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Solid state polymerization of bis-(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol

Part 1 *X-ray diffraction and spectroscopic observations*

D. BLOOR, L. KOSKI*, G. C. STEVENS, F. H. PRESTON, D. J. ANDO
Department of Physics, Queen Mary College, University of London, UK

The thermal polymerization of bis-(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol has been studied by optical and Raman spectroscopy and X-ray diffraction. Single phase polymerization is revealed by continuous changes in the spectra of polymer chains in polymerizing crystals. Spectroscopic and X-ray measurements on extracted polymer are interpreted in terms of random polymer formation. Polymer formed initially is strained but this anneals to a strain-free conformation in the fully converted polymer or on extraction from the monomer lattice. Possible causes of the variations in polymerization rate are discussed.

1. Introduction

The solid state polymerization of diacetylenes produces polymers with a wide range of morphologies. These polymerizations have been known for many years [1–3] but it is only recently that their true nature has been appreciated, due principally to the work of Wegner and his collaborators [4–9]. The reaction scheme is shown diagrammatically in Fig. 1. Diacetylene monomers, with suitable end groups, stack in a regular array in the monomer crystal. Polymerization to an all trans planar polymer chain can be initiated by heat and ultra-violet or ionizing radiation. The polymer chain structure is shown in Fig. 1. This structure is very stable and occurs in polymers made from triacetylene [9] and cyclic diacetylene [10] monomers. Complete conversion can be obtained with a product which can be amorphous [11], mesomorphic [8], single crystal fractured by internal stress [12] or highly perfect single crystals [4, 8, 13]. In some cases a stable crystal is obtained with a limiting conversion of less than 100% [4, 12].

The production of large polymer crystals led to the proposal that the solid state polymerization proceeded via a perfect solid solution of monomer and polymer [8]. This contrasts with the phase segregation that occurs in the solid state polymerization of monomers such as trioxane, which leads to a fibrous crystalline product [14]. Baughman [12] has considered the polymerization of model rigid rod diacetylene molecules. He showed that the requirements for solid-state reactivity, crystal packing, proximity of reacting molecules and least motion of the reacting molecules could be met in many diacetylene monomer crystals. Monomer reactivity is related to the degree to which each of the requirements is satisfied. Baughman identified four possible phase diagrams for the reactive materials. In each case the molecular contribution to the change in free energy during polymerization is assumed to decrease linearly in proportion to the amount of more stable polymer present. The rearrangement of the crystal lattice during polymerization also contributes to the change in free energy. This will have a large maximum if the monomer and polymer lattices are incompatible and a single phase polymerization will not be possible. If the lattice contribution has a small maximum then a single phase polymerization may be possible. If the lattice contribution has no maximum then a single phase polymerization is favoured. This can proceed to 100% conversion if the lattice energy is least for the polymer or to a

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* Present address: Technical Research Centre of Finland, Helsinki, 18, Finland.

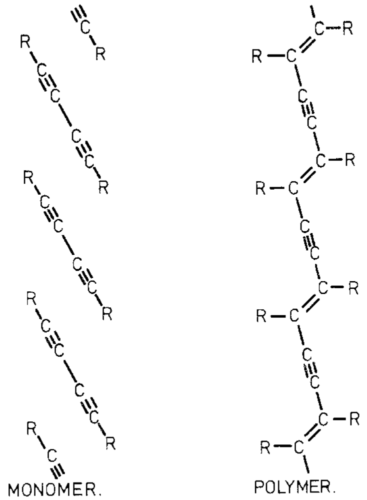

Figure 1 Left: stacking of diacetylene monomers in a reactive crystal. Right: diacetylene polymer chain. R represents the endgroups in the monomer and sidegroups in the polymer.

stable limiting conversion if the lattice energy has a deep minimum for less than 100% conversion.

These ideas receive support from the observation of well defined X-ray diffraction from partially polymerized crystals [8, 11]. These measurements are restricted, at room temperature, to the less reactive diacetylenes since the more reactive monomers are rapidly polymerized by the X-ray beam. One highly reactive monomer, which produces large polymer crystals with striking optical spectra [15], is the bis-(*p*-toluene sulphonate) derivative of 2,4-hexadiyne-1,6-diol. We have investigated the thermal polymerization of this monomer by a number of less direct methods. In the present paper we will present the results of optical and Raman spectroscopy and X-ray diffraction measurements on partially polymerized crystals and extracted polymer. A second paper, Part 2, will describe the results of optical and scanning electron microscope studies. These measurements provide enough information to enable us to determine the nature of the polymerization.

2. Materials preparation

The bis-(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol was prepared by the method due to Wegner [16]. Single crystals of monomer with lateral dimensions greater than 1 cm were grown by slow evaporation of acetone solution. The purest samples of monomer gave small diamond shaped crystals with well developed crystallographic facets. The larger pseudo-hexagonal or coffin shaped crystals have a pair of non-singular faces, the effect of these on polymer perfection is discussed in Part 2. Small crystals with both morphologies are shown in Fig. 2. Growth by slow cooling of a seeded saturated solution enabled faceted crystals up to 1 ml in volume to be grown. The crystals were initially pale yellow in colour but rapidly turned pink on exposure to light or when heated. Crystals heated above 50° C turn deep red then black and finally develop a golden metallic lustre characteristic of the polymer. The reflectivity is highly dichroic with a structured spectrum, rising to nearly 100% reflectivity at low temperatures, for light polarized along the polymer chain and a constant low value for light polarized perpendicular to the chain, see [15] and Fig. 2.

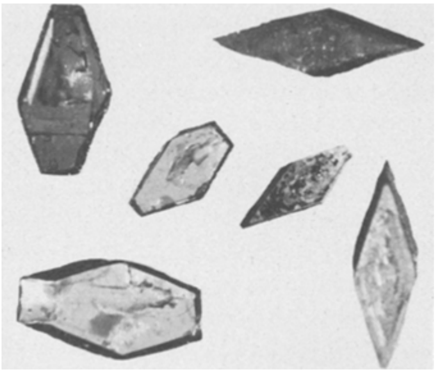

Figure 2 Small diamond and coffin shaped single crystals of bis-(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol photographed in polarized light. Monomer crystals are at the left, polymer crystals at the right. The electric vector of the light is horizontal.

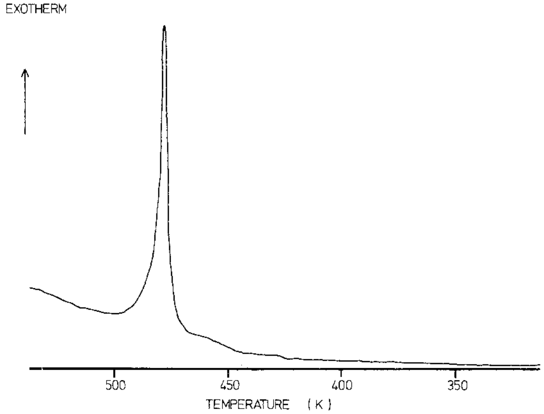

Figure 3 Typical thermogram of bis-(*p*-toluene sulphonate) diacetylene polymer, heating rate 8° C min^{-1}.

The polymer crystals decompose dramatically at 210° C on rapid heating in air or inert gas. A typical thermogram is shown in Fig. 3, the large exotherm resulting from decomposition is the main feature. However, decomposition also occurs after prolonged heating at much lower temperatures. This has been investigated by esr and mass spectroscopy and has been found to be complex. No decomposition occurs during or after polymerization at 60° C. Large and irreversible changes in free radical concentration are observed on heating the polymer so obtained above 100° C [15]. Polymer crystals heated above 100° C become black and fracture, structural damage is seen in the scanning electron microscope as described in Part 2, and decomposition products are detected in the mass spectrometer. At 70 and 80° C the free radical concentration begins to rise shortly after the samples are converted to polymer. This rise is preceded by the detection of decomposition in the mass spectrometer. Further details of these measurements will be given elsewhere [17]. Surface decomposition occurs in crystals exposed to sunlight giving them a tarnished appearance. In order to avoid these effects samples were polymerized at 60° C, except when polymerization at a higher temperature was being studied, and stored in the dark in a refrigerator.

The spectra of partially polymerized crystals were recorded using several thin slices cleaved from a single monomer crystal. These were thermally polymerized under identical conditions for different times and stored at 0° C until the spectra were recorded. The percentage conversions were determined for the same conditions. Unreacted monomer was dissolved in acetone with vigorous stirring and the insoluble polymer fraction was extracted. This process was repeated several times to ensure complete removal of monomer. At high conversions the crystals were pulverized between extractions for the same purpose. At low percent conversion, up to 5 g of monomer were used. This improved the accuracy of the measurement and also enabled sufficient polymer to be extracted for subsequent measurements over a wide range of conversions. The conversion curves determined in this way for thermal polymerization of degassed monomer under an argon atmosphere at 60, 70 and 80° C are shown in Fig. 4. Our results at 60° C agree well with those of Wegner [16] for polymerization in nitrogen in the dark. We found that the normal light levels in the laboratory had no observable effect on the measured polymerization.

The polymerization curves all have a similar shape; an initial slow polymerization up to about 10% conversion, a very rapid rise to nearly complete conversion and a final slow increase to a limiting value. The final phase goes to 100% conversion at 60 and 70° C but at 80° C the decomposition, which sets in just after the rapid rise, gives a lower limiting value. The rapid polymerization becomes faster at higher temperatures, the change from 15 to 80% conversion occurs in about 2 h at 60° C, 30 min at 70° C and 5 min at 80° C. The possible causes of this behaviour will be discussed in Section 5.

Measurements were not made for polymerization in air. Visual observations suggest that the process is similar to that in argon since the initial slow deepening in colour of the crystals is followed by a rapid appearance of the metallic lustre. The optical spectra and X-ray diffraction patterns are identical for air and argon polymerized samples. Some differences occur in the esr spectra of such samples; these are expected because of the paramagnetism and electron affinity of oxygen. We conclude, therefore, that there are no major differences in the physical properties of the two types of material. The measurements reported below were made on both types of material with the exception of the extracted polymer which was all obtained from crystals grown and polymerized in an argon atmosphere.

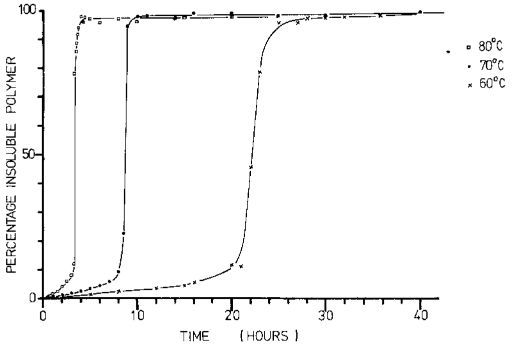

Figure 4 Percentage conversion of bis-(p-toluene sulphonate) diacetylene crystals heated to 60, 70 and 80° C in an argon atmosphere.

3. Measurements on single crystals

Single crystals of thermally polymerized bis-(p-toluene sulphonate) diacetylene produced X-ray diffraction patterns in rotation and Weissenberg cameras with spot sizes set by the instruments. The crystal structure of the polymer has been

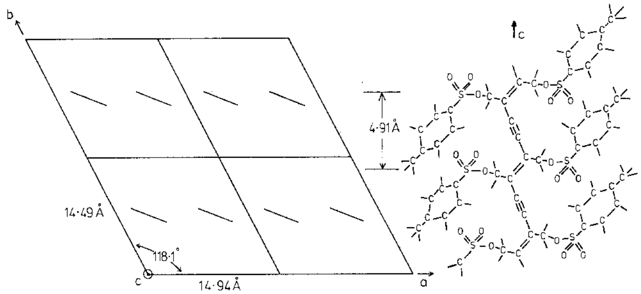

Figure 5 Crystal structure of bis-(*p*-toluene sulphonate) diacetylene polymer according to Kobelt and Paulus [18]. Left: projection on to the *a*–*b* plane showing orientation of the plane of the polymer chains. Right: projection of a single chain normal to the plane of the chain.

determined by Kobelt and Paulus [18] and is shown in Fig. 5. Kobelt and Paulus report the crystal symmetry to be $P2_1/c$, in the second setting with the *b*-axis unique. We prefer to use the equivalent symmetry $P2_1/b$, in the first setting with the *c*-axis unique. In this case the polymer chain is extended in the *c*-direction in accord with common usage for polymers. In Fig. 5 the projection on to the *a*–*b* plane, in which the orientation of the plane of the polymer chain is shown by a straight line, and a projection of a polymer chain normal to the plane of the chain are shown. Our single crystal structural data, though less accurate, agrees with that of Kobelt and Paulus.

The structure of the monomer could not be determined because single crystals polymerized rapidly in the X-ray beam. However, polycrystalline residues on the surfaces of crystals were observed to be partially polymerized long after thermal polymerization of the crystal was complete. Monomer precipitated from solution as a microcrystalline powder had similar stability so that it was possible to obtain data on a scanning diffractometer without any visible polymerization. Polymer powder samples were prepared for comparison purposes, one was obtained by pulverizing small, thin 100% polymer crystals and a second by similar treatment of polymer extracted at 96% conversion. The latter sample appeared crystalline in the scanning electron microscope but was sufficiently fibrous to allow it to be reduced to a fine powder. Similar treatment of large fully converted crystals produced a flaky material which showed strong prefered orientation in the diffractometer. The diffraction patterns were recorded on a Philips PW1050/25 diffractometer using Cu*Kα* radiation. Up to thirty reflections could be measured accurately and the lattice parameters were refined until there was no significant improvement in the quality of the fit to the experimental data. The parameters determined for the monomer and polymer samples are listed in Table I together with the parameters of Kobelt and Paulus [18]. The values of the lattice parameters for the two polymer samples agree with those of Kobelt and Paulus within the accuracy of our measurements, *a*, *b* and *c* to ± 0.02 Å and γ to ± 0.1°. The lattice parameters of the monomer are significantly different, in particular the value of *c* is about 5% larger than in the polymer.

In order to eliminate the possibility that the precipitated monomer was in an unreactive crystal modification we measured the change in volume on polymerization for a large single crystal and compared it with that calculated from the parameters of Table I. These changes were 7.0 ± 1.0% and 6.0% respectively, a satisfactory agreement which indicates that there was no major difference

TABLE I Lattice parameters of bis-(*p*-toluene sulphonate) diacetylene monomer and polymer, symmetry $P2_1/b$. Cell dimensions in units of 10^{-10} m, cell angle in degrees.

	Polymer			Monomer
	Kobelt and Paulus [18]	This work 100% conversion	This work 96% conversion	This work
a	14.936(1)	14.91	14.93	15.02
b	14.493(8)	14.48	14.50	14.60
c	4.910(3)	4.93	4.90	5.15
γ	118.14(4)	118.0	118.2	118.4

between the precipitated powder and macroscopic crystals. The much greater stability of the former material has two possible causes, first the bulk of the energy imparted to the powder by the X-rays will be dissipated at crystal surfaces rather than in initiating polymerization and secondly the lengths of the polymer chains produced by each initiation will be limited by the size of the crystals.

Although the measured change in c is quite large the volume change is similar. Thus, as can be seen from the lattice parameters the change in the lateral dimensions of the crystal is small and the retention of the crystal structure by a single phase polymerization is likely. We have no direct X-ray evidence for this but we can obtain information on the intermediate state of the crystal by optical and Raman spectroscopy.

The absorption spectra recorded during the polymerization at 80° C of a 7 μm thick monomer crystal mounted between glass slides are shown in Fig. 6. These show an intense electronic absorption with weaker phonon sidebands on the high frequency side [15]. After 2 h the absorption becomes very intense for light polarized parallel to the polymer chain and the true absorption cannot be measured due to depolarization and stray light in the optical system. The absorption can be observed for light polarized perpendicular to the polymer chain as the absorption coefficient is finite provided the light is not polarized perpendicular to the plane of the polymer chain [15 19]. Although the features in the spectra are quite broad a distinct bathochromic shift occurs during polymerization. There are two alternative explanations for this shift, first that it is due to the increase in length of the conjugated chains during polymerization and secondly it is due to the change in length of effectively infinite chains produced by changes in the lattice dimensions during a single phase polymerization.

We reject the first alternative since the observed shift is too small. We find that the monomer absorbs at 272.5 nm, in agreement with Armitage and Whiting [20], and the polymer at 620 nm, see Fig. 6 and [15]. These values are comparable with those observed for other conjugated molecules [21, 22]. The observed shift requires an increase from sixteen to an infinite number of repeat units [21]. This is incompatible with the stability and insolubility of the polymer extracted at very low conversion. A range of chain lengths would produce a broad absorption in partially polymerized samples whereas the spectra observed are well defined particularly at low temperatures, see Fig. 8. This results from the fact that the absorption intensity of the electronic absorption increases rapidly as the length of the conjugated chain increases. The peak absorption for light polarized parallel to the polymer chain can be measured correctly only by the use of very thin samples even when there is 0.1%, or less, polymer present. This, together with the insolubility of polymer extracted from such samples and the molecular weight measurements by Wegner [16], leads us to conclude that the spectra we observe are due to very long polymer chains isolated in the monomer matrix in accord with the model of Kaiser *et al.* [8]. These chains are essentially infinite in that variations in length have a negligible effect on the absorption frequency and intensity, which are close to the limiting values for truly infinite chains.

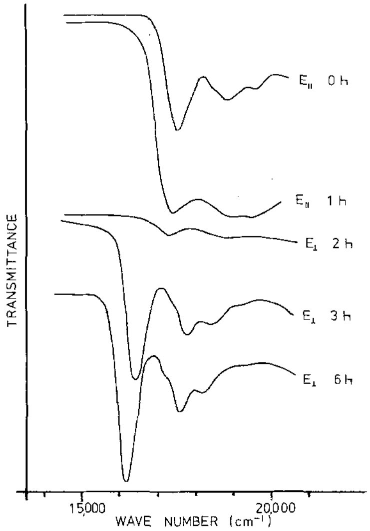

Figure 6 Room temperature transmission spectra of a thin bis-(p-toluene sulphonate) diacetylene crystal recorded during thermal polymerization at 80° C. Polarization of light with respect to the c-axis and polymerization time are given to the right of the spectra.

The frequency of the electronic absorption as function of polymerization time at 80° C is plotted in Fig. 7. This has the same form as the polymerization curve at 80° C, Fig. 4. The absorption frequency decreases as the crystal c-axis contracts. The same effect has been observed in partially polymerized crystals subjected to hydrostatic pressure [23]. The similarity of the curves for absorption frequency and percent conversion

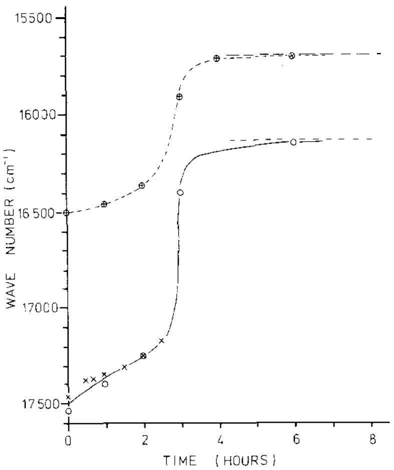

Figure 7 Frequency shifts of the electronic absorption peak in crystals polymerized at 80° C. Lower curve: spectra recorded at room temperature, ○ – from spectra of Fig. 6, x – from spectra of cleaved crystal. Upper curve: spectra recorded at 4.2 K, lower frequency peak. Horizontal lines at right are peak positions for polymer crystals polymerized at 60° C.

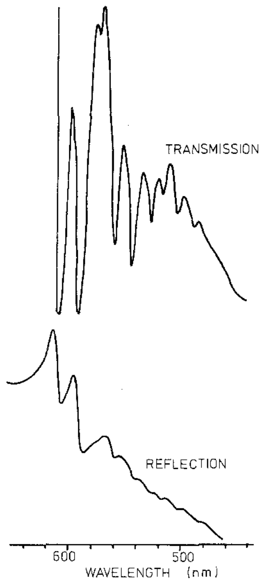

Figure 8 Transmission and reflection spectra of a partially polymerized crystal of bis-(p-toluene sulphonate) diacetylene at 4.2 K. These spectra are not corrected for background intensity variations.

suggests simple relationships between these quantities and the c-axis dimension. Similar results are obtained for spectra recorded at low temperatures, which have much sharper reflection peaks and absorption lines, see Fig. 8. The electronic absorption and the phonon sidebands are split into pairs. A similar splitting occurs in polymer crystals [15]. The frequencies and shifts can be found more accurately from these spectra. The frequency of the lower absorption peak for samples polymerized at 80° C is plotted in Fig. 7. The frequency shift for the other peak is similar.

The low temperature spectra show an additional frequency shift due to the contraction of the crystals on cooling to 4.2 K. At room temperature a negative c-axis thermal expansion coefficient has been reported for a bis-phenylurethane diacetylene polymer [24]. Below 150 K, where two sharp peaks can be resolved, the observed frequency shift indicates normal behaviour. This follows since the torsional modes responsible for the negative value will not be excited at low temperatures. The frequency shift on cooling is less for the polymer than for partially polymerized crystals. This reflects the weaker molecular interactions and the absence of a negative expansion region in the monomer.

A possible cause of the splitting of the absorption peaks is a phase transition in the crystal below room temperature. However, the presence of similar splittings in crystals with either very little or 100% polymer, which have different molecular structures, renders this unlikely. Detailed studies of the spectra as a function of temperature are being performed to establish the origin of the splitting. Preliminary measurements indicate that the apparent loss of structure in the spectra at room temperature is due to line broadening and not to a sharp transition.

Raman spectroscopy can provide additional information about the polymer chains in partially polymerized crystals [25–27]. The Raman scattering from the polymer is resonantly enhanced due to the interaction of the exciting radiation with the electronic absorption of the polymer chain. Only those vibrations which couple with the electronic states of the polymer will be enhanced. Thus, the vibrations of the polymer chain will appear in the Raman spectra while those of the sidegroups will not. This effect has been clearly demonstrated for the bis-(p-toluene sulphonate) diacetylene polymer [27]. The large sidegroups have many possible Raman active vibrational modes, however, the Raman spectrum excited with red light has just five strong components. Lines at 2086, 1486 and 1467 cm^{-1} are assigned to the stretching vibrations of the triple and double bonds in the polymer chain while lines at 1205 and 955 cm^{-1} are assigned to motions involving bond bending and stretching of single bonds [27]. The frequencies of these vibrations are sensitive to the bond lengths [26] and bond angles in the polymer chain.

In partially polymerized crystals the enhancement of the polymer Raman spectrum is greater than that of the monomer because the exciting radiation is closer to the polymer absorption than to the monomer absorption. The spectra shown in Fig. 9 were recorded using a dye laser tuned to 620 nm just below the peak absorption for partially polymerized crystals. At very low conversion the monomer triple bond vibration can just be discerned at 2260 cm^{-1}. The five polymer lines are observed but for low conversion the four higher frequency lines are shifted to lower frequencies compared to the polymer. The unshifted line involves mainly stretching of the single bond between the polymer chain and the sidegroups and will be insensitive to deformation of the chain. During the slow initial polymerization, below about 10% conversion, the line frequencies increase with increasing conversion. The peaks are broad, particularly the triple bond vibration, and the two double bond peaks have comparable intensity. Above about 10% conversion sharp lines appear at the same frequencies as in the polymer. The broad features, again most noticeably the triple bond vibration, merge with these peaks and disappear with the exception of the lower frequency double bond line, which remains as a weaker feature in the polymer spectrum.

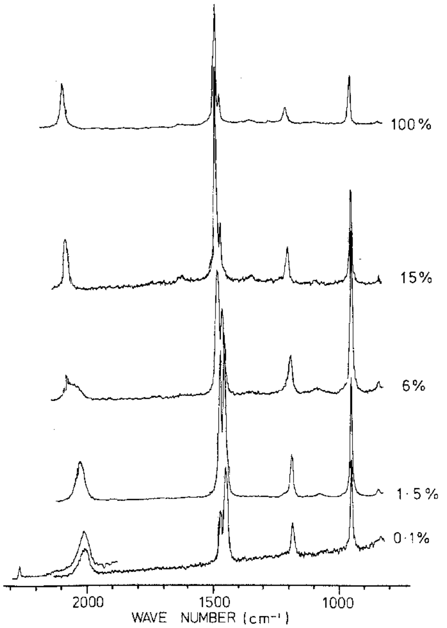

Figure 9 Raman spectra of bis-(*p*-toluene sulphonate) diacetylene crystals during thermal polymerization. Percent conversion is shown at the right of the spectra. 620 nm dye laser excitation and a resolution better than 1 cm^{-1} were used.

These changes are obviously related to the percentage polymerization and the changes in the *c*-axis dimension. At low conversion the polymer chain is extended by about 5%, producing changes in bond lengths and angles. The increases in length are largest for the single and triple bonds as their vibrations have the largest frequency shifts, 25 and 75 cm^{-1} relative to the polymer respectively. The width of the triple bond line indicates some variation in bond lengthening. Using accepted correlations [26] the actual changes in bond lengths are very small so that bond angle deformation must account for most of the increase in chain length. As the *c*-axis contracts during polymerization the bonds shorten and at about 10% conversion can adopt their final lengths with the *c*-axis extension taken up solely in bond angle deformation.

Both the optical and Raman spectra of crystals show systematic changes during thermal polymerization, which can be explained as the response of long polymer chains to a slowly changing crystalline environment during a single phase polymerization.

4. Measurements on extracted polymer

Samples of polymer were extracted from crystals polymerized for different times at 60° C in an argon atmosphere. These samples were examined

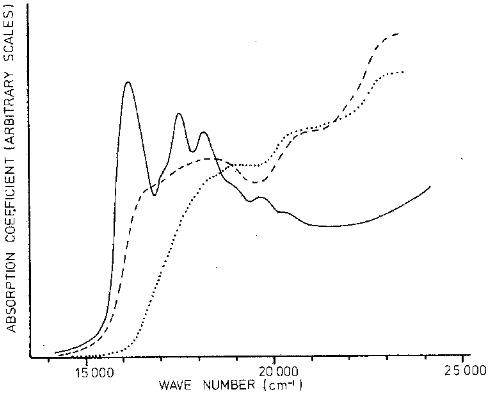

Figure 10 Diffuse reflectance spectra of extracted polymer powders, dotted curve – 0.1% conversion, dash curve – 11.7% conversion. Full curve – absorption coefficient for light polarized perpendicular to the *c*-axis of a polymer crystal. Vertical scales for the curves are arbitrary.

by optical and Raman spectroscopy and X-ray diffraction.

At low percent conversions the extracted polymer is a finely divided powder. Transmission spectra cannot be measured because of strong light scattering by the samples. However, the absorption coefficient can be determined, to an arbitrary multiplicative factor, from the diffuse reflectance spectrum. The results for samples extracted at conversions of 0.1 and 11.7% are shown in Fig. 10. The results for samples extracted at 2.4 and 4.6% are similar to those for the 0.1% sample. These results agree with the visual observation that at low conversions the extracted polymer is orange but becomes red, like the unextracted polymer, at higher conversions. Comparison with the absorption coefficient for single crystal polymer shows that the 11.7% sample has broad peaks in the region of the electronic absorption and phonon sidebands. This indicates some degree of crystallinity in this sample. At 0.1% conversion these peaks are absent and the shift in the absorption edge suggests that the length of chain with uninterrupted conjugation is reduced. As the absorption coefficients contain unknown factors the apparent increase in absorption in the blue for the extracted polymer is probably due to incorrect scaling in the figure. Previously we have attributed the spreading out of the absorption edge in crystal samples to an increase in defect density [15]. Spreading is also observed in the extracted samples again suggesting lower perfection on extraction at lower percent conversion.

This conclusion is confirmed by X-ray diffractometer traces obtained for similar samples. Fig. 11 shows the patterns observed for samples extracted at 2.4, 5.5, 11.7, 79 and 96% conversion. The diffraction peaks for the 2.4% sample are barely visible but are clearer for the 5.5 and 11.7% samples and sharp and distinct for the 79 and 96% samples. Thus, at 2.4% conversion the sample appears amorphous but for 5.5 and 11.7% conversion there is considerably more long range order in the extracted polymer. At high conversions the samples are essentially single crystals with diffraction peaks broadened by disorder introduced on removal of the residual monomer.

These results also agree with the solid solution model of Kaiser *et al.* [8]. At low conversion the polymer chains are isolated and on extraction from the monomer matrix collapse to form an amorphous powder. Though this material has the lowest molecular weight [16] as shown in Section 3 the chains are not short enough to affect the absorption spectrum. Thus, the reduction in length of conjugation, shown by the spectrum of the extracted polymer, must result from the deformation of the chains on extraction. As the conversion increases more chains occur as close neighbours which on extraction retain some of the crystalline order. At high percent conversion removal of the monomer produces defects in an otherwise single crystal material, for example slip adjacent to voids. This produces a mosaic structure which broadens the X-ray diffraction peaks. Direct observation of these effects is described in Part 2.

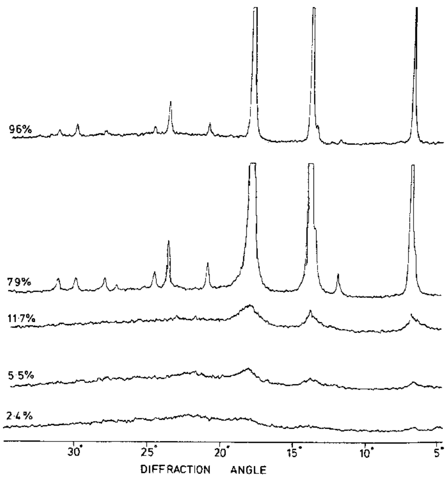

Figure 11 X-ray diffractometer traces of extracted polymer samples. Percent conversion is given at the left of each trace.

X-ray diffraction is sensitive to long range order and allows the dimensions of the unit cell of the extracted polymer to be determined. As shown in Fig. 11 the positions of the diffraction peaks do not change so that, within the limits imposed by the widths of the peaks, the unit cell dimensions are the same for all extracted samples and equal to those of fully polymerized crystals. Raman spectroscopy is sensitive to short range order and can provide information about the conformation of the polymer chain. The Raman spectra of extracted powders are shown in Fig. 12. The main Raman lines occur at the same frequencies as for a polymer crystal. Thus, the polymer chain retains exactly the same dimensions in the extracted polymer as in the single crystal in agreement with the X-ray results. For the low conversion samples this is true for only part of the material since additional lines shifted to higher frequency occur. We have interpreted these as due to a second

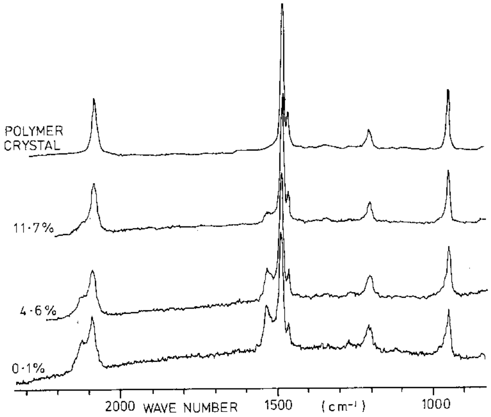

Figure 12 Raman spectra of extracted polymer powders, percent conversion is noted at the left of the spectra. The uppermost spectrum is that of a polymer crystal. 620 nm dye laser excitation and a resolution of just over 1 cm^{-1} were used.

distinct conformation of the polymer chain produced as the chains collapse on extraction at low conversion [27]. These lines disappear as the conversion and the crystallinity of the samples increases. This interpretation receives support from the changes in reflectance spectra which suggest the introduction of kinks into the polymer chain on extraction.

Thus, we arrive at the conclusions that the polymerization of bis-(*p*-toluene sulphonate) diacetylene is a homogeneous single phase transformation and that the final polymer crystal contains polymer chains in their equilibrium conformation since both the X-ray and Raman measurements show that the extracted and fully crystalline polymer adopt the same conformation no matter what the degree of conversion prior to extraction.

5. Discussion

A single phase polymerization to produce a lattice with minimum free energy must possess a free energy diagram close to the ideal case discussed by Baughman [12], in which the free energy of the single phase system falls continuously as polymerization proceeds. The details of the change in free energy may produce some variation in polymerization rate but these are unlikely to be as great as those observed for the bis-(*p*-toluene sulphonate) diacetylene. Initiation, nucleation and chain length are more likely to be important factors in the polymerization kinetics.

The problems of initiation and nucleation are complex and we will make some simplifying assumptions. First following Papissov and Kabanov [28], since the polymerization occurs in a single phase we assume that the interfacial energy between polymer and monomer is small and that single polymer chains can form supercritical nuclei. Furthermore we assume, following Semenov [29] and Adirovich [30], that once initiated the polymerization proceeds as an excitation wave, an exciton plus a lattice displacement wave, until the excitation is trapped or decays into inactive excitations. This means that each initiation leads almost instantaneously to the production of a long polymer chain. These assumptions seem reasonable since the optical spectra and measured viscosities [16] require the presence of long chains even at low conversions.

If we assume that the initiation rate controls the polymerization rate then we require the energy for initiation to be high during the initial slow polymerization and to fall dramatically during the rapid polymerization. This seems reasonable since the rapid phase is auto-catalytic in character. However, Arrhenius plots of the data in Fig. 4, although not very accurate, show that the activation energy is approximately constant for both regions.

A second possibility is that the distance of propagation of the excitation wave controls the polymerization rate. In the initial slow region the Raman spectra show that the polymer in the monomer matrix is strained. The loss of energy to strained bonds will limit the lifetime of the excitation wave and the molecular weight of the polymer produced During rapid polymerization the polymer chains formed have equilibrium bond lengths and are close to the conformation of the chains in the polymer crystal. Little energy is dissipated as strain energy in the polymer so that the excitation wave lifetime and the molecular weight of the polymer are both increased. This is in agreement with the increase in viscosity of the polymer during polymerization observed by Wegner [16].

We can describe the single phase monomer-polymer system by a simple model of two elastic systems acting along the *c*-axis. When coupled together one, the monomer, is in compression and the other, the polymer, is in extension. The change in *c*, assuming Hookean behaviour, as a function of conversion and the ratio of the elastic moduli of the two systems is shown in Fig. 13. The total change in *c* is set equal to that observed for the

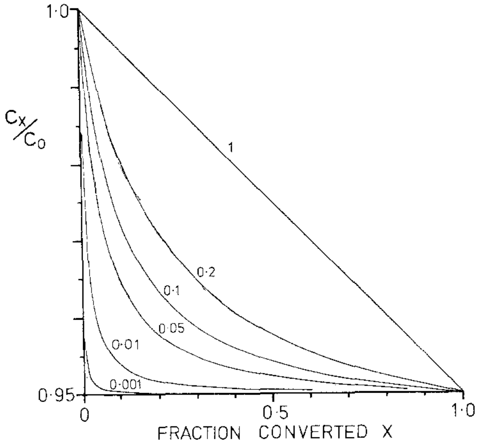

Figure 13 Change in c as a function of fractional conversion X for perfectly elastic monomer and polymer in a single phase. The numbers on the curves give the ratio of the monomer elastic modulus to that of the polymer.

bis-(p-toluene sulphonate) diacetylene. As the ratio of the monomer to polymer elastic constant decreases the initial decrease in c becomes more rapid. A ratio of 0.01 results in a change in c with a knee at about 10% conversion. This curve can be used to explain the experimental observations described in Sections 2 and 3. Below 10% conversion the polymer will be highly strained while above 10% it will be close to its equilibrium conformation. The initial strain and its disappearance are seen clearly in the frequency shifts and linewidth changes in the Raman spectra. The change in strain energy stored in the polymer chains was used above to explain the changes in polymerization rate in terms of changes in chain length. The calculated change in c will produce changes in the optical spectrum which occur ahead of the changes in polymer content of the crystal. Comparison of Figs. 4 and 7 show that this is in fact what happens. The ratio of the elastic constants of weakly bonded molecular crystals, e.g. benzene, and covalently bonded crystals, e.g. diamond, is about 10^{-3}. A ratio of about 0.01 is reasonable for this system because of additional interaction between the polar sidegroups in the monomer. In reality the elastic forces will be non-Hookean but this should not affect the general results deduced on the basis of perfectly elastic behaviour.

The final stage of polymerization proceeds at a low rate. This is explained by the presence of short unreacted sequences and material in highly defected or impure regions of the crystal where polymerization is inhibited. At the higher temperatures decomposition prevents complete conversion. This may result from the channelling of excitation-wave energy into localized excitations capable of breaking bonds.

We have assumed that the initiation is random in accord with the uniformity of colouration of partially polymerized crystals and the variation in crystallinity of the extracted polymer. Schermann *et al.* [31] report the growth of polymer at dislocation etch pits in this system. However, this only occurs in the fast polymerization region and in either the $+c$ or $-c$ directions but not both. This suggests that the anisotropic force field around the dislocation favours faster polymerization on one side of the dislocation earlier than in the bulk of the crystal.

Most of the strained polymer formed in the initial phase of polymerization anneals out during the rapid phase. The persistence of a second double bond vibration in the final polymer suggests that the annealing is incomplete. However, the appearance of this line with the same relative intensity in the extracted polymer suggests a more fundamental origin. The initial strain is evident in esr spectra since the intrinsic polymer radical concentration falls during polymerization [17]. The final radical concentration is too low for the minor double bond to be a bond defect. Further investigations of this Raman line are in hand.

The observed changes in the electronic absorption are consistent with those produced by hydrostatic pressure. They can be understood in general terms since a compression will tend to equalize the bond lengths in the polymer chain and reduce the excitation energy to zero [19]. However, the Raman spectra show only small bond length changes and imply large bond angle changes. This is consistent with accepted force constants for bond bending and stretching. Simple Hückel molecular orbital calculations, where the interactions depend only on bond length, cannot be used in this situation. More complex molecular orbital calculations are rarely exact and are unlikely to add to the understanding of the polymerization process.

To summarize, the optical and Raman spectra of polymerizing crystals of bis-(p-toluene sulphonate) diacetylene show smooth changes which we attribute to a continuous change in lattice parameters during a single phase polymerization. Spectroscopic and X-ray diffraction measurements of extracted polymer show a random initiation of chain growth leading to collapse of the isolated polymer chains on extraction at low conversion. Fully polymerized crystals contain chains with an unstrained conformation as exhibited by extracted polymer. The strain observed in polymer chains in the monomer matrix has been described by a simple model of interacting elastic systems. The presence of two clearly different regions of high and low strain can be used to explain the observed polymerization kinetics in terms of the excitation wave model of Semenov. This model is also favoured by the presence of very long polymer chains at all stages of polymerization.

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References

1. A. BAEYER and L. LANDSBERG, *Ber. Deut. Chem. Ges.* **15** (1882) 57.
2. F. STRAUSS, L. KOLLECK and W. HEYN, *ibid* **63** (1930) 1868.
3. F. STRAUSS, L. KOLLECK and H. HAUPTMANN, *ibid* **63** (1930) 1886.
4. G. WEGNER, *Z. Natforschung.* **24b** (1969) 824.
5. *Idem, J. Polymer Sci. Polymer Letters* **9** (1971) 133.
6. *Idem, Die Makromol. Chemie* **134** (1970) 219.
7. *Idem, ibid* **154** (1972) 35.
8. J. KAISER, G. WEGNER and E. W. FISCHER, *Israel J. Chem.* **10** (1972) 157.
9. J. KIJI, J. KAISER, G. WEGNER and R. C. SHULZ, *Polymer* **14** (1973) 433.
10. R. H. BAUGHMAN and K. C. YEE, *J. Polymer Sci. Polymer Chem.* **12** (1974) 2467.
11. R. H. BAUGHMAN, *J. Appl. Phys.* **43** (1972) 4362.
12. *Idem, J. Polymer Sci. Polymer Phys.* **12** (1974) 1511.
13. E. HADICKE, E. C. MEZ, C. H. KRAUCH, G. WEGNER and J. KAISER, *Angew. Chemie Int. Edit.* **10** (1971) 266.
14. E. H. ANDREWS and G. E. MARTIN, *J. Mater. Sci.* **9** (1974) 1507.
15. D. BLOOR, D. J. ANDO, F. H. PRESTON and G. C. STEVENS, *Chem. Phys. Letters* **24** (1974) 407.
16. G. WEGNER, *Die Makromol. Chemie* **145** (1971) 85.
17. D. BLOOR and G. C. STEVENS, to be published.
18. D. KOBELT and E. F. PAULUS, *Acta Cryst.* **B30** (1974) 232.
19. E. G. WILSON, *J. Phys. C: Solid State Phys.* **8** (1975) 727.
20. J. B. ARMITAGE and M. C. WHITING, *J. Chem. Soc.* (1952) 2005.
21. J. R. PLATT, *J. Chem. Phys.* **25** (1956) 80.
22. M. BEER, *J. Chem. Phys.* **25** (1956) 745.
23. D. N. BATCHELDER and A. C. COTTLE, private communication.
24. R. H. BAUGHMAN, *J. Chem. Phys.* **58** (1973) 2976.
25. A. J. MELVEGER and R. H. BAUGHMAN, *J. Polymer Sci. Polymer Phys.* **11** (1973) 603.
26. R. H. BAUGHMAN, J. D. WITT and K. C. YEE, *J. Chem. Phys.* **60** (1974) 4755.
27. D. BLOOR, D. J. ANDO, F. H. PRESTON and D. N. BATCHELDER, to be published in "Structural studies of macromolecules by spectroscopic methods", edited by K. J. Ivin (Wiley).
28. I. M. PAPISSOV and V. A. KABANOV, *J. Polymer Sci. C* **16** (1967) 911.
29. N. N. SEMENOV, *J. Polymer Sci.* **55** (1961) 563.
30. E. I. ADIROVICH, *Dokl. Akad. Nauk, SSSR* **136** (1961) 117.
31. W. SCHERMANN, J. O. WILLIAMS, J. M. THOMAS and G. WEGNER, *J. Polymer Sci: Polymer Phys.* **13** (1975) 753.

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