

Polymorphism on the cyclic hexamer of *p*-phenylene sulfide

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The cyclic hexamer of *p*-phenylene sulfide (CHPS) is extracted and isolated from commercial poly(*p*-phenylene sulfide). The crystal structure change, from the α -form to the β -form, in the CHPS is reported for the first time. Optical microscopy is used to observe the characteristics of the crystals under cross-polarized light. Fourier transform infrared and Raman spectroscopy are used to examine the vibrational characteristics of the crystal as a function of temperature. Scanning electron microscopy is used to examine the shape of the crystals. Differential scanning calorimetry is used to observe the thermal characterization of the sample. Molecular modelling is employed to examine possible conformations. The X-ray powder diffraction pattern is also compared for the two structures. A theory on the crystal structure change is proposed. © 1998 Elsevier Science Ltd.

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INTRODUCTION

Recently there has been considerable interest in cyclic compounds containing aromatic rings as polymeric precursors. One example is the cyclic trimer of polyethylene terephthalate, which is known to have multiple crystal forms¹. Other examples are the cyclic phenylene sulfides^{2,3} (CPS). This paper reports a crystal structure change observed in a CPS for the first time. Cyclic phenylene sulfides are known to occur as a by-product in the polymerization of poly(*p*-phenylene sulfide) (PPS)⁴. The CPS were first identified by Kaplan and Reents⁵, and the cyclohexa(phenylene sulfide) (CHPS) was first isolated by Sergeev et al.⁶ Previously, the i.r. and Raman spectral characteristics of PPS and CHPS have been reported³. As expected, the bands present for CHPS are nearly the same as those of PPS except for those related to crystal packing. One of the most important regions for identifying crystal structure has been determined to be the C–H out-of-plane mode region, which will be utilized in the present work to study the polymorphism observed in CHPS.

The X-ray single crystal structure of the CPS hexamer⁷, along with the tetramer⁸, pentamer⁹, heptamer¹⁰ and octamer¹⁰, are known. Each cyclic crystallizes in a different structure owing to the varying conformations in the ring. The columnar structure of the hexamer and octamer are known to entrap solvent.

EXPERIMENTAL

Extraction of low molecular weight PPS (Ryton V-1, Phillips) was performed for 16 h with tetrahydrofuran (THF) (Aldrich). The solution was allowed to stand for 72 h, which produced colourless needles of CHPS (m.p. 348°C). The average size of the crystals was 1 mm \times 30 μ ,

and the yield was 0.1 %. Cyclohexa(phenylene sulfide) was also obtained by selective extractions and recrystallization from chloroform^{4,11}. Pellets of KBr were made for FTi.r. analysis. Annealing of the crystals was done at 325°C for 20 min in air unless stated otherwise. No discoloration was observed.

Melting points were obtained using differential thermal analysis (Mettler FP84HT). Differential scanning calorimetry (d.s.c.) was done using a TA Instruments, DSC 2910. FTi.r. spectroscopy was performed with a Bomem Michelson MB spectrometer with a liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) detector at a resolution of 2 cm⁻¹. A FTi.r. heated cell was used to ramp the temperature at 5°C min⁻¹. The specific detectivity, D^* , of the MCT detector was 1×10^{10} cm Hz^{1/2} W⁻¹. Raman spectroscopy was performed with a Dilor XY dispersive spectrometer equipped with a triple monochromator and an 18 bit charge-coupled device detector. The excitation source is a Coherent Model 890 Ti:Sapphire laser at 750.7 nm pumped by a Coherent Innova Model 305 argon ion laser. Output laser power was 350 mW. The integration time was 60 s. Resolution at the excitation line was 3 cm⁻¹. Molecular modelling was performed using the SYBYL software package. A Philips X-ray powder diffractometer with CuK α radiation at a slit width of 0.1° was used. The sample was lightly ground.

RESULTS

Cyclohexa(phenylene sulfide) and structure change

Using size-exclusion chromatography and FTi.r., the low molecular weight cyclic nature of the compounds was established. Therefore, the melting point of the CHPS along with the crystal shape confirms that CHPS has been successfully obtained. In the present work, crystals were obtained by crystallization from THF. Previously, the

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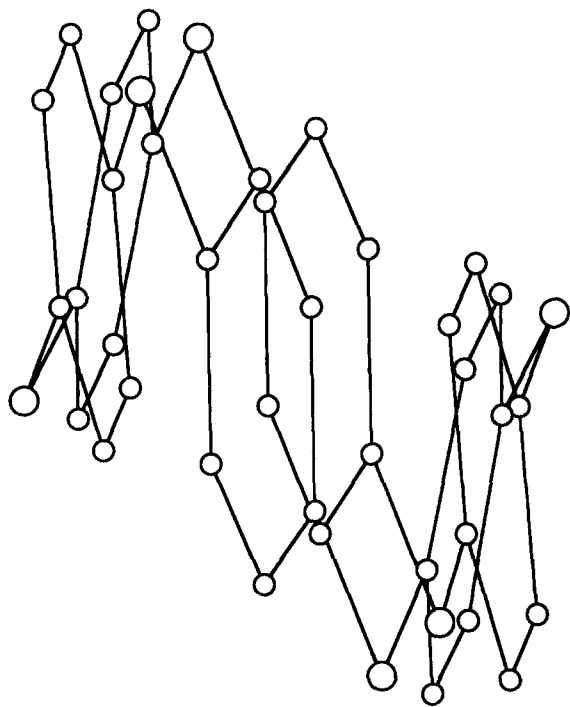


Figure 1 Molecular structure for hexamer crystallized from chloroform⁷

structure of the crystal hexamer crystallized from chloroform has been reported. The crystal structure obtained from the published coordinate data is shown in Figure 1⁷. The shape of the molecules is being termed as 'Z' conformation. The molecules stack and are known to entrap chloroform in the channels of the crystal, but not THF³.

Heating of these crystals, with or without solvent, results in a transition from what is being termed the α -form to the β -form. This transition was first seen by using FTi.r. and observing a significant change in the C-H out-of-plane bend region, which has been shown to be sensitive to the crystal structure³. This region is shown in Figure 2 for crystals obtained by recrystallization from chloroform or THF. There is essentially no difference between the spectrum of the two hexamer crystals, and therefore it can be concluded that the same transition is occurring. The larger (and solvent-free) crystals grown from THF were used throughout this work. By using FTi.r. and also optical microscopy and d.s.c., it is possible to determine at what temperature this transition occurs.

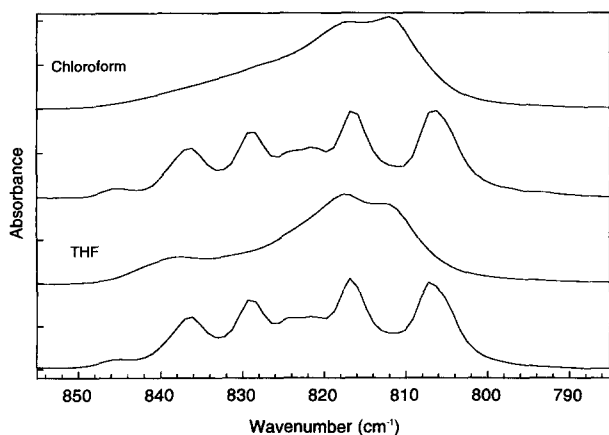


Figure 2 FTi.r. spectrum of hexamer crystallized from chloroform and THF for the C-H out-of-plane bending region before (top) and after (bottom) heating at 240°C for 40 h

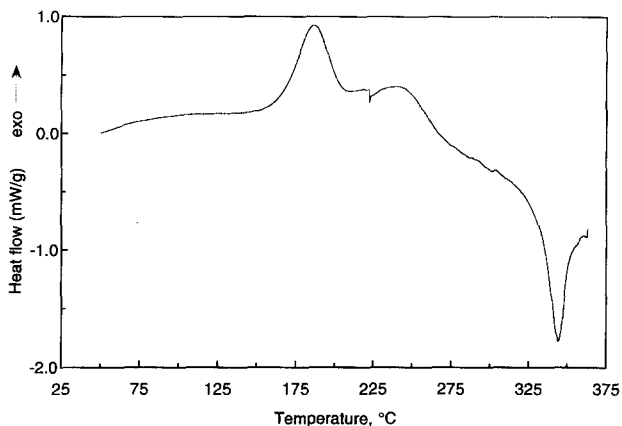


Figure 3 DSC scan of the CPS hexamer at a heating rate of $5^{\circ}\text{C min}^{-1}$ showing the exothermic crystal structure change

Onset of transformation

Three techniques were used to determine the onset of transformation: optical microscopy, d.s.c. and FTi.r. In each, the same heating rate of $5^{\circ}\text{C min}^{-1}$ was employed. Using optical microscopy, it is observed upon heating of the crystals that there is a sufficient energy release to cause the crystal to jump. Often, the crystals leave the $500\ \mu$ field of view. Micrographs were taken with an exposure time of 1 min. After 15 trials, it was determined that the first movement is seen at $140 \pm 8^{\circ}\text{C}$. Some crystals are observed to move even up to 220°C .

A d.s.c. scan of the CHPS is shown in Figure 3, which clearly shows the exothermic nature of the transition. There are clearly two peaks that can only be the result of a crystal transformation. The first extends from 150 to 200°C . The second, which is significantly weaker, extends from 225 to 250°C .

Fourier Transform i.r. is generally not regarded as a useful thermal technique, since the band position and intensity change as a function of temperature. Therefore, the band position and intensity alone cannot be used to detect a structure change. However, if there is a sudden change in the rate of the change of the band position, then it can be assumed that this is due to a crystal structure change.

The spectra of CHPS in a KBr pellet were taken at 30-s intervals as the sample was heated. The band position as a function of temperature is shown in Figure 4 for the bands at 1010 and $1097\ \text{cm}^{-1}$ for two heating scans. The $1010\ \text{cm}^{-1}$ band position is nearly linear for both scans and is believed

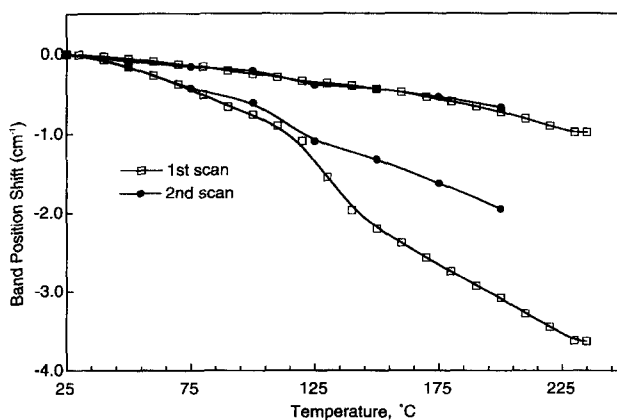


Figure 4 Band position as a function of temperature for the $1010\ \text{cm}^{-1}$ (top) and $1097\ \text{cm}^{-1}$ (bottom) bands at a heating rate of $5^{\circ}\text{C min}^{-1}$ for two heating cycles

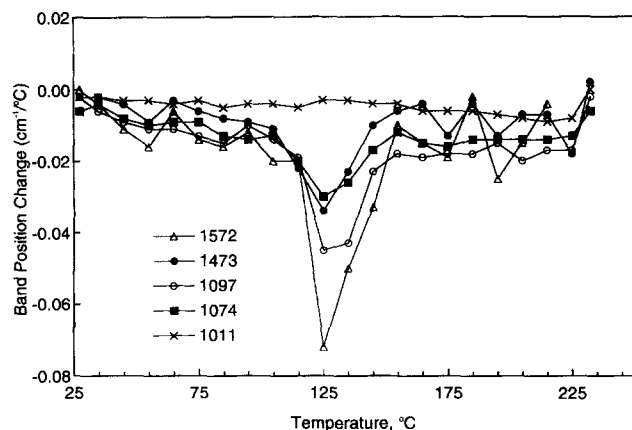


Figure 5 Derivative of the FTi.r. band position as a function of temperature for bands at 1574, 1097, 1073 and 1010 cm^{-1} at a heating rate of 5°C min^{-1} showing the onset of transformation

to be insensitive to the change. However, the band at 1097 cm^{-1} clearly shows a considerable shift on the first scan and only a minor shift on the second. Clearly, a non-reversible structure change has occurred. *Figure 5* shows the derivative for the first heating scan for selected bands and indicates a structural change at $\sim 130^\circ\text{C}$ if the shape of the peak is assumed to be symmetric. This onset of transformation by FTi.r. is lower than either the d.s.c. or the optical microscopy indicates. This is because the crystals in the pellet are under pressure, which has been shown to induce the crystal structure change after several hours at room temperature.

Infrared and Raman spectroscopy

The spectral characteristics of the hexamer have been examined elsewhere³ and the bands that are unique to the polymer and cyclic have been identified. The spectra of the hexamer are shown in *Figure 6* at two different heating temperatures, which are compared with the non-annealed sample. The largest change occurs in the C–H out-of-plane bending region that is shown enlarged in *Figure 2* before and after heating. The position of these peaks is reproducible. In *Figure 6*, an intermediate step can be observed. Upon heating, there is an emergence of strong peaks at 807, 817, 829 and 836 cm^{-1} . None of these bands is observed for the polymer, therefore it is clear that the ring has not opened. Even after 2 h at 325°C , there is no evidence of polymerization. The sharp bands arise from a more

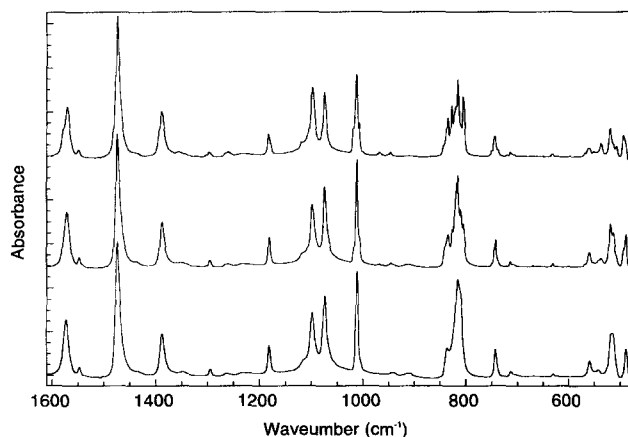


Figure 6 FTi.r. spectrum of CPS hexamer recrystallized from THF as-obtained (bottom) annealed at 225°C for 20 min (middle) annealed at 325°C for 20 min (top)

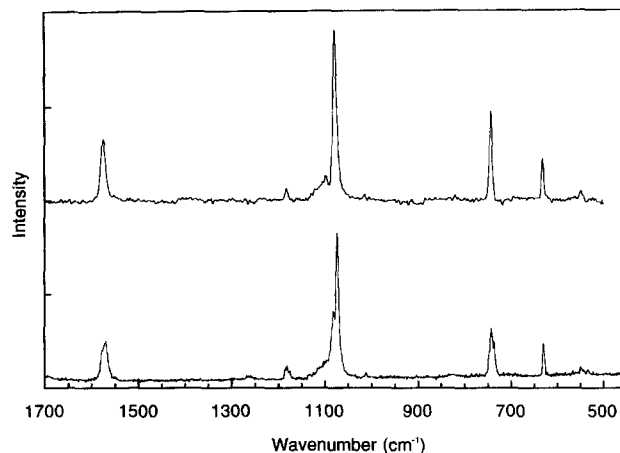


Figure 7 Raman spectrum of hexamer before (top) and after (bottom) heating

restricted conformational state, which could come from increased packing. Initially the cyclic is presumed to have a centre of inversion and, therefore, a high degree of symmetry. The emergence of new, strong bands indicates that this symmetry is no longer present. Even a slight distortion of the cyclic ring could cause this.

There is also a significant change in the long-range order bands, in particular the band at 520 cm^{-1} . There is a change in the structurally sensitive modes at 1074 and 1097 cm^{-1} . With increasing symmetry, the antisymmetric phenyl–S stretching mode at 1074 cm^{-1} decreases. This phase change could be a strain-relieving mechanism. As seen in *Figure 6*, there is a considerable change in the C–H out-of-plane mode around 820 cm^{-1} , before the change in the phenyl–S stretch is observed. This would seem to indicate that there is an initial change in packing of the molecules followed by rotation about the phenyl ring relieving some of the strain in the S–phenyl–S group. The 1574 cm^{-1} aromatic ring mode shows the same behaviour. Another unusual aspect of the spectrum after heating is the multiple bands observed at 554, 742, 1010, 1180, 1292 and 1575 cm^{-1} . The 1010 cm^{-1} is a fundamental band and is known to be insensitive to substitution. The side peaks are therefore unexpected, but must come from the 1010 cm^{-1} mode, since there is an accompanying decrease in height. Initially, there is a slight shoulder, therefore this mode is likely to be present initially but is enhanced in the heating process.

The Raman spectrum of the crystal before and after heating is shown in *Figure 7*. The same multiple-line effect that was observed in FTi.r. is seen in Raman at 742, 1180 and 1574 cm^{-1} . There is also the emergence of a peak at 1097 cm^{-1} , which is known to be the antisymmetric component of the phenyl–S stretch.

Microscopy

SEM micrographs of a hexamer crystal before and after heating are shown in *Figure 8*. Initially, the crystal has a nearly hexagonal shape, and four of the angles and sides of the crystal face are nearly equal. After heating, there are several changes that occur. First, there is the appearance of significant microcracking caused by the stress imparted to the sample. The symmetry of the crystal face has changed from three twofold rotation axes to one twofold rotation axis. There is still a centre of inversion. The ratio of the lengths of the crystal face after heating is not constant, but there is always the same symmetry. Another interesting aspect is that material appears to have been squeezed out of

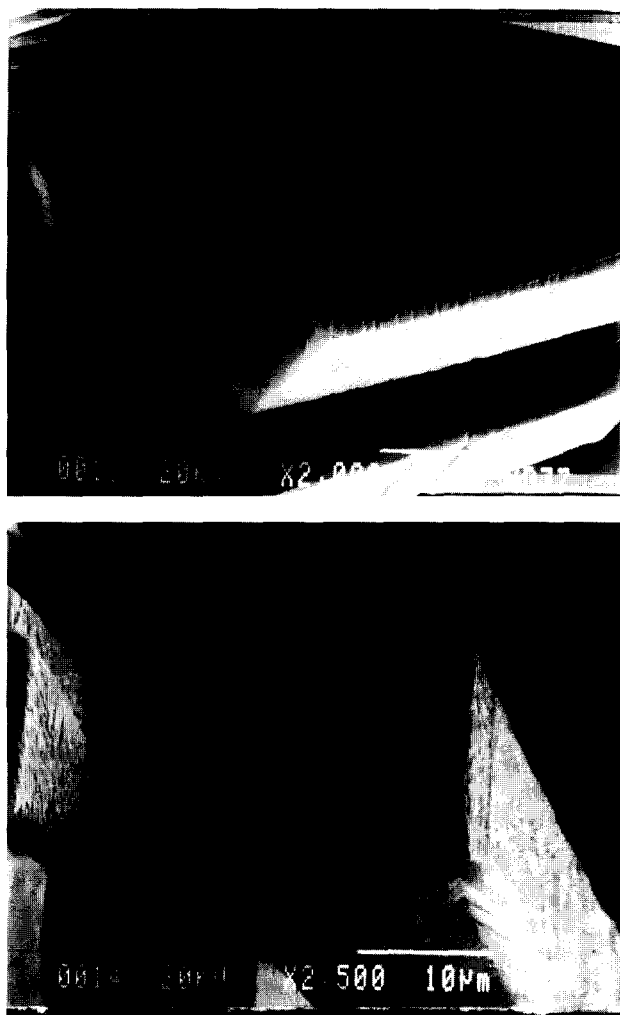


Figure 8 SEM micrograph of a CPS hexamer crystal before (a) and after (b) heating

the crystal in two places, which can be seen in the lower portion of *Figure 8b*. There is no indication of this type of structure before heating, therefore it must be the result of the crystal structure change.

Optical microscopy was used to examine the onset of transformation and also the appearance of the crystals. Initially, the crystal is transparent and shows birefringence under cross-polarized light. It is also extremely straight. After heating, the crystal appears brown with many spots, which is due to the microcracking seen in *Figure 8b*. The

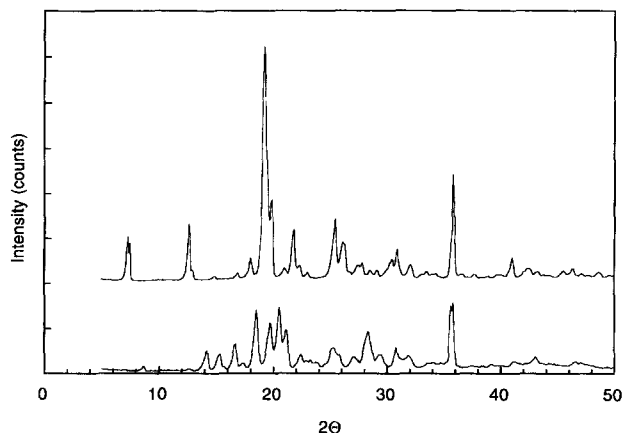


Figure 9 X-ray powder diffraction pattern before (top) and after (bottom) heating using $\text{CuK}\alpha$ radiation at $0.1^\circ/\text{scan}$

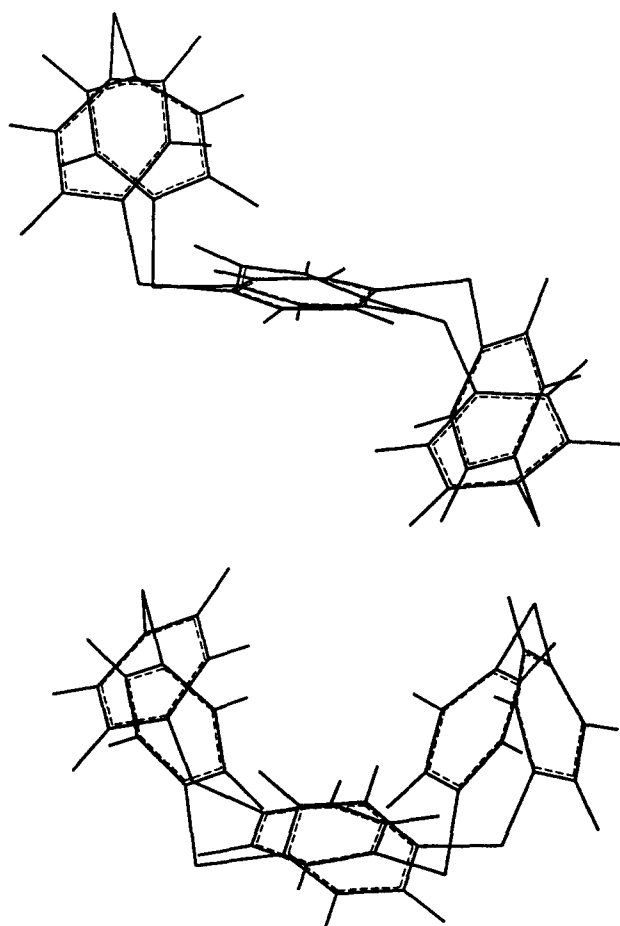


Figure 10 Schematic of the molecular modeling results: chair (top) and boat (bottom)

crystal is also observed to be kinked or curved. In rare cases, the curvature of the crystal can be up to 90° . A dark line is seen in the crystal, which is a result of the material that is squeezed out of the crystal as was seen using SEM.

X-ray powder diffraction

The powder diffraction pattern before and after heating for the CPS hexamer is shown in *Figure 9*. The crystal size is slightly larger than ideal for a powder pattern (roughly $20\ \mu$). The sample was ground lightly, since excessive grinding results in a material that is difficult to handle. As a result, there is an orientation effect in the powder photograph. The sharp enhancement of the 19.5° line is a result of this. Upon annealing, the crystals become kinked and undergo crystal structure change which can be seen by a significant number of new reflections that are tightly spaced between 14 and 23° . The new reflections are due to a change in the phenyl ring orientation. The reflection at 36° does remain constant although, with the diminished orientation effect, the shoulder is more enhanced and appears as a doublet. This d -spacing ($2.5\ \text{\AA}$) corresponds to $[020]$ and does not appear to change.

Molecular modelling

Molecular modelling was undertaken to see if there is an energy consideration for the hexamer assuming the 'Z' conformation or whether that is a result of crystal lattice effects. Various conformations were energy minimized, accounting for electrostatics. Two examples of energy-minimized structures obtained from different starting points are shown in *Figure 10*. The boat conformation was

Table 1 Summary of results obtained from molecular modeling and comparison to known structures¹⁰

Molecule	Mean S-C distance (Å)	Mean C-S-C angle (deg)
Boat ^a	1.780	98.0
Chair ^a	1.771	99.5
Tetramer	1.784	98.7
Pentamer	1.778	102.5
Hexamer	1.779	102.5
Heptamer	1.775	103.5
Octamer	1.781	103.7
Diphenyl sulfide	1.771	103.7
<i>p</i> -(OHs) ₂ C ₆ H ₄	1.780	106.6
Polymer	—	110

^aPresent work

obtained from an initial planar molecule. A summary of the results is shown in *Table 1*. The bond lengths obtained for each structure are very close to that for the CHPS⁷. The ϕ -S- ϕ bond angles were generally less than those obtained in the crystal structure and are more strained than those found in PPS and diphenyl sulfide, indicating that the structures obtained, although energy minimized, do have some energy that could potentially be reduced further. Molecular modelling predicts a torsional angle of approximately 60°, which is close to the 62° angle observed by X-ray. There appears to be no energy consideration for assuming the reported 'Z' conformation. Based on molecular modelling, there does not seem to be a preferred orientation for the overall cyclic structure; however, in no energy-minimized structure (20 attempts) was an acute angle like that in the 'Z' conformation ever observed.

DISCUSSION

The needle-like crystals of the hexamer have been grown as long as 1.5 mm. However, owing to the limited diameter of the crystals (max. 30 μ) and tendency to have multiple crystals, single crystal X-ray analysis has not been possible. Therefore, the most important evidence in proposing a theory are the SEM pictures. The crystal structure is known to be monoclinic, which can result in a hexagonal cross-section. The unit cell is nearly orthorhombic since β is almost 90° ($\beta = 91.8^\circ$), with the columns displaying a twofold screw axis. Upon annealing, shifting of these columns, relative to each other could result in the symmetry that was observed in the SEM micrograph. This is analogous to the change observed in terephthalic acid¹², where packing rearrangement is seen and the unit cell angle is decreased. However in this case the molecule is a ring. The behaviour can also be compared to that of discotic columns; however, there is no linear flexible group¹³.

Once a column 'slips' relative to another, a series of chain reactions occurs analogous to a fault line in an earthquake. If there are multiple initiation points, eventually two propagating events come together resulting in material that appears to be squeezed out, which was seen in the SEM. This would be a rapid event like that observed in optical microscopy. The long-range order is destroyed, as seen by the FTi.r.; however, the local order is maintained. The crystallographic symmetry appears to be destroyed based on the appearance of more distinct C-H stretch regions in the FTi.r. spectrum. Therefore, a change in the phenyl ring orientation does occur, which appears to precede the more drastic change as seen by the FTi.r. spectra in *Figure 6*. Molecular modelling does indicate a variety of possible conformations. However, the 'Z' conformation does not

appear to be one of them, and therefore it is likely that this structure is also changed upon annealing. This could be the source for causing the crystal columns to change their packing, resulting in the crystal structure change.

CONCLUSIONS

Above approximately 140°C, a transformation from the α -form to the β -form occurs in the cyclic hexamer crystals of phenylene sulfide. The initial structure is metastable and at long times changes to the β -form under pressure at room temperature. The β -form is stable at room temperature, and the structure change can be observed using FTi.r. spectroscopy, d.s.c., X-ray powder diffraction patterns, optical microscopy and SEM. It is proposed that this change is occurring owing to a change in the columnar structure and slight distortion of the cyclic ring.

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