979) and Enkelmann (1983).

Neutron diffraction study of pFBS monomer

The relatively low thermal reactivity of pFBS monomer would permit a room-temperature study. However, for easier comparison with previous work on pTS monomer (Aimé, Lefebvre, Bertault *et al.*, 1982), the data were collected at 220 K. A colorless trapezoidal crystal, approximately $4 \times 2 \times 1$ mm, was mounted on the four-circle neutron diffractometer D8 at ILL, Grenoble. Lattice parameters were measured using 18 reflections in the range $14 < \theta < 52^\circ$. 1265 independent reflections, with $(\sin\theta)/\lambda \leq 0.697 \text{ \AA}^{-1}$ and maximum $h, k, l = 21, 8, 22$, were collected. Intensities of standard reflections did not change during the measurements. 1180 reflections with $I \geq 1.5\sigma(I)$ were used and given equal weight. No absorption correction was applied. Program XRAY72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for structure refinement, with Fermi lengths 0.665 for C, 0.566 for F, -0.374 for H, 0.580 for O and 0.28 for S (Koester, 1977). After introduction of anisotropic thermal factors for all atoms, the final reliability values were $R = 0.056$ and $wR = 0.061$.

Unit-cell dimensions were determined at several temperatures between 200 and 300 K, using 16 intense reflections throughout reciprocal space, $14 < \theta < 52^\circ$, on the same diffractometer.

X-ray diffraction study of pFBS polymer

A crystal plate, $0.5 \times 0.4 \times 0.15$ mm, was polymerized thermally at 333 K (brown color with golden metallic lustre) and studied at room temperature by X-ray diffraction, using an Enraf-Nonius CAD-4 diffractometer, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\omega/2\theta$ scan ($D_x = 1.60 \text{ g cm}^{-3}$). Unit-cell parameters were determined by least-squares refinement of the setting angles for 25 reflections ($\theta_{\text{max}} = 20^\circ$). 2248 reflections were measured and 1493 independent reflections [$I > \sigma(I)$, $R_{\text{int}} = 0.014$, 146 parameters] were used for $2\theta \leq 54^\circ$, $(\sin\theta)/\lambda = 0.639 \text{ \AA}^{-1}$ maximum $h, k, l = 17, 6, \pm 18$; standard reflections: 113, 300, 411; intensity variation $\pm 0.05\%$ with no appreciable decay during the measurements. The structure was solved by direct methods.

Table 1. Monomer unit-cell dimensions

	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	Ref.
pFBS						
221 K	13.932	5.147	14.062	114.32	919	(1)
295 K	13.992	5.187	14.091	114.20	933	(1)
295 K	13.94	5.18	14.09	114.1	929	(2)
110 K	13.89	5.07	13.93	118.0	866	(3)
pTS						
221 K	14.630	5.133	14.845	118.55	979	(4)
295 K	14.656	5.178	14.942	118.81	994	(5)

References: (1) this work; (2) Yee (1979); (3) Enkelmann (1983); (4) Aimé, Lefebvre, Bertault *et al.* (1982); (5) Kobelt & Paulus (1974).

Table 2. Atomic positions and equivalent isotropic thermal parameters for pFBS monomer and polymer

	x	y	z	B_{eq} (Å ²)
(a) pFBS monomer at 221 K				
S	0.7298 (4)	0.2499 (10)	0.3966 (5)	3.16
F	0.9222 (4)	0.9661 (10)	0.2071 (4)	7.14
O1	0.6704 (2)	0.4335 (5)	0.4455 (2)	3.42
O2	0.6542 (2)	0.0969 (5)	0.3161 (3)	4.17
O3	0.8090 (3)	0.1302 (6)	0.4855 (3)	4.58
C1	0.5150 (2)	0.9058 (5)	0.4748 (2)	3.41
C2	0.5412 (2)	0.7401 (5)	0.4293 (2)	3.56
C3	0.5720 (2)	0.5447 (4)	0.3730 (2)	3.36
C4	0.7875 (2)	0.4661 (4)	0.3387 (2)	2.91
C5	0.8733 (2)	0.6134 (5)	0.4040 (2)	3.69
C6	0.9190 (2)	0.7832 (5)	0.3581 (2)	4.28
C7	0.8779 (2)	0.8015 (5)	0.2515 (3)	4.50
C8	0.7931 (2)	0.6572 (7)	0.1851 (3)	5.06
C9	0.7476 (2)	0.4855 (6)	0.2314 (2)	4.02
H3A	0.5137 (4)	0.3900 (11)	0.3465 (6)	5.99
H3B	0.5836 (5)	0.6374 (13)	0.3089 (5)	6.13
H5	0.9018 (5)	0.5938 (14)	0.4875 (5)	6.32
H6	0.9892 (5)	0.8980 (15)	0.4052 (7)	7.79
H8	0.7645 (7)	0.6794 (2)	0.1024 (6)	8.87
H9	0.6817 (5)	0.3647 (15)	0.1838 (5)	6.83
(b) pFBS polymer at 295 K				
S	0.72372 (3)	0.25141 (9)	0.40505 (3)	3.410 (8)
F	0.9170 (1)	0.9704 (4)	0.2058 (1)	8.90 (4)
O1	0.66641 (8)	0.4417 (3)	0.45660 (8)	3.44 (2)
O2	0.6470 (1)	0.0911 (3)	0.3276 (1)	4.71 (3)
O3	0.8035 (1)	0.1258 (3)	0.4908 (1)	5.44 (3)
C1	0.5039 (1)	0.8801 (3)	0.4936 (1)	2.41 (3)
C2	0.5147 (1)	0.5992 (3)	0.4747 (1)	2.26 (3)
C3	0.5598 (1)	0.5302 (3)	0.3969 (1)	2.76 (3)
C4	0.7805 (1)	0.4721 (4)	0.3451 (1)	2.90 (3)
C5	0.8709 (1)	0.6105 (4)	0.4049 (1)	3.81 (4)
C6	0.9168 (2)	0.7796 (4)	0.3566 (2)	5.01 (5)
C7	0.8711 (2)	0.8051 (5)	0.2517 (2)	5.06 (4)
C8	0.7835 (2)	0.6738 (6)	0.1927 (1)	5.51 (5)
C9	0.7358 (2)	0.5028 (5)	0.2388 (1)	4.30 (4)
H3A	0.522 (1)	0.382 (4)	0.354 (1)	4.
H3B	0.556 (1)	0.687 (4)	0.352 (1)	4.
H5	0.903 (1)	0.588 (4)	0.478 (1)	4.
H6	0.970 (1)	0.862 (4)	0.390 (1)	4.
H8	0.750 (1)	0.688 (4)	0.127 (1)	4.
H9	0.677 (1)	0.414 (4)	0.201 (1)	4.

After isotropic, then anisotropic refinements, the H atoms were found with electron densities between 0.37 and 0.77 e Å⁻³. With the isotropic thermal coefficients of the H atoms fixed, the best full-matrix refinements yielded $R = 0.033$, $wR = 0.031$, $S = 1.5$; x , y , z , β_{ij} for non-H atoms; x , y , z for H atoms. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Crystal and molecular structure of pFBS monomer

As already known (Yee, 1979; Enkelmann, 1983), the space group is monoclinic $P2_1/c$ with $Z = 2$, iso-

Table 3. Bond lengths (Å) and bond angles (°) of pFBS monomer and polymer

(a) pFBS monomer at 221 K			
S—O1	1.588 (8)	C4—C9	1.381 (4)
S—O2	1.424 (6)	C5—C6	1.387 (5)
S—O3	1.423 (6)	C5—H5	1.076 (8)
S—C4	1.757 (7)	C6—C7	1.370 (5)
F—C7	1.343 (7)	C6—H6	1.101 (7)
O1—C3	1.448 (3)	C7—C8	1.383 (4)
C1—C2	1.209 (4)	C8—C9	1.396 (5)
C2—C3	1.449 (4)	C8—H8	1.064 (9)
C4—C5	1.394 (3)		
O1—S—O2	109.1 (4)	C5—C4—C9	122.0 (3)
O1—S—O3	103.3 (4)	C4—C5—C6	118.0 (3)
O1—S—C4	104.1 (3)	C4—C5—H5	119.8 (5)
O2—S—O3	120.7 (4)	C6—C5—H5	122.2 (4)
O2—S—C4	108.2 (4)	C5—C6—C7	119.2 (2)
O3—S—C4	110.2 (4)	C5—C6—H6	121.5 (6)
S—O1—C3	116.2 (3)	C7—C6—H6	119.2 (6)
C1—C1—C2	179.5 (3)	F—C7—C6	119.0 (3)
C1—C2—C3	178.9 (3)	F—C7—C8	117.0 (3)
O1—C3—C2	107.3 (2)	C6—C7—C8	124.0 (3)
O1—C3—H3A	108.0 (4)	C7—C8—C9	116.7 (3)
O1—C3—H3B	109.5 (4)	C7—C8—H8	120.7 (6)
C2—C3—H3A	110.4 (5)	C9—C8—H8	122.6 (6)
C2—C3—H3B	109.0 (4)	C4—C9—C8	120.1 (2)
H3A—C3—H3B	112.4 (6)	C4—C9—H9	119.3 (5)
S—C4—C5	118.2 (3)	C8—C9—H9	120.7 (5)
S—C4—C9	119.8 (2)		
(b) pFBS polymer at 295 K			
S—O1	1.583 (1)	C4—C5	1.384 (2)
S—O2	1.424 (1)	C4—C9	1.382 (2)
S—O3	1.416 (1)	C5—C6	1.383 (2)
S—C4	1.748 (1)	C5—H5	0.957 (15)
F—C7	1.349 (2)	C6—C7	1.363 (3)
O1—C3	1.453 (2)	C6—H6	0.81 (2)
C1—C2	1.425 (2)	C7—C8	1.338 (3)
C2—C2	1.366 (2)	C8—C9	1.385 (2)
C2—C3	1.506 (2)	C8—H8	0.86 (2)
O1—S—O2	108.43 (6)	S—C4—C9	119.8 (1)
O1—S—O3	103.55 (6)	C5—C4—C9	120.9 (1)
O1—S—C4	105.43 (6)	C4—C5—C6	119.0 (2)
O2—S—O3	120.53 (8)	C4—C5—H5	122. (1)
O2—S—C4	108.62 (6)	C6—C5—H5	119. (1)
O3—S—C4	109.23 (7)	C5—C6—C7	118.7 (2)
S—O1—C3	119.91 (8)	C5—C6—H6	121. (1)
C1—C1—C2	121.1 (1)	C7—C6—H6	120. (1)
C1—C2—C3	117.5 (1)	F—C7—C6	118.0 (2)
O1—C3—C2	105.91 (9)	F—C7—C8	118.6 (2)
O1—C3—H3A	108.7 (9)	C6—C7—C8	123.1 (2)
O1—C3—H3B	112.7 (9)	C7—C8—C9	119.4 (2)
C2—C3—H3A	110. (1)	C7—C8—H8	127. (1)
C2—C3—H3B	111.2 (9)	C9—C8—H8	114. (1)
H3A—C3—H3B	108. (1)	C4—C9—C8	118.8 (2)
S—C4—C5	119.3 (1)	C4—C9—H9	120. (1)
		C8—C9—H9	121. (1)

morphous with the room-temperature structure of monomer pTS; unit-cell dimensions at 221 K are given in Table 1.

The corresponding atomic positions and anisotropic thermal factors are given in Table 2,* bond lengths and bond angles in Table 3. An *ORTEP* drawing of one asymmetric unit, with numbered atoms, is given in Fig. 1. Projections of the structure on planes (010) and (102), perpendicular and parallel respectively to the polymer chain growth direction, the binary axis, are shown in Figs. 2(a) and 3(a).

* Lists of structure factors and anisotropic thermal parameters for pFBS monomer and polymer have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51138 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Between 200 and 300 K, lattice parameters vary linearly with T within the experimental accuracy; the corresponding thermal expansion factors are given in Table 4. They can be used to obtain, by extrapolation,

lattice parameters at temperatures where thermal polymerization is actually performed.

Comparison of pFBS and pTS monomers: structure and reactivity differences

Topotactic solid-state chemical reactions are usually discussed in terms of the structure of the reacting matrix.

The molecular geometries of pFBS and pTS monomers in their respective crystals are very similar, as shown by comparison of Table 2 with Table 8 of Aimé, Lefebvre, Bertault *et al.* (1982). The slightly different benzene-ring geometries are, as expected, due to the strongly σ -electron-withdrawing character of fluorine. Domenicano & Murray-Rust (1979) have shown that the effects of two substituents in *para* position on a benzene ring are additive, and they tabulated the bond-angle distortions due to many substituents, including F and Me, but not $\text{SO}_3\text{CH}_2\text{R}$ [this problem has been further discussed by Murray-Rust (1982)]. From their table, and assuming additivity, one expects

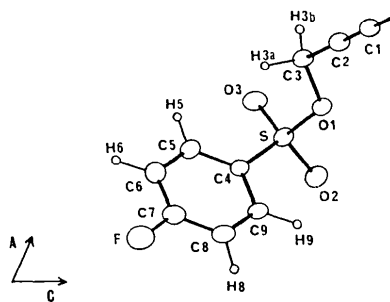


Fig. 1. ORTEP (Johnson, 1965) drawing of one-half of a pFBS monomer unit on the plane (010), in the crystal at 221 K, showing the numbering of the atoms.

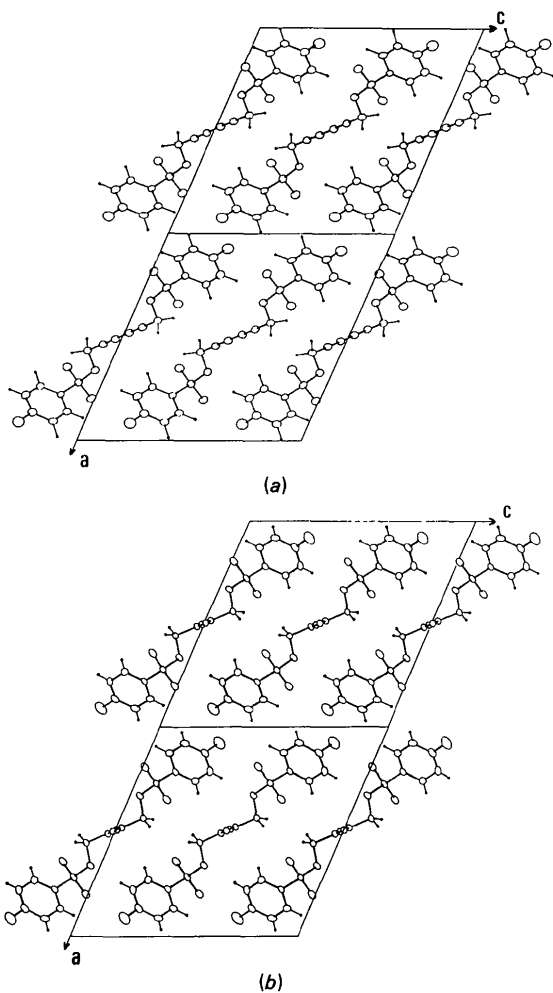


Fig. 2. Projections of the pFBS structure on the plane (010), along the chain growth direction b : (a) monomer at 221 K, (b) polymer at 295 K.

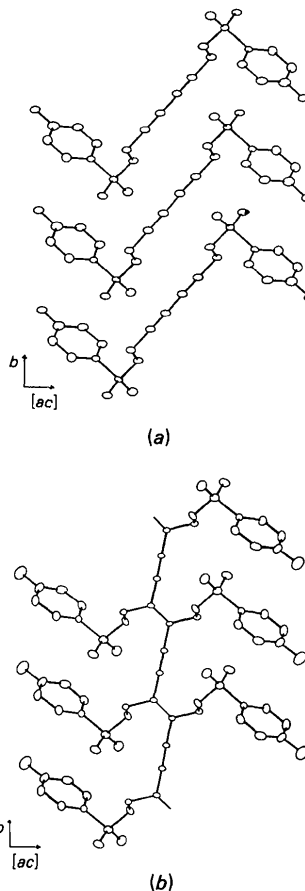


Fig. 3. Projection of the pFBS structure on the plane (102), which contains the polymer growth direction b , showing the packing of neighboring reacting diacetylenes: (a) monomer at 221 K, (b) polymer at 295 K.

Table 4. Thermal expansion factors (10^{-6} K^{-1}) of monomers pFBS and pTS between 200 and 300 K

Errors indicated in parentheses are mean-square deviations of experimental data, neglecting possible systematic errors. ϕ_0^+ in degrees is the angle between the a axis and the first principal axis, corresponding to α_1 .

	pFBS	pTS*
α_a	40 (6)	35 (1)
$\alpha_z = \alpha_b$	85 (10)	107 (4)
α_c	66 (9)	106 (10)
α_β	-25 (3)	23 (5)
α_1	33 (10)	8 (19)
α_3	94 (15)	107 (24)
ϕ_0^+	-18 (4)	31 (5)
Volume expansion	213 (3)	222 (2)

* Values for pTS single crystals, from Aimé (1983) and Aimé *et al.* (1988). Other thermal expansion measurements are also discussed in Bloor, Day *et al.* (1985).

the following angle changes from pTS to pFBS (Table 5): C(6)–C(7)–C(8) should increase by $\sim 5^\circ$, C(5)–C(6)–C(7) should decrease by $\sim 3^\circ$ and other changes should be within experimental accuracy. Since the room-temperature phase of monomer pTS is disordered, atomic positions are less well defined, so the present results should instead be compared to pTS geometry in the low-temperature phase. Of the two sites in that phase, site I is the less perturbed by its crystal environment, as shown by the nearly perfect planarity of the benzene group (Aimé, Lefebvre, Bertault *et al.*, 1982, Table 5). A comparison between the geometries of pFBS at 221 K and of pTS, site I, at 120 K, given in Table 5, fully confirms the expectation. Furthermore, no bond length differs significantly from its theoretically expected value. As for pTS (Aimé, Lefebvre, Bertault *et al.*, 1982), the pFBS molecule is not strained in the monomer lattice.

The unit-cell volume of pFBS monomer is about 7% smaller than that of pTS and, as we shall see, the same is approximately true of the corresponding polymers. Most, if not all, of the effect can be accounted for by the difference in van der Waals volumes of F and CH_3 respectively. Comparison of thermal motions in pFBS (Table 2) and pTS (Aimé, Lefebvre, Bertault *et al.*, 1982, Table 2) clearly shows that pFBS has a normal nondisordered structure: the U_{eq} of the methyl C atom of pTS is 50% larger than that of F; for the neighboring C7 atom the difference is 30% and for the opposite C4 atom, 20%.

Packings are very similar. Intermolecular close contacts are few, approximately the same, and at the same distances. For instance, contacts between molecules corresponding to a translation of \mathbf{b} or an operation C_2^b are compared in Table 6. Distances between reactive diacetylene C atoms differ only slightly (3.64 and 3.56 Å respectively); the angle θ between \mathbf{b} and the diacetylene group direction is 45.6° in pFBS and 43.8° in pTS at 221 K. Since thermal

Table 5. Comparison of benzene-ring geometries in pFBS and pTS

Differences (diff.) are pFBS values minus pTS values. Experimental uncertainties on these values are at least $\pm 0.8^\circ$. C atoms are numbered as shown in Fig. 1.

Angle	Monomers				Polymers			
	pTS 221 K	Site I pTS 120 K	pFBS 221 K	Expl diff.	Expected diff.	Expl diff.	pTS 295 K	pFBS 295 K
9-4-5	120.1	121.5	122.0	0.5	0.4±0.4	0.5	120.4 (3)	120.9
4-5-6	120.0	118.7	118.0	-0.7	0.1±0.2	0.1	118.9 (4)	119.0
5-6-7	120.5	120.9	119.2	-1.7	-3.0±0.2	-2.8	121.5 (3)	118.7
6-7-8	118.9	118.9	124.0	5.1	5.3±0.4	4.6	118.5 (3)	123.1

Table 6. Comparison of intermolecular contacts (Å) at 221 K

	pTS	pFBS
$T(\mathbf{b})$		
C1–O3	3.19	3.23
C3–O3	3.25	3.28
H2–O3	2.52	2.55
C5–O2	3.27	3.17
C_2^b		
H1–O3	2.63	2.73
C3–O3		3.19

expansion along \mathbf{b} is smaller in pFBS (Table 4), we expect these differences to be smaller at room temperature and even more so at the temperatures at which polymerization is performed. Calculated values of \mathbf{b} at 333 K are the same within 10^{-3} Å in pFBS and pTS.

Still, thermal polymerization at 333 K is about eight times faster in pTS than in pFBS. Formation of new polymer chains in the mixed monomer–polymer crystal matrix results from three reaction steps: initiation, propagation and termination. A lower reactivity can be due to faster termination, slower propagation, lower initiation rate, or a combination of factors. The former two processes would on average lead to shorter chains. However, the absorption spectra of polymer chains diluted in the monomer matrix are not significantly different (Bloor & Preston, 1976; Bara & Bauer, 1986). Since in pTS their length is about 20 to 30 monomer units (Albouy, Keller & Pouget, 1982), significant shortening would make the spectrum distinctly different. Therefore, the difference in polymerization rates of pFBS and pTS should mainly be due to differences in the initiation step. A word of caution is, however, necessary: in some pTS–pFBS mixed crystals, soluble, and presumably short, oligomers were found (Enkelmann, 1983). One cannot exclude, even in pure pFBS, the formation of short oligomers in addition to normal chains. The different reactivities of pFBS and pTS correspond to different activation energies: 109 kJ mol^{-1} for pFBS (Yee, 1979) compared to 94 kJ mol^{-1} in pTS (Chance & Sowa, 1977; Bertault, Schott, Brienne & Collet, 1984). Using the ratio of experimental thermal reactivities at 333 K, these values imply that the pre-exponential factor is larger in pFBS than in pTS

(another determination in the case of pFBS might be worthwhile). So, differences in the energetics of the initiation process, not directly related to the geometry, should also be considered.

Clearly, the repeat distance along the polymerization direction and the angle θ are not sufficient indicators of reactivity: purely one-dimensional geometrical considerations cannot explain reactivity differences. Should the complete three-dimensional geometry be considered? In pTS, unit-cell dimension variations in the ac plane during polymerization (Aimé, 1983; Bloor, Day, Ando & Motevalli, 1985; Aimé, Bertault, Lefebvre & Schott, 1988) indicate that there is a coupling between uniaxial stress corresponding to polymerization along b and transverse elastic constants. Introducing plausible values of S_{ij} in the one-dimensional theory of Baughman indeed yields lattice-parameter changes in the ac plane which agree qualitatively with observation, but are too small by a factor of four (Aimé, 1983). So, it is fair to say that the effect on polymerization of this axial-transverse elastic coupling is not well understood. In pFBS, the elastic constants are unknown. The variation of the unit cell with polymer content has been studied only in the induction period, below about 15% polymer (Bara, 1985). These and the present results suggest that pFBS might be slightly stiffer than pTS. So, although further discussion is premature, one is left with the impression that geometric considerations do not completely determine the topotactic solid-state polymerization reaction.

Libration modes of the diacetylene moiety certainly play an important role in the reaction, as they bring reacting C atoms closer to each other. Niederwald & Schwoerer (1983) in their analysis of the room-temperature photopolymerization of pTS, propose that phonons with an energy of a few wavenumbers are important [see also Bässler's discussion (1984)]. Phonon dispersion studies on monomer pTS (Aimé, Lefebvre, Pouget & Schott, 1982) have shown the existence of very low energy (below 10 cm^{-1}) optic modes, which may be related to the phase transitions occurring in this material. So, one can speculate that the difference in reactivity of pTS and pFBS might be more directly related to differences in the phonon spectrum than to purely structural differences. Clearly, more work is necessary.

Another remark, not related to crystal reactivity, is of interest here. Shortly after the discovery of the incommensurate phase of pTS, it had been suggested that the mere existence of the modulation was a consequence of the influence of polymer chains in the monomer lattice (Patillon, Robin, Albouy, Pouget & Comes, 1981). Further studies showed that the modulation is present, essentially unchanged, even at very small polymer content (Aimé, 1983). The absence of the modulation in pFBS in similar conditions of lattice parameters and polymer content, although not a proof, is further

Table 7. *Poly-pFBS unit-cell dimensions at 295 K*

	This work	pFBS Ref. (1)	Ref. (2)	pTS Ref. (3)
a (Å)	13.957 (6)	13.93	13.89	14.49
b (Å)	4.914 (2)	4.90	4.91	4.910
c (Å)	14.103 (6)	14.06	14.10	14.94
β (°)	113.56 (4)	113.3	113.2	118.14
V (Å ³)	887	881	884	937

References: (1) Yee (1979); (2) Enkelmann (1983); (3) Kobelt & Paulus (1974).

evidence that the origin of the incommensurate phase should be looked for elsewhere than in the presence of polymer chains.

Crystal and molecular structure of pFBS polymer

This structural determination may be of interest for two reasons, corresponding to two problems of current interest concerning diacetylenes and polydiacetylenes: the ground-state geometry of the polymer backbone, and the influence of crystal field and side groups on it; and the relation between monomer and polymer structure, and its influence on the topochemical polymerization reaction.

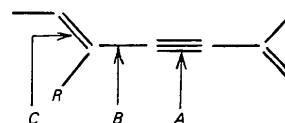
As already found by Yee (1979) and Enkelmann (1983), poly-pFBS is monoclinic, space group $P2_1/c$, $Z = 2$ as for the room-temperature phase of poly-pTS (Kobelt & Paulus, 1974). Differences from Enkelmann's results will be discussed below. The unit cell is compared in Table 7 with literature values and poly-pTS lattice parameters (Kobelt & Paulus, 1974). Atomic positions and anisotropic thermal factors are given in Table 2, and bond lengths and bond angles in Table 3, for comparison with monomer values. Projections on planes (010) (perpendicular to the chain direction) and (102) (parallel to it) are given in Figs. 2(b) and 3(b) respectively.

Comparison of Tables 1 and 7 shows that unit-cell differences between monomer and polymer are similar in the pTS and pFBS systems, the 'lateral' changes in the ac plane being much smaller in pFBS. Packings are shown as projections on the ac plane in Figs. 4(a) and 4(b). There is very little change between monomer and polymer. An investigation of the unit-cell and thermal-expansion changes with polymer content in pFBS, as was done for pTS (Aimé, 1983; Bloor, Day *et al.*, 1985; Aimé *et al.*, 1988), would help to understand the coupling of compression along b due to polymerization with lateral strains, and its influence on the reaction process.

Polymer backbone structure

Although it is at present quite generally accepted that the relaxed polydiacetylene structure is of enyne type, only a few such structures have been determined

crystallographically. Besides pTS, these were MBS, DCH, HDU-I and THD (Enkelmann, 1984; Schott & Wegner, 1987). The pFBS polymer backbone geometry found here is a typical enyne structure, in fact identical to that of pTS within experimental uncertainties. It differs notably from the geometry found by Enkelmann, as shown in Table 8. We believe our structure is essentially correct. Several checks of the quality of the data are possible; for instance, the differences in

Table 8. *Polymer backbone geometries*

Bond	This work	Ref. (1)	pTS Ref. (2)
A	1.204 (3)	1.17 (2)	1.191 (4)
B	1.426 (3)	1.39 (3)	1.428 (4)
C	1.357 (5)	1.42 (3)	1.356 (4)

References: (1) Enkelmann (1983); (2) Kobelt & Paulus (1974).

Table 9. *Comparison of monomer and polymer unit cells for pFBS and pTS at 295 K*

	pFBS		pTS	
	Monomer	Polymer	Monomer	Polymer
a (Å)	13.992	13.957	14.656	14.493
b (Å)	5.187	4.914	5.178	4.910
c (Å)	14.091	14.103	14.942	14.956
β (°)	114.20	113.56	118.81	118.14
V (Å ³)	933	887	994	937
$ac \sin \beta$ (Å ²)	179.8	180.4	191.9	190.9

benzene-ring bond angles with poly-pTS are exactly as expected (Table 5), the C–F bond length is exactly equal to that in FC_6H_5 (Nygaard, Bojesen, Pedersen & Rastrup-Andersen, 1968). The C–C bond lengths of the benzene ring are, on average, shorter in the X-ray polymer than in the neutron monomer, by ≈ 0.015 Å. This is exactly what is expected for an X – N difference: similar observations were made in pyrene, for instance (Hazell, Larsen & Lehmann, 1972). Thus, one may be quite confident in the accuracy of the present data. The inaccuracy of the data of Enkelmann (1983) may simply reflect a poor statistical situation, since only 472 unique reflections were used – less than a quarter of the number used here – for 124 parameters, since the H-atom parameters were not refined. The criteria introduced by Hamilton (1965) to identify satisfactory refinement conditions are not met. In fact, it is surprising that, with only 4 data per parameter, the R factor is not lower than 0.069. This leads us to suspect another origin for the discrepancy. As already discussed elsewhere (Schott & Wegner, 1987), incomplete polymerization may lead to systematic errors by which bond B (see Table 8) is apparently shortened and bond A lengthened, as found in Enkelmann (1983). In the present study, great care was taken to push thermal polymerization to completion; polymerization was continued well beyond the time when either exothermic effects could be detected by DSC or residual monomer extracted.

The great similarity of poly-pTS and poly-pFBS crystals (Table 9) and the identity of ground-state chain geometries, suggest that these systems could be used for investigating the effect of environment on transition

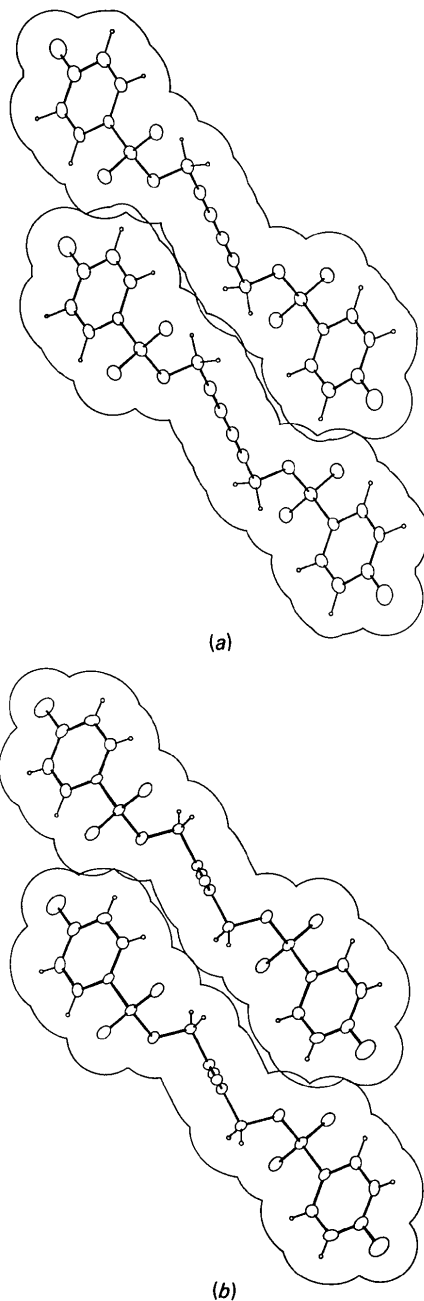


Fig. 4. Projection of the pFBS structure on the ac plane, showing the packing around the diacetylene groups: (a) monomer at 221 K, (b) polymer at 295 K.

energies, using the multipolar moments of the side groups and the dielectric tensors.

Data on a partially polymerized crystal

A monomer-polymer mixed crystal was prepared by isothermal polymerization at 333 K. From the time spent at 333 K, and the known isothermal polymerization kinetics, a polymer content of 18% was calculated. The sample was therefore at the beginning of the autocatalytic polymerization region.

The crystal was studied at 220 K by neutron diffraction in the same experimental conditions as the pure monomer. 512 reflections were collected. This is not enough to allow a complete refinement of the structure (it is only three times the number of refined parameters). The diffuse-scattering component was not studied. Rather, information about the average structure was sought: the calculated atomic positions are weighted averages of all configurations existing in the system. Results of the refinement are given on Tables 2 and 3; they are not meant to be a structure determination. The excellent final R of 0.036 is simply the result of the small number of reflections used.

The existence of a well defined average structure is shown by a single set of well defined Bragg peaks in the experiment, and well defined atomic positions in the refinement. This is perfectly consistent with a homogeneous, random distribution of polymer in the mixed crystal. Since the data were not refined as a disordered structure, disorder would show up as an increase of thermal-motion ellipsoids. In general, this was not observed. For the C1 to C4 atoms, the thermal motion component along b , u_{22} , increases by 30 to 60%, whereas a slight reorganization perpendicular to b upon reaction is suggested by decrease of u_{33} and u_{13} by a corresponding amount.

We argued above and elsewhere (Schott & Wegner, 1987) that a small amount of monomer in polymer would show up as anomalous bond lengths. The present data indeed show that polymer present in monomer shows up as anomalous values for bond lengths C1-C2 and C2-C2'. Other bond lengths, which would not be expected to change upon reaction, for instance S-C4, differ from the monomer value, which is also the normally expected one. This may in part be due to insufficient data. We believe however that this is instead caused by relative atom displacement during polymerization: C4 moves somewhat, as well as the benzene ring, whereas S does not. This is further evidence of coupling of axial (along b) and lateral motions and strains.

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