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A Spectroscopic Study of the Second Order Phase Transition in Bis (*p*-toluene sulfonate) Diacetylene Polymer Crystals

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The second order phase transition at 195 K which occurs in bis (*p*-toluene sulfonate) diacetylene polymer crystals has been studied by optical reflection and transmission, Raman and far-infrared spectroscopy. Order parameter fitting to the data suggests that at low temperatures the transition has a two dimensional character while closer to the transition it appears to be three dimensional. There are indications of a broad transition region which might be expected for a predominately two dimensional phase transition in which fluctuations dominate the behaviour of the system. Analysis of new X-ray crystallographic data gives some support to a structural model in which the transition would have a substantial two dimensional character.

INTRODUCTION

The occurrence of a second order phase transition in crystals of both the monomer and polymer of the bis (*p*-toluene sulfonate) of 2,4-hexadiyne-1,6-diol [TS] is now well established. The crystal structure of the low temperature phase has been determined[1,2] and the gradual onset of order in the low temperature phase has been observed in X-ray studies.[3,4]

The low temperature phase has two inequivalent polymer chains. This difference in structure gives rise to splittings of some features which appear in the optical and vibrational spectra of the high temperature phase, as originally suggested by Bloor *et al.*[5] and recently discussed in detail by Schott *et al.*[6] Though numerous studies have been made of the optical[7-10] and Raman[11-12] spectra at ambient and high pressure,[13,14] few have attempted to deduce details of the nature of the phase transition from the data. In the cases where a fit of an order parameter of the form

$$\frac{\Delta}{\Delta_o} = \left[1 - \frac{T}{T_c}\right]^{\beta} \qquad (1)$$

has been attempted, the experimental results were not adequate to display more than the second order nature of the transition.[7,10,11]

We report here more careful measurements of the optical and Raman spectra and new measurements of the low lying vibrational modes by far-infrared spectroscopy. Careful analysis of these results shows that the behaviour of TS is not simple and is worthy of further study. Though a similar phase transition occurs in both fully and partially polymerized crystals we describe here measurements on fully polymerized samples only.

OPTICAL SPECTRA

Optical spectra were measured by reflection spectroscopy[10] (with subsequent Kramers-Kronig analysis) and by transmission through thin samples cleaved from crystals with adhesive tape. In general the latter were too thick to record spectra for light polarized parallel to the chains.[15] The spectra for light polarized perpendicular to the chains are in fact easier to interpret since the refractive index of the polymer is virtually constant for this polarization and so the maxima of ε_2, k, absorption coefficient and sample loss coincide. This is not true for the case of parallel polarization.[16] The optical splitting as a function of temperature is shown in Figure 1. The agreement between data from reflection and transmission spectroscopy is satisfactory. Near 200 K the line width is too great to measure the splitting directly, the values being deduced from the excess line broadening.

From 4 K to about 120 K the splitting can be described by Eq. 1 with T_c = 175 K and $\beta = 0.125$. Closer to the transition temperature an order parameter with T_c = 185 K and $\beta = 0.34$ gives a better fit. A composite fit with the two sets of parameters gives a much better fit than a single curve with T_c = 185 K and an intermediate value of 0.2 for β. The splitting exhibits a tail above 185 K which is observable up to the X-ray determined transition temperature of 195 ± 2 K.[4]

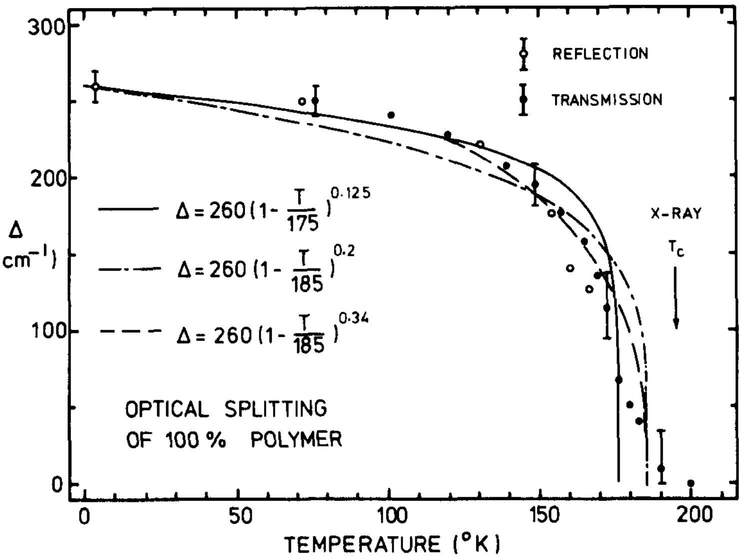

FIGURE 1 Temperature dependence of the splitting, Δ, of the peaks in the imaginary part of the dielectric constant, ε_2, as determined by reflection and transmission spectroscopy of TS polymer crystals. At 300 K ε_2 has a single peak at 16050 cm^{-1}. The best fit to the data is given by a composite order parameter with $\beta = 0.125$, $T_c = 175$ K up to 120 K, and $\beta = 0.2$, $T_c = 185$ K at higher temperatures.

RAMAN SPECTRA

The splittings of the Raman lines at 1203 and 952 cm^{-1}, which are predominately bending modes about the double and triple bonds,[17] are only a few cm^{-1}. The temperature dependences are shown in Figure 2, but within experimental accuracy the data do not differentiate clearly between the order parameters used to fit the optical spectra. Although the temperature dependences of the optical and Raman data indicate that the two types of splitting are closely related, measurements at high pressure indicate that this is not necessarily so. Figure 3 shows that at 90 K the relative splittings in the optical spectra decrease with increasing hydrostatic pressure while those of the Raman spectra remain constant.

FAR-INFRARED SPECTRA

Far-infrared spectra show several well polarized narrow vibrational absorptions at 4 K. As the sample temperature is increased a parallel polarized band centered at 32 cm^{-1} shows a soft mode behaviour. In addition a

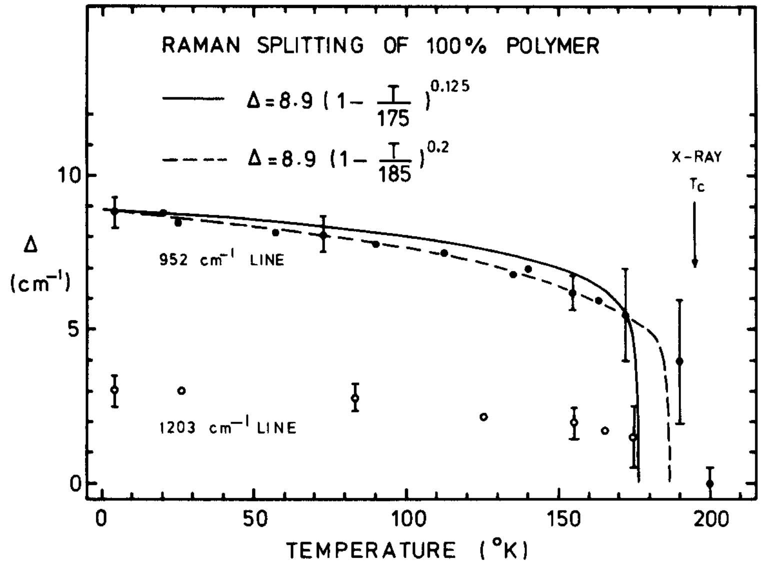

FIGURE 2 Temperature dependence of the splitting, Δ, of the two Raman lines at 952 and 1203 cm^{-1}. The 952 cm^{-1} splitting data are insufficient to discriminate between the two types of order parameter. The split lines were observed individually by tuning the dye laser to the appropriate absorption peak so that strong resonant enhancement was only experienced by one of the pair.

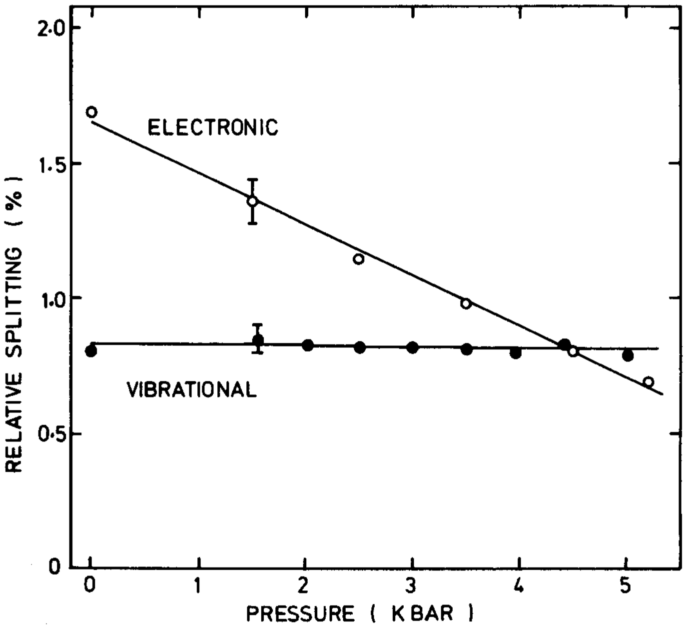

FIGURE 3 Relative splittings of the peaks in ε_2 (electronic) and the 952 cm^{-1} Raman lines (vibrational) as a function of hydrostatic pressure at 86 K. The difference in pressure dependences indicates that the splittings are not highly correlated in spite of the similarities in Figures 1 and 2.

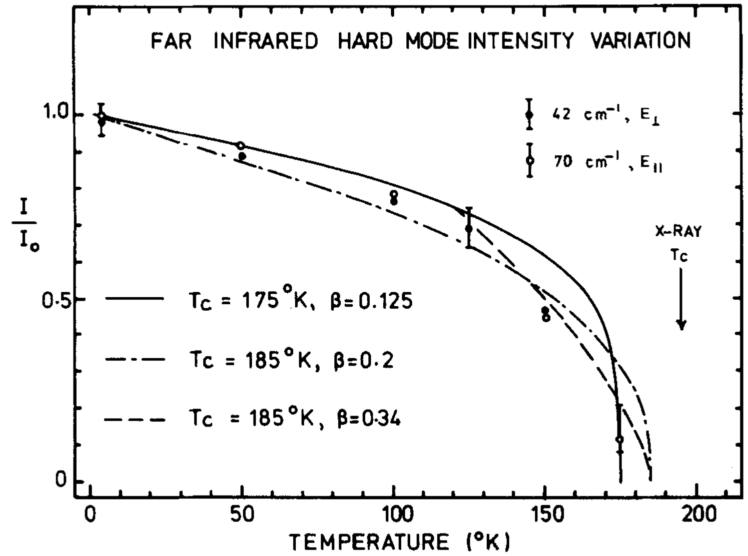

FIGURE 4 Temperature dependences of the intensities of two "hard" vibrational modes as observed in far-infrared absorption spectroscopy. The 42 cm^{-1} line (at 4 K) was observed for radiation with the electric field vector polarized perpendicular to the polymer chain, while for the 70 cm^{-1} line the polarization was parallel to the chain. The various curves have been drawn assuming I/I_0 proportional to $(\Delta/\Delta_o)^2$. The best fit to the data occurs with a composite order parameter as in Figure 1.

number of bands show typically hard mode behaviour with gradually decreasing intensities as the transition temperature is approached. Results for two hard modes are shown in Figure 4. The transition dipole of such modes will derive from a second order term which is dominated in the transition region by the contribution of the soft mode. Thus the intensity should follow the square of the order parameter. The composite curve used to describe the optical splitting fits well to this data. Further details of these measurements will be given elsewhere.[18]

CONCLUSIONS FROM THE ORDER PARAMETER ANALYSIS

At low temperatures the results suggest that TS is characterised by two dimensional disorder since the critical exponent β takes the theoretical value obtained for the two dimensional Ising model.[19] Near the transition a value of β close to that found in three dimensional second order transitions gives a better fit. However in both cases the value of T_c used is substantially lower than 195 K, the temperature at which additional reflections appear in the X-ray diffraction pattern. This suggests that neither model is correct

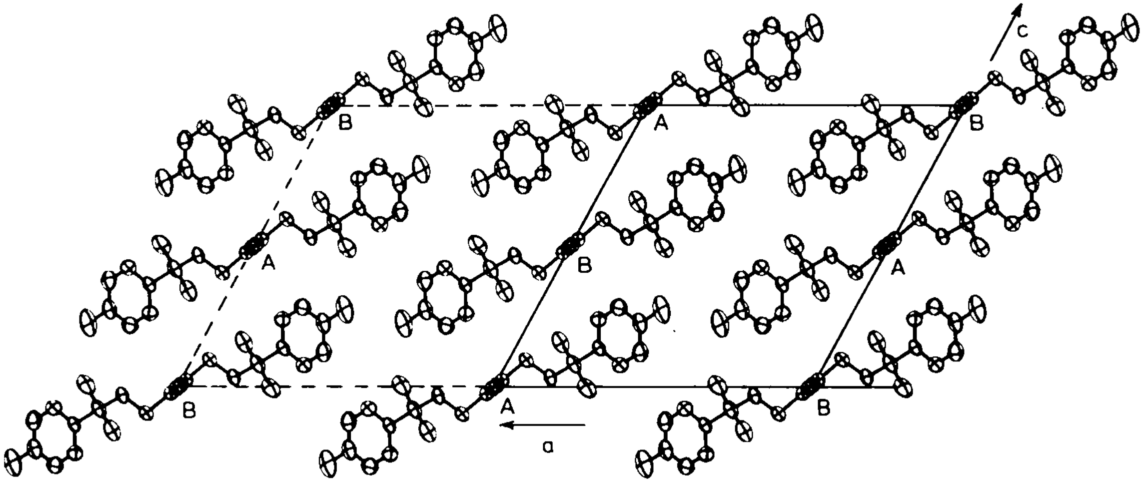

FIGURE 5 Projection of the $P2_1/c$ unit cell of TS polymer at 300 K onto the *a–c* crystallographic plane. The polymer backbone is parallel to the *b* axis which is perpendicular to the *a–c* plane. The atoms, which are identified in Figure 6, are represented by their thermal ellipsoids. The solid lines outline the unit cell in the high temperature phase. In the low temperature phase with $P2_1/n$ structure, the unit cell is doubled in the *a* direction (dotted lines) and there are two inequivalent polymer chains, A and B, in the unit cell.

closer than 10 K to the transition. Such discrepancies may be expected for a predominately two dimensional phase transition with a wide transition width in which fluctuations dominate the behaviour of the system.[20]

X-RAY DIFFRACTION ANALYSIS

In order to investigate possible models for a two dimensional second order transition in TS we have re-investigated the low and high temperature crystal structures. X-ray intensity data were collected for 1486 unique reflections at 120 K and 1294 reflections at 300 K. Figure 5 shows a projection of the $P2_1/c$ unit cell onto the a–c plane. The doubling of the unit cell in the a direction, which occurs in the low temperature $P2_1/n$ structure, is also indicated. The structures were solved by direct methods and subsequent anisotropic refinement gave R factors,

$$R = \frac{\Sigma|(|F_o| - |F_c|)|}{\Sigma|F_o|} \tag{2}$$

of 0.045 and 0.061 for the structures at 300 K and 120 K respectively, F_o and F_c being the observed and calculated structure factors. In general our structures agree well with those reported previously for both the high[21] and low[1,2] temperature phases. Despite the improvement in accuracy we were still unable to detect any structural differences between the backbones of the two types of polymer chain (those with type A and those with type B sidegroups) which are present in the low temperature phase.

Figure 6 shows the anisotropic thermal motion of the non-hydrogen atoms in TS. The central figure is a plot of a backbone segment and one sidegroup of a TS molecule at room temperature, and the plots labelled A and B are similar parts of the two distinct types of TS molecule at 120 K. The degree of thermal motion for the two molecules at 120 K is, of course, lower than the level of thermal motion at room temperature. Despite the fact that the molecules labelled A and B occupy positions which are slightly displaced from the positions they would have occupied at room temperature, it can be seen that the thermal ellipsoids of molecules A and B in Figure 6 could be completely enveloped within the thermal ellipsoids of the room-temperature molecule.

This last observation led us to ask if the structures determined at room temperature truly represent the configuration of TS molecules at room temperature. It seemed possible that the derived, room-temperature, structures could represent either an average of a random distribution of A and B type molecules distributed throughout the TS crystal at room-temperature,

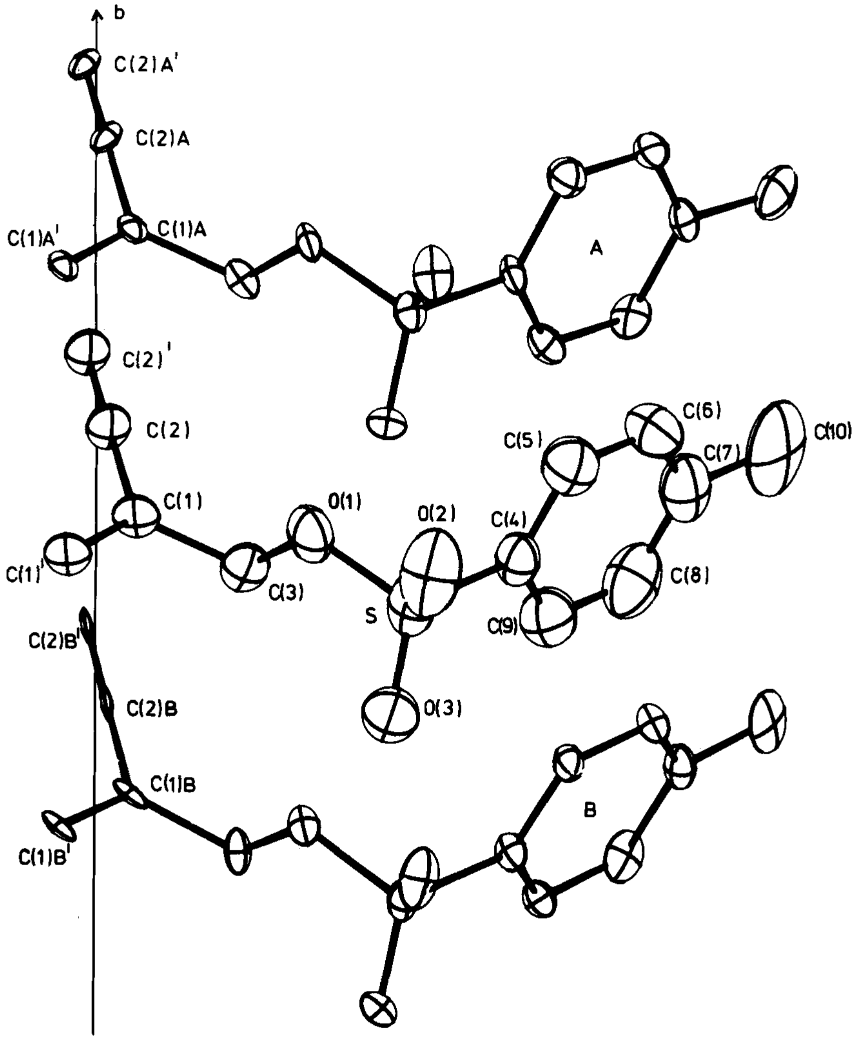

FIGURE 6 Comparison of the structure of a TS sidegroup at 300 K (center diagram) with that of the two structures (top and bottom diagrams labelled A and B) in which sidegroups are found in the low temperature phase at 120 K. The anisotropic thermal motion is depicted by 50% probability ellipsoids for the non-hydrogen atoms. The atomic labels are: C, carbon; O, oxygen; S, sulfur. For clarity the hydrogen atom ellipsoids have not been included. Atoms $C(1)^1$, C(1), C(2), and $C(2)^1$ are on the backbone with the vector **b** defining the polymer chain direction.

or molecules at room-temperature which possess sufficient thermal motion to pass freely between states A and B.

These ideas were tested using a model for the room-temperature structure which was a superposition of the two low-temperature structures, A and B, with each atomic site having half occupancy. This hybrid structure was refined using 1294 X-ray reflections which had been measured, using a four-circle diffractometer, from a crystal of TS at room-temperature. The 1294 reflections were all of an intensity (I) for which $I > 1.5\ \sigma(I)$. The hybrid structure refined to give an R factor of 4.2%. The best refinement of a room-temperature structure using singly occupied atomic positions had an R factor of 4.5%.

It has thus not been possible to resolve by X-ray observations whether the true picture of the room-temperature structure is one of molecules which possess thermal motion which is large enough to encompass the two sites of side-groups A and B, or of molecules which can spend a time in either configuration A or B which is larger than the time taken for a molecule to make the transition from configuration A to configuration B.

A TWO-DIMENSIONAL PHASE TRANSITION?

Using the second model for the crystal structure of the high temperature phase of TS it is possible to consider the phase transition as one having a high degree of two dimensionality. A study of the interatomic interactions in the polymer has indicated that there is likely to be a high degree of correlation between the structures of adjacent sidegroups along any given chain. If a particular sidegroup on a chain has type A structure then it is highly probable that every other sidegroup stacked on the same side of the polymer chain will be of type A. In the low temperature phase these stacks are ordered while the high temperature phase would consist of a random array of A and B stacks. Such a transition would be a purely two dimensional one as there would be no structural information in the third dimension parallel to the chain axis. The third dimension would only be important for a stack in the process of changing from A to B or vice versa. Presumably energy considerations would prevent this taking place instantaneously as in, for example, the case of the flipping of a spin. It would appear likely that the flipping of a stack would be initiated locally and propagate in the fashion of falling dominoes. At low temperatures the flipping of stacks would be unlikely and the behaviour would be predominately two dimensional. At temperatures where fluctuations are important the three dimensional character would become more important. Thus the composite curves used to fit the experimental data seem plausible in terms of this model.

CONCLUSIONS

Spectroscopic studies of the second order phase transition in crystals of toluene sulfonate, diacetylene polymer indicate that the transition has some two dimensional character. It is possible to interpret X-ray structural data in a highly speculative way so as to give a possible explanation for the source of this two dimensionality.

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