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Static and Dynamical Properties of Both Monomer and Polymer pTS-D Crystals: A Comparative Study

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Microcalorimetry and neutron and Raman scattering spectroscopy were used to make a static and dynamic comparative study of the structural instabilities of the disubstituted and fully deuterated diacetylene 2,4-hexadiynylene bis(*p*-toluenesulfonate) (pTS-D) in the monomer and polymer crystalline states. Monocrystals of monomer pTS-D undergo solid-state polymerization yielding monocrystals of conjugated polymer. We try to make a determination of the order parameter with the aim to understand the mechanism which leads to the structural instabilities observed in the two states. From an analysis based on the theoretical model "Φ^4", we show that these instabilities present an intermediate character between order–disorder and displacive, with a more pronounced displacive character in the polymer than in the monomer.

I. Introduction

To perform neutron scattering experiments, we had to make large-size monocrystals of fully deuterated pTS-D. pTS-D is the symmetrical diacetylene compound R—C≡C—C≡C—R where R is $CD_3C_6D_4SO_2OCD_2$. pTS-D (as hydrogenated pTS-H)[1] undergoes in crystalline state progressive and topochemically solid-state polymerization along the *b* axis; this reaction is initiated by irradiation or by thermal annealing,[2] but no polymerization of the monomer is induced by the interaction of the sample with neutrons. Indeed no variation of the *b* parameter has been observed on our overall 45-day experiments using the same monomer crystal (see also refs 3 and 4) at subambient temperature in order to prevent thermal polymerization. It is possible to obtain, from large size monomer crystals (0.5 cm^3), mixed monomer–polymer monocrystals with any intermediary and controlled polymer content and, finally, conjugated polymer crystals. pTS-D monomer and polymer are isomorphous at room temperature[5,6] and exhibit in crystalline state structural instabilities at low temperature. As in pTS-H, there is an intermediate incommensurate phase in the monomer and a single-phase transition in the polymer;[7] these instabilities are associated to motions of the polar side groups and yield to a doubling of cell *a* dimension.

Polymerization kinetics of diacetylene crystals has been extensively investigated:[8] it shows an induction period followed by an autocatalytic acceleration of the reaction rate by about 2 orders of magnitude. However, the mechanism of polymerization still awaits a satisfactory explanation. A very small chemical change can strongly modify the reaction rates and even prevent the polymerization. For example in pFBS, which differs from pTS solely by replacement of the terminal methyl groups by F atoms, the actual rate is about 1 order of magnitude smaller with a same general reaction kinetics as pTS.[9] Replacement of the terminal methyl groups by Br or Cl atoms prevents the reaction. The side groups play an important role in the reactivity of diacetylenes but it is far from being well understood. That's why the evolution of the phase transitions during polymerization of pTS, which are associated with motions of the side groups, can bring informations on the mechanism of the reaction (pFBS does not show any phase transition).

We have performed static and dynamical studies of the structural instabilities in pTS-D monomer and polymer by microcalorimetry and by neutron and Raman scattering.

II. Static Properties

(A) Calorimetric Results. Figure 1 shows the variation of specific heat as a function of temperature in the range 140–225 K for pTS-D monomer and polymer monocrystals. These results were obtained on Perkin-Elmer DSC7 differential scanning calorimeter on crystalline samples weighting about 40–60 mg. Mono-pTS-D and poly-pTS-D samples present a qualitatively similar behavior when considering the endotherms characteristic of the continuous transitions in the range 170–200 K. In the two cases the C_p anomalies present first an increase then a smoother decay which spread about over 30 K. The maximum of the specific heat jumps (mono-pTS-D, $\Delta C_p = 5 \times 10^{-3}$ J/g K and poly-pTS-D, $\Delta C_p = 10^{-2}$ J/g K) and the transition temperatures (respectively ca. 189 and 180 K) are on the same order in both crystals. The corresponding variations of entropy are small as compared to the value given by $R \ln 2$ for an ideal order–disorder transition. In addition the C_p anomaly observed at T_I = 155 K is the signature of the incommensurate-commensurate phase transition (lock in) in mono-pTS-D; this

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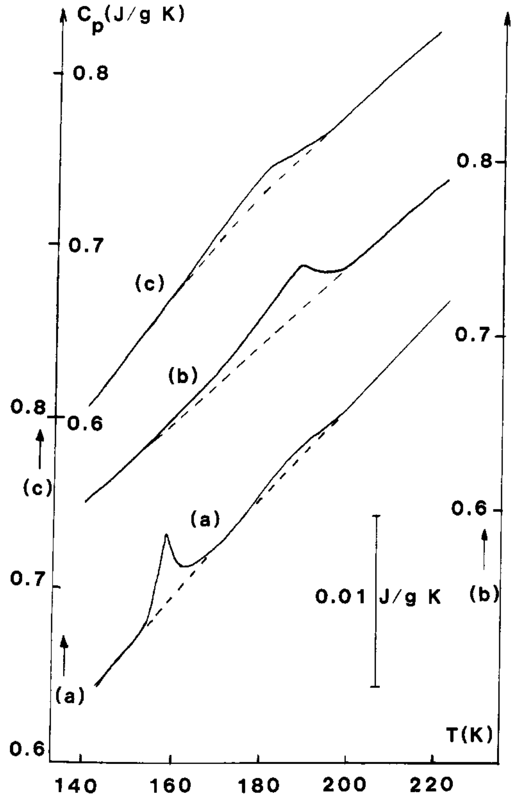

Figure 1. Heat capacity as a function of temperature, measured on pTS-D monomer and polymer and pTS-H polymer crystals: (a) pTS-D monomer crystal; (b) pTS-H polymer crystal; (c) pTS-D polymer crystal. The scale used for C_p is the same in the three cases.

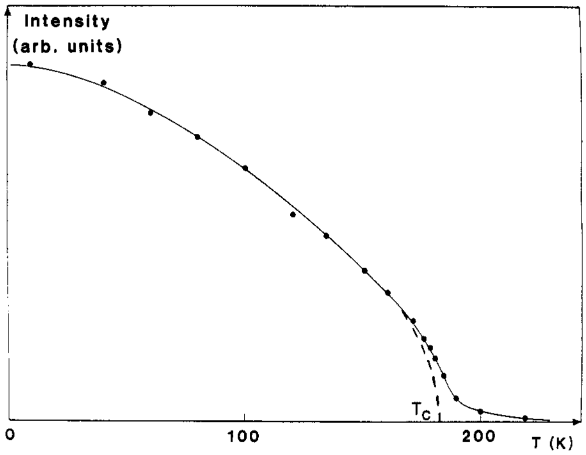

Figure 2. Integrated intensity of the (6.5, 1, 0) superlattice reflection as a function of temperature (k = 2.662 Å^{-1}) in poly-pTS-D crystal. The broken line going to T_c (T_c = 182 K is determined after drawing of the full width at half maximum of the (6.5, 1, 0) as a function of temperature) is a guide for eyes to show the existence of critical scattering near T_c assuming its value at $T \leq T_c$ is twice as small as the same value measured at $T \geq T_c$.

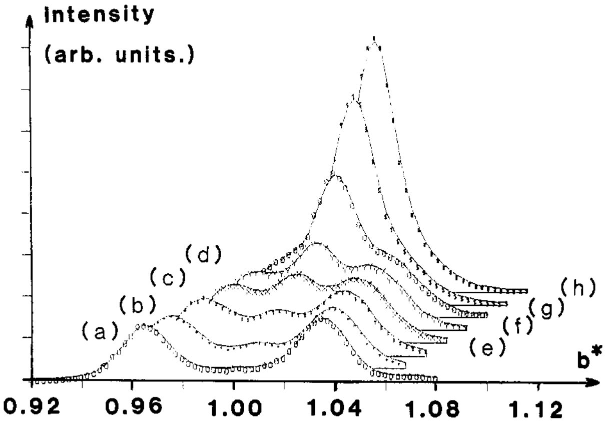

Figure 3. Intensity evolution as a function of temperature near lock in transition of the satellites characteristic of the incommensurate phase in a pTS-D monomer crystal at the (3.5; 1 ± δ, 0) point of the reciprocal lattice (k_i = 1.4 Å^{-1}; scans in the b^* direction). Temperatures: (a) 161.4 K; (b) 160 K; (c) 158.6 K; (d) 157.6 K; (e) 157.1 K; (f) 155 K; (g) 154.4 K; (h) 153.2 K.

endotherm has a first-order like shape. The intermediate phase between T_c and T_I corresponds to a modulation along the b axis. This calorimetric study shows that mono and poly-pTS-D have a behavior which is nearly similar as mono and poly-pTS-H.[2,10,11] This fact led us to perform a dynamical study of pTS-D crystals in order to try to know the dynamical properties of pTS.[12,13]

(B) Elastic Neutron Scattering Study. The variation of the integrated intensity for superlattice reflections as a function of temperature gives the possibility to obtain the evolution of $\langle \eta^2 \rangle$ where η is the order parameter for a continuous phase transition. In poly-pTS-D the intensity of superlattice reflections decreases continuously to T_c = 182 ± 2 K when determined after drawing the variation of the full width at half-maximum of the (6.5, 1, 0) superlattice reflection as a function of temperature. Above T_c, only strong diffuse scattering is observed, indicating the existence of pretransitional critical fluctuations associated with short-range order. Figure 2 shows the variation of the integrated intensity for the (6.5, 1, 0) superlattice reflection as a function of temperature. Taking into account the fact that critical scattering supplies around T_c an additional contribution to the intensity, and assuming the value of this contribution at $T \leq T_c$ is twice as small as the value measured at $T \geq T_c$, the corrected intensity follows the power law $I = I_0(T_c - T)^{2\beta}$ with $\beta = 0.25$ on a large temperature range going from T = 8 K to about T_c.[14] The diffuse scattering is centered on the (0.5; 0; 0) zone boundary point and not on incommensurate positions as in the monomer crystal.[6]

Figure 3 shows, as a function of temperature when approaching T_I, the intensity variation of the satellites characteristic of the incommensurate phase in mono-pTS-D ((0.5; ± δ; 0) point in the Brillouin zone). When temperature decreases from 161.1 to 153.2 K, the two satellites transform into the superlattice reflection characteristic of the low-temperature phase. We point out that there is a coexistence of the satellites and superlattice reflection over about 5 K.

Figure 4 shows in mono-pTS-D the integrated intensity for the (3.5, 1 ± δ, 0) superlattice satellite reflection as a function of temperature. The integrated intensity below T_I and the sum of the integrated intensities of satellites between T_I and T_c permit to obtain the evolution of $\langle \eta^2 \rangle$ as a function of T: $\langle \eta^2 \rangle$ decreases continuously to T_c = 195 ± 2 K, following the power law $I = I_0(T_c - T)^{2\beta}$ on a

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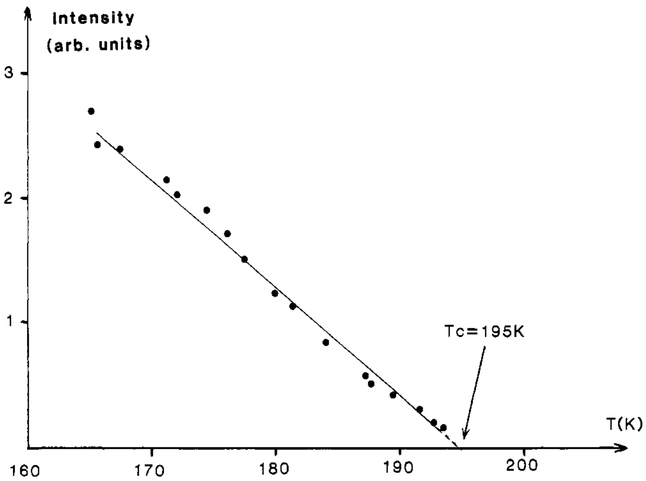

Figure 4. Integrated intensity of the (3.5, 1 ± δ, 0) superlattice satellite reflection as a function of temperature (k = 1.4 Å^{-1}) in mono-pTS-D crystal.

large temperature range going from at least T = 150 K to T_c. As the experiments were made at ki = 1.4 Å^{-1}, the energy resolution was enhanced by a 7.5 factor (220–30 GHz) when compared to the resolution of the neutron study of the polymer crystal. Diffuse scattering attached to the soft mode (section III.A) is then strongly reduced.

In this case however the critical exponent $\beta \approx 0.5$ is higher than that obtained for poly-pTS-D ($\beta \approx 0.25$).[14] For mono-pTS-D, the critical exponent value $\beta \cong 0.5$ is then consistent with that predicted by the Landau theory for a second-order phase transition. On the other hand explanation of the difference between the values of β in mono- and poly-pTS-D is not obvious. Indeed there is no significant difference (see later) between mono- and poly-pTS-D concerning the pretransitional dynamics or the analysis used to determine the order parameter. It seems a reasonable interpretation on the low value of β in poly-pTS-D to say this system, either is near a tricritical point, or undergoes a weakly first-order transition. So it has been observed that in these cases the value of β coefficient can decrease from 0.5 to 0.16.[15,16]

(C) Analysis of Thermal Motions by X-ray. Thermal motions of atoms in mono and poly-pTS-D were analyzed by X-ray using the method of rigid group motions.[17,18] The phenyl rings can be used in this case as rigid groups because the study of both high- and low-temperature structures has shown that the structural instabilities are associated to motions of the polar side groups. In both cases the librational tensor is strongly anisotropic: it has a very high value along one particular axis.[5,14] In mono- and poly-pTS-D the directions of this axis and of the main axis of the phenyl ring are not the same (Figure 5). As the orientation of the side group dipoles can be considered to have the same direction as this main axis, our study shows then a change in dipole interactions in the low- and high-temperature phases. A dielectric study confirms that the transition has an antiferroelectric character;[19] however, it does not appear clearly from this study if the order parameter should be identified with the orientation of the permanent dipole.

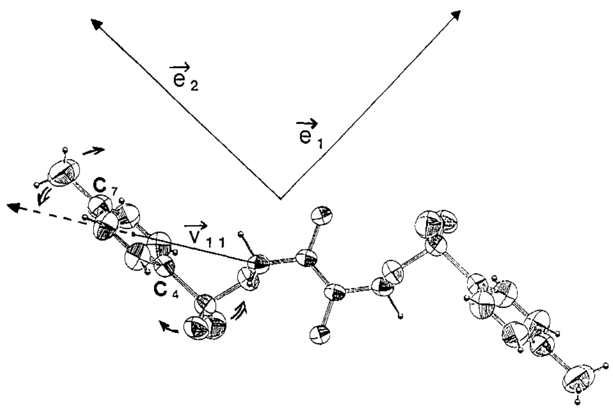

Figure 5. The poly-pTS-D molecule as viewed in the ($\mathbf{e}_1$, $\mathbf{e}_2$) plane; the $\mathbf{e}_1$ vector is perpendicular to the phenyl ring; the $\mathbf{e}_2$ vector is parallel to the C_4–C_7 direction. $_{v11}$ represents the principal axis of the side-group rotations.

Our comparison of mono- and poly-pTS-D properties and a study of mono-pTS-D under hydrostatic pressure[20,21] show indeed that steric interactions (short-range forces) play a role in the mechanism of the structural instabilities. Hydrostatic pressure or polymerization, which can be considered as an "uniaxial constraint" for side groups in pTS, increases the relative strength of short range intermolecular interactions, in particular along the b axis. Then either one or the other process may change the likely delicate balance between short- and long-range interactions, these latter being less sensitive to a decrease of the relative distances between rigid groups. It is also a possible explanation for the modulation disappearing of side group orientations along the b axis (incommensurate phase) in poly-pTS-D and in mono-pTS-D under pressure.

The analysis of thermal motions in mono and poly-pTS-D leads to another interesting result: the main eigenvalue of the librational tensor corresponds to a rotation angle of about ±5–6°.[5,14] This result is in good agreement with the static displacement observed in the low-temperature phases. It shows again that the thermal motions in the high-temperature phases are probably far from T_c the precursors of the structural changes which occur at T_c.

III. Dynamical Study

(A) High-Temperature Phases: Inelastic Neutron Scattering. The critical wave vector $\mathbf{q}_c$ for both mono- and poly-pTS-D is located at the A point of the Brillouin zone (zone boundary at $\mathbf{q}$ = (0.5;0;0)). It corresponds to a doubling of the unit cell along the axis with two inequivalent sites. That is why we can study the pretransitional dynamics in the high-temperature phases only by neutron scattering. The frequency ν_c of the soft mode in poly-pTS-D (Figure 6) has a mean-field behavior in agreement with the following expression $\nu_c^2 = a(T - T_0)$ where T_0 = 190 K and $a = 7.3 \times 10^{-4}$ T Hz^2 K^{-1}.[14] In mono-pTS-D the frequency ν_c of the soft mode is a similar function of T (Figure 6): $\nu_c^2 = a'(T - T_c)$ with T_c = 195 K and $a' = 7.7 \times 10^{-4}$ T Hz^2 K^{-1}.[6]

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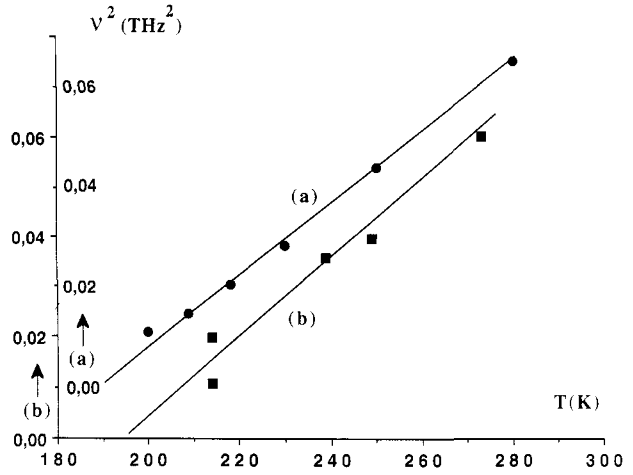

Figure 6. Temperature dependence of ν^2 (ν being the soft mode frequency). The variations of ν^2 for poly-pTS-D (a) and for mono-pTS-D (b) are linear as a function of temperature. The slopes are very close.

These results show then surprisingly that mono- and poly-pTS-D have approximately the same behavior. However differences exist: first (as shown in part B) the critical fluctuations for mono-pTS-D are centered not exactly at $\mathbf{q}_c$ but on incommensurate positions $\mathbf{q}_s$ near $\mathbf{q}_c$ (δ is small: $\delta \leq .06$).[6] It means that the dispersion curve of the soft mode does not condense exactly at the zone boundary, as shown by inelastic neutron scattering. Second, the damping of the soft mode is slightly more important in mono-pTS-D. That explains why the soft mode becomes overdamped at $T_c + 80$ K in mono-pTS-D and at $T_c + 50$ K in poly-pTS-D.[6] In these temperature ranges, critical fluctuations spectra are merely described by the scattering cross section of relaxation processes. Although this fact does not show that the pretransitional dynamics has a pure order–disorder behavior near T_c, it shows nevertheless that the transition is displacive (soft mode) but with some order–disorder character. The transition is then slightly more displacive in the case of poly-pTS-D.

We made also the dispersion curves of the soft mode in the a^* and b^* directions in both mono- and poly-pTS-D. In the two cases the values of critical correlation lengths along a^* (ξ_a) and b^* (ξ_b) are of the same order and always slightly higher in the b^* direction. This result is in complete disagreement with a two-dimensional character of the phase transition involving the (a^*,c^*) plane; this conclusion is based on the previous analysis of the order parameter deduced from spectroscopic measurements.[22] On the other hand it is consistent with our interpretation (section II.B) that the low value of the β exponent in poly-pTS-D is consistent with a weakly first-order phase transition.

(B) Low-Temperature Phases: Raman Scattering. The analysis of space group symmetries in both high- and low-temperature structures of mono- and poly-pTS-D (respectively $P2_1/c$ and $P2_1/n$) leads to the compatibility relations between the A point above T_c and the Γ point below T_c:

$T > T_c$	$T < T_c$
A point	Γ point
A_g	B_g
B_g	A_g (soft mode)
A_u	B_u'
B_u	A_u

This table shows clearly that the soft mode can be observed only in the low-temperature phases by Raman scattering with (a,a), (b,b), (c,c), or (a,c) polarization. It was indicated[23] that this mode was observed by far-infrared spectroscopy although it is forbidden by symmetry. In this case however it is possible that modes coupled to the order parameter have been observed.

In the low-temperature phase of poly-pTS-D we have observed by Raman scattering a soft mode; a soft amplitudon mode is also seen in the incommensurate phase of mono-p-TS-H[24] and mono-pTS-D.[6] In both cases the evolution of the soft mode as a function of temperature is characterized by a frequency decreasing and a large damping; however, that decreasing does not follow a Landau type power law in the low-temperature phase.[6,14]

The square of the soft modes frequencies does not vary linearly as a function of T. The decay of ν_c is smoother far from T_c and becomes steeper near T_c with a large increase of damping. Furthermore the slope ratio of the soft mode frequency squared from $T < T_c$ to $T > T_c$ is much larger than the standard ratio 2 predicted by the mean-field theory.[16] Finally we point out that an unexpected line-width broadening of the other low-frequency modes appears near T_c in both mono- and poly-pTS-D. Our interpretation is that the structural instabilities present some order–disorder character; it can be related to the progressive setting of disorder with temperature increase. Indeed the crystal is spatially inhomogeneous when disorder exists.[14,25]

IV. Discussion

Using microcalorimetry and elastic and inelastic coherent neutron and Raman scattering results and the analysis of thermal motions, we have succeeded in obtaining a coherent description of the dynamical and static properties of the structural instabilities in mono- and poly-pTS-D.

The order parameter is identified with a rotation of the side-groups around the so-called v_{11} axis (Figure 5). The instability is related to a delicate balance between dipole–dipole and steric interactions. This balance is influenced by the polymerization process: there is a change from second order to weakly first order of the transition character. This change leads also to the disparition of the incommensurate modulation along b^* in mono-pTS-D; it can be considered as the result of a triangular inter-ring interaction between phenyl rings of two neighboring stacks.[26] Another case is on the one hand biphenyl which undergoes an incommensurate phase transition of second order[27] and on the other hand paraterphenyl where exists only a commensurate transition of weakly first order.[28] The pretransitional dynamics of mono- and poly-pTS-D are remarkably close. The process is only slightly more

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displacive in the polymer state than in the monomer state. This behavior can be connected to the contraction along the stack *b* axis during solid-state polymerization, which hinders the motions of the side groups. Displacive transitions with a strong order–disorder character (large soft mode damping) exist in other organic crystals as A-TCNB,[29] paraterphenyl, and quaterphenyl under high pressure.[30]

Our results can be discussed from the theoretical point of view using the "Φ^4 model".[31] It describes the crossover between displacive and order–disorder behavior. The hindering of side-groups motions in the polymer state corresponds to a decrease of the "hump height" of the double-well potential. In other words the side-groups are more constrained to rotate around a position which is the average position in the high-temperature phase. The "Φ^4 model" also shows that the standard slope ratio of 2 given by the mean-field (Landau) theory[16] is accurate only in the purely displacive limit case, and if one assumes that the local orientations are coupled by long-range interactions. These two conditions do not apply to mono- and poly-pTS-D.

In the short-range coupling limit, the slope ratio values stretch from 6 to at least 10.5 for transitions with an intermediary character between order–disorder and displacive. Then the importance of short-range steric interactions in mono and poly-pTS-D may explain the high values of the observed slope ratios.

The control of the polymerization procedure permits us to obtain mixed crystals with any polymer content X, so as to be able to study different samples with a well defined X in all the range between 0 and 1.[11] The understanding of static and dynamical properties of mono- and poly-pTS-D is important for interpretation of the more complex situation encountered in the mixed crystals. The system presents some analogies with orientational glasses,[32] as in mixed-crystals solids, but, in our case, with another type of static disorder. Further studies on mixed crystals of pTS-D are now in progress by the experimental methods described in this paper and by methods as D-NMR and dielectric measurements in order to investigate the local properties of the structural instabilities.

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