Crystal structure of poly[1,2-bis(*p*-methoxybenzenesulphonyloxymethyl)-1-buten-3-ynylene]

Richard L. Williams, David J. Ando and David Bloor
Department of Physics, Queen Mary College, Mile End Road, London E1 4NS, UK

and Michael B. Hursthouse
Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, UK

The crystal structure of poly[1,2-bis(*p*-methoxybenzene-sulphonyloxymethyl)-1-buten-3-ynylene] is presented. The structure is compared with that of the well-studied toluene sulphonate polymer. The similarities in the structures of the two polymers imply similarities in those of the monomers. Since the Raman spectra show similar lattice distortions during polymerization for both materials, it is concluded that the different polymerization kinetics indicate that lattice strain is not the dominant factor influencing the kinetics.

INTRODUCTION

Topochemical polymerization has been shown to occur in crystals of many disubstituted diacetylenes under the influence of heat or radiation[1–3]. The reaction is shown schematically in *Figure* 1. In a few cases the reaction results in the production of almost defect-free polymer single crystals. One of the most widely-studied materials which can be obtained in this form is poly[1,2-bis(*p*-tolylsulphonyloxymethyl)-1-buten-3-ynylene] (IIa of *Figure* 1)[4]. Recently a number of studies of closely-related sulphonate monomers have been reported[5–9]. These show that while Ia occurs in a single reactive form, many of the related sulphonate monomers exhibit several modifications, only one of which is reactive in the solid state. Monomers which behave in this manner are 2,4-hexadiynylene-di-*p*-chlorobenzene sulphonate (Ib) and 2,4-hexadiynylene-di-*p*-methoxybenzene sulphonate (Ic).

For both Ib and Ic the inactive form is readily crystallized and crystal structures have been obtained for both materials[10,11]. However, the active forms can be obtained only from highly supersaturated solutions[6,8], conditions which are not conducive to the production of macroscopic single crystals of good quality. In addition, in the case of Ic the more crystalline samples are highly reactive and convert to polymer in a few weeks even when stored at 253K. Thus, as yet, it has not been possible to obtain crystal structure data on the reactive forms of the monomers Ib and Ic. Fortuitously, we have obtained crystals of Ic large enough for X-ray structural studies; these were thermally polymerized to give the polymer IIc in the form of stable samples for structural analysis. We report the results of this analysis and compare the structure of IIc with that obtained previously for IIa[12].

EXPERIMENTAL

Synthesis of monomer and polymer

The monomer Ic was synthesized by the reaction of *p*-methoxybenzenesulphonyl chloride with 2,4-hexadiyne-

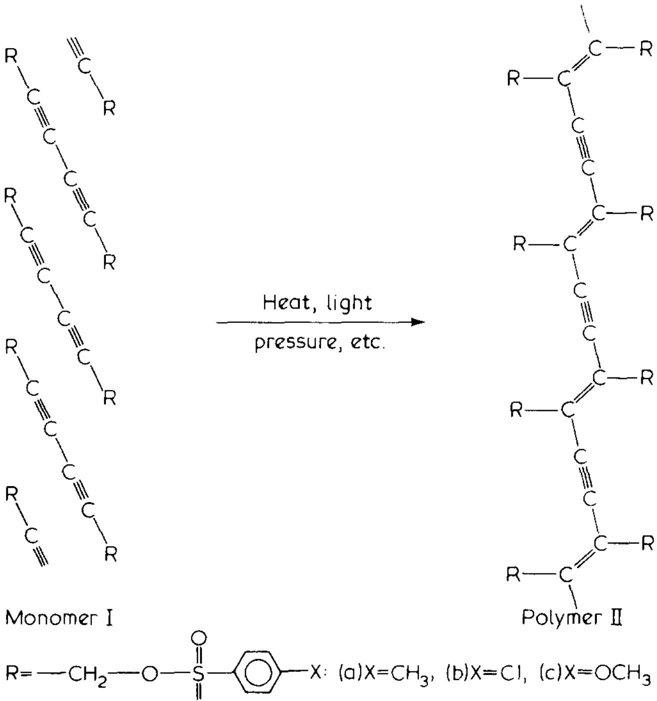

Figure 1 Topochemical polymerization of a disubstituted diacetylene (I) stacked in a crystal lattice to form a polydiacetylene (II) chain. Typical side groups R are indicated; full chemical names are given in the text

0032 3861/80/111269 04$02.00

Table 1 Unit cell parameters of poly[1,2-bis(*p*-methoxybenzenesulphonyloxymethyl)-1-buten-3-ynylene] (IIc) at 209K. The unit cell symmetry is $P\bar{1}$. Standard deviations in the least significant figures are given in parentheses

a	= 4.9017 (12) Å	α	= 78.719 (13)°
b	= 8.5427 (14) Å	β	= 77.220 (16)°
c	= 12.7237 (19) Å	γ	= 70.416 (12)°

Table 2 Atomic coordinates for poly[1,2-bis(*p*-methoxybenzenesulphonyloxymethyl)-1-buten-3-ynylene] (IIc); the atoms are labelled as shown in *Figure 2*. Standard deviations in the least significant figures are given in parentheses

	Coordinate		
Atom	*x*	*y*	*z*
C1	−0.3835 (29)	0.0134 (18)	0.4974 (11)
C2	−0.1238 (29)	0.0512 (19)	0.4920 (11)
C3	−0.1445 (31)	0.2452 (18)	0.4553 (13)
C4	−0.1239 (32)	0.5550 (19)	0.2360 (12)
C5	−0.1791 (40)	0.5343 (20)	0.1376 (14)
C6	−0.4035 (42)	0.6567 (21)	0.0907 (14)
C7	−0.5621 (37)	0.7945 (21)	0.1415 (14)
C8	−0.5044 (42)	0.8145 (23)	0.2395 (16)
C9	−0.2796 (37)	0.6923 (21)	0.2877 (15)
C10	−0.9520 (46)	1.0555 (22)	0.1388 (17)
S1	0.1569 (9)	0.3963 (5)	0.2937 (4)
O1	0.0238 (24)	0.2456 (12)	0.3424 (8)
O2	0.2213 (26)	0.4564 (14)	0.3778 (11)
O3	0.3846 (25)	0.3241 (14)	0.2115 (10)
O4	−0.7792 (27)	0.9066 (15)	0.0913 (10)
H5	−0.0556 (250)	0.4199 (151)	0.1057 (94)
H8	−0.6084 (307)	0.9082 (180)	0.2763 (115)

1,6-diol using the general procedure adopted for the preparation of the toluene sulphonate monomer Ia[13,14]. The active crystal modification was obtained by the moderately rapid evaporation of small volumes of acetone solution. In general this produced either a microcrystalline or dendritic crystalline powder, which was adequate for polymerization studies[6], but inadequate for crystal structure determination. One batch of crystals was obtained with typical dimensions 0.3 x 0.15 x 0.1 mm and a number of these were annealed at 333K to give a polymer content in excess of 95%. 100% conversion to polymer was not possible as the approach to full conversion is extremely slow[6] (see *Figure* 5).

X-ray structural determination

The structure was determined at room temperature from X-ray data recorded on a Nonius CAD-4 diffractometer using experimental procedures described in detail previously[11]. A summary of the crystal data obtained is given in *Table* 1. The structure was solved by direct methods and refined by least-squares using the SHELX[15] program to an R value of 0.13; anisotropic temperature factors were assigned to all atoms (C,O,S). In order to see if this high R value and some uninterpretable peaks left on the difference map were due to incomplete polymerization of the sample, it was annealed at 343K for a further 120h. However, possibly due to stresses induced during mounting, the crystal was found to be cleaved after annealing so that it was not possible to obtain further diffraction data. No significantly better samples could be found amongst those available.

RESULTS AND DISCUSSION

This polymer structure occurs in the triclinic space group $P\bar{1}$ with one independent 'molecule' (i.e. monomer equivalent) in the cell. Because of the limitations in the accuracy of the intensity data it was only possible to locate two hydrogen atoms with certainty. The atomic coordinates of these hydrogens and the heavy atoms are listed in *Table* 2. The molecular structure is shown in *Figure* 2, which also shows the 50% probability thermal ellipsoids[16].

Comparison of this polymer with the bis(*p*-toluene sulphonyl) polymer IIa shows that except for the extremity of the side groups the two polymer chains have very similar structures. This is shown in *Figure* 3, which gives an equivalent projection for IIa to that used for IIc in *Figure* 2. A more detailed comparison of bond lengths and angles (see *Tables* 3 and 4) confirms this visual similarity. However, the lattice packing of the two chains is very different since the structure of IIc lacks the diad screw axis between

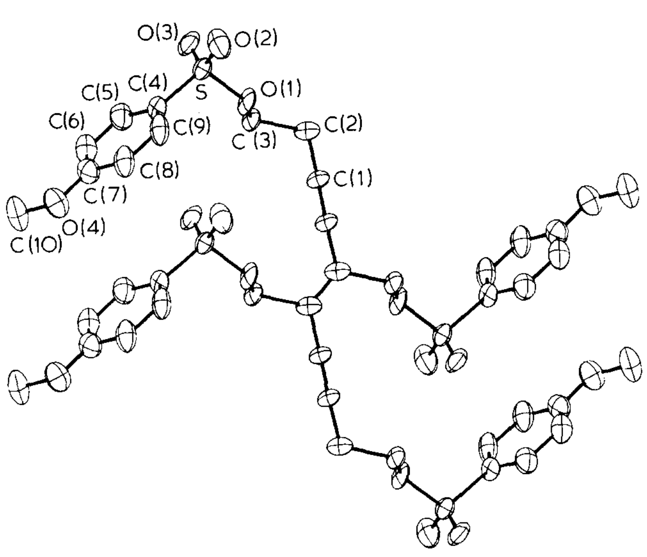

Figure 2 Molecular plot of polymer IIc viewed perpendicular to plane containing polymer chain and diacetylene unit; 50% probability ellipsoids are shown for the atoms whose coordinates are listed in *Table 2*

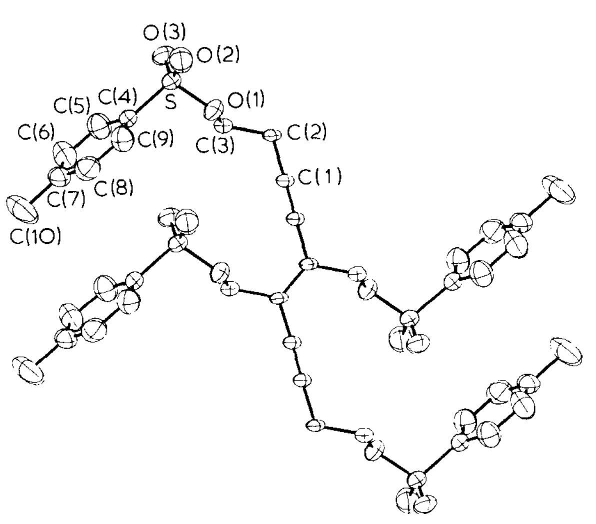

Figure 3 Molecular plot of polymer IIa viewed perpendicular to plane containing polymer chain and diacetylene unit; 50% probability ellipsoids are shown. Data obtained from ref 23

Table 3 Comparison of bond lengths in IIa and IIc. Estimated standard deviations in the least significant figures are given in parentheses. Atoms are labelled as in *Figures 2* and *3*. Data for IIa obtained from ref 23

Bond	Bond length (Å/0.1 nm)	
	IIa	IIc
S1–O1	1.580 (2)	1.594 (9)
S1–O2	1.420 (2)	1.408 (13)
S1–O3	1.423 (2)	1.412 (12)
S1–C4	1.746 (3)	1.754 (15)
O1–C3	1.460 (3)	1.490 (17)
C3–C2	1.506 (4)	1.606 (19)
C2–C1	1.424 (3)	1.400 (18)
C1–C1	1.195 (5)	1.223 (25)
C2–C2	1.364 (5)	1.268 (28)
C4–C5	1.380 (4)	1.393 (23)
C5–C6	1.389 (5)	1.391 (24)
C6–C7	1.372 (5)	1.367 (23)
C7–C8	1.372 (5)	1.391 (25)
C8–C9	1.377 (5)	1.399 (24)
C9–C4	1.373 (4)	1.368 (22)
C7–O4	–	1.355 (19)
O4–C10	–	1.432 (21)

Table 4 Comparison of bond angles in IIa and IIc. Estimated standard deviations are given in parentheses. Atoms are labelled as in *Figures 2* and *3*. Data for IIa taken from ref 23

	Bond angle (°)	
	IIa	IIc
O2–S1–O1	108.5 (0.1)	110.1 (0.6)
O3–S1–O1	103.4 (0.1)	101.2 (0.7)
O3–S1–O2	121.0 (0.2)	120.2 (0.8)
C4–S1–O1	105.2 (0.1)	105.3 (0.7)
C4–S1–O2	108.4 (0.1)	108.5 (0.8)
C4–S1–O3	109.1 (0.2)	110.4 (0.8)
C3–O1–S1	119.3 (0.2)	117.8 (0.9)
C3–C2–C1	117.7 (0.2)	115.1 (1.2)
C2–C3–O1	106.0 (0.2)	102.8 (1.1)
C5–C4–S1	119.7 (0.2)	117.5 (1.3)
C9–C4–S1	120.1 (0.2)	120.0 (1.3)
C9–C4–C5	119.9 (0.4)	122.5 (1.5)
C6–C5–C4	119.0 (0.3)	118.9 (1.6)
C7–C6–C5	121.3 (0.3)	119.4 (1.7)
C8–C7–C6	118.5 (0.3)	121.3 (1.7)
C9–C8–C7	121.4 (0.3)	119.9 (1.8)
C8–C9–C4	119.6 (0.3)	118.0 (1.8)
C6–C7–O4	–	115.7 (1.7)
C8–C7–O4	–	122.9 (1.7)
C7–O4–C10	–	119.0 (1.5)

chains found in IIa, as illustrated in *Figure* 4. In the case of Ia the crystal symmetry remains unchanged during polymerization[17]. Raman spectroscopy suggests that this is also the case for Ic[18], and that the molecular deformation produced by the solid-state polymerization is similar in both cases. Thus, it seems reasonable to assume that the molecular structure of both monomers is similar, but that a single stack aligned along the *a*-axis occurs for Ic, while a pair of symmetry related stacks occurs in Ia.

On the basis of this structural data it might be expected that the polymerization kinetics of the two monomers would be similar. This is also the conclusion of the Raman spectroscopic studies on the basis that the lattice strain is similar throughout polymerization for the two materials. A model, in which lattice strain controls the polymerization kinetics, has been shown to be applicable to Ia[19]. However, the kinetics of Ic have been found to be very different[5,6], as shown in *Figure* 5. This fact, together with the reported sensitivity of the polymerization kinetics of Ia to isotopic substitution[20], hydrostatic pressure[21] and to the incorporation of Ib and Ic as substitutional

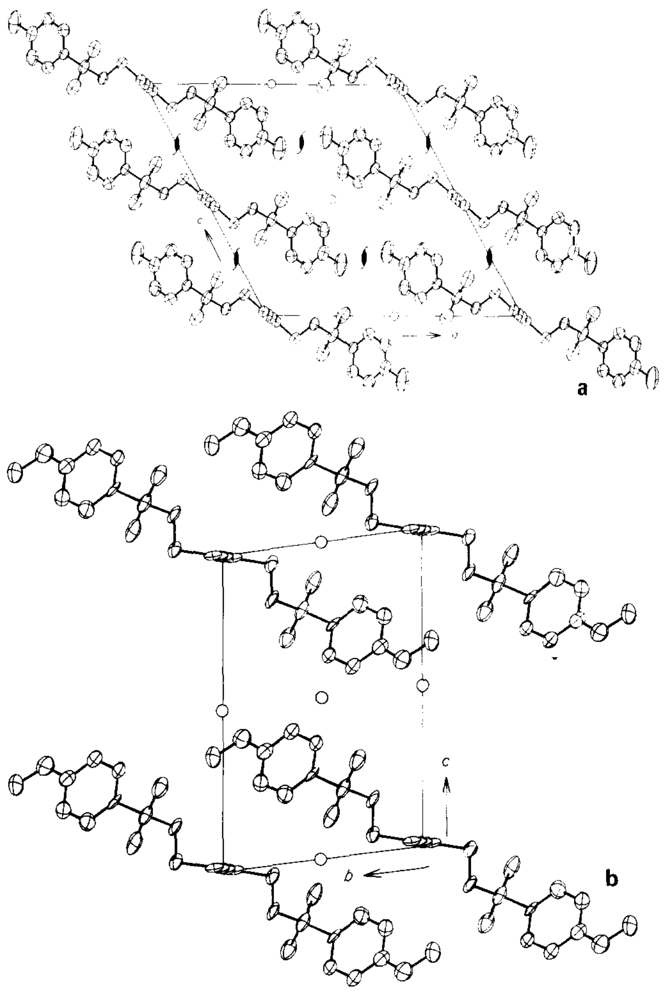

Figure 4 Molecular plots of polymers IIa (a) and IIc (b) viewed along the directions of the polymer chain, showing diad screw axes (a) and inversion centres (b). Data for IIa obtained from ref 23. Inversion centres occur at the centre of each molecular unit

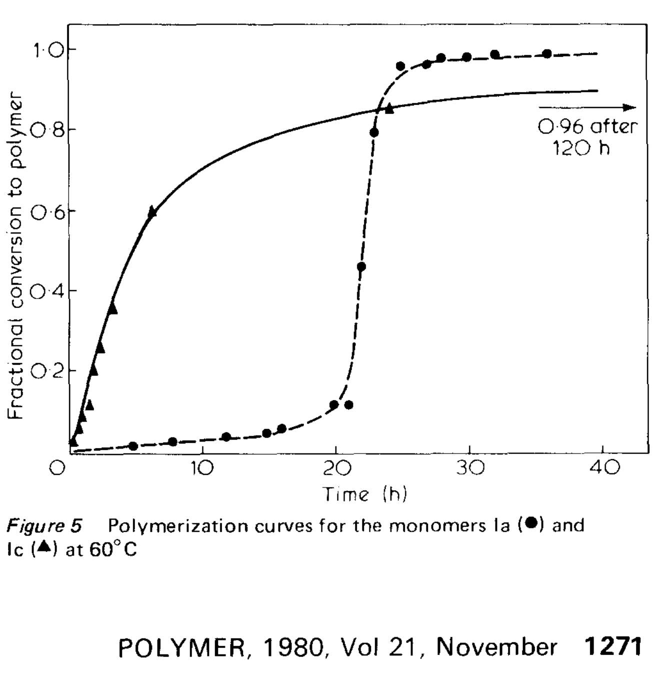

Figure 5 Polymerization curves for the monomers Ia (●) and Ic (▲) at 60°C

impurities[7,8,22], suggests strongly that lattice strain is not the dominant factor determining the polymerization kinetics in diacetylenes.

REFERENCES

1 Wegner, G. *Z. Naturforsch.* (*B*) 1969, **24**, 824
2 Wegner, G. 'Chemistry and Physics of One-Dimensional Metals', (Ed. H. J. Keller) Plenum Press, New York, 1977, pp. 297–314
3 Baughman, R. H. and Chance, R. R. *Ann. New York Acad. Sci.* 1978, **313**, 705
4 Wegner, G. in 'Molecular Metals' (Ed. W. E. Hatfield) Plenum Press, New York, 1979, pp. 209–242
5 Bloor, D., Ando, D. J., Fisher, D. A. and Hubble, C. L. in 'Molecular Metals' (Ed. W. E. Hatfield) Plenum Press, New York, 1979, pp. 249–253
6 Ando, D. J., Bloor, D., Hubble, C. L. and Williams, R. L. *Makromol. Chem.* 1980, **181**, 453
7 Enkelmann, V. *Makromol. Chem.* 1978, **179**, 811
8 Enkelmann, V. *J. Mater. Sci.* 1980, **15**, 951
9 Yee, K. C. *J. Org. Chem.* 1979, **44**, 2571
10 Mayerle, J. J. and Clarke, T. C. *Acta Crystallogr.* (*B*) 1978, **34**, 143
11 Fisher, D. A., Ando, D. J., Bloor, D. and Hursthouse, M. B. *Acta Crystallogr.* (*B*) 1978, **35**, 2075
12 Kobelt, D. and Paulus, F. *Acta Crystallogr.* (*B*) 1974, **30**, 231
13 Wegner, G. *Makromol. Chem.* 1971, **145**, 85
14 Stevens, G. C., Ando, D. J., Bloor, D. and Ghotra, J. S. *Polymer*, 1976, **17**, 623
15 Sheldrick, G. M. 'SHELX program for crystal structure determination', University of Cambridge (1976)
16 Further structural information can be obtained from the authors.
17 Enkelmann, V., Leyrer, R. J. and Wegner, G. *Makromol. Chem.* 1979, **180**, 1787
18 Bloor, D., Ando, D. J., Hubble, C. L. and Williams, R. L. *J. Poly. Sci.* (*Polym. Phys. Edn*), 1980, **18**, 779
19 Baughman, R. H. *J. Chem. Phys.* 1978, **68**, 3110
20 Kröhnke, C. *Thesis* University of Freiburg (1979)
21 Lochner, K., Bässler, H. and Henrichsen, Th. *Ber. Bunsenges, Phys. Chem.* 1979, **83**, 899
22 Ando, D. J., Bloor, D. and Tueke, B. *Makromol. Chem.* 1980, **1**, 385
23 Cottle, A. C. unpublished results