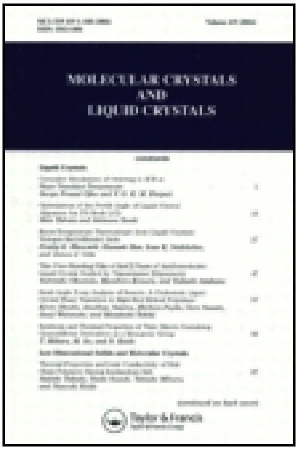

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X-ray Study of the Incommensurate Phase of Bis-(p-toluene Sulfonate) of 2, 4-Hexadiyne-1, 6 Diol as a Function of Polymer Conversion

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X-ray Study of the Incommensurate Phase of Bis-(p-toluene Sulfonate) of 2,4-Hexadiyne-1,6 Diol as a Function of Polymer Conversion

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The incommensurate modulated structure earlier observed between 206 K and 163 K in monomer single crystals is studied as a function of polymer conversion. The temperature range of existence of this phase gradually decreases with increasing polymer conversion and disappears in the autocatalytic region. At this stage a single phase transition is observed to the low temperature commensurate superstructure $2a \times b \times c$. In the region around 50% polymer conversion the width of the satellite reflexions at the wave vector $(0.5a^*, \delta b^*, oc^*)$ reveals a slightly disordered structure. The dependence of the incommensurate wave vector component δ along b^* is found to be continuous in temperature and polymer conversion.

I INTRODUCTION

Among substituted diacetylenes which are highly reactive in the solid state, bis-p-toluene sulphonate of 2,4-hexadiyne-1,6 diol (PTS) has been the most extensively studied.[1] The main motivation for the interest in these compounds is that by exposure to radiations or by annealing they undergo a progressive topochemical polymerization. In the case of PTS for instance, large single crystal of the monomer transforms into nearly defect free polymer single crystal. In particular it has been observed directly by X-ray diffuse scattering experiments[2] that the mechanism of polymerization proceeds homogeneously inside the single crystal. In the early stages of polymerization and up to nearly

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50% conversion, isolated polymer chains grow along the stacking direction *b* and are distributed at random throughout the lattice. Another unexpected property of PTS has been recently revealed by the observation of an incommensurate modulated phase.[2,3] This phase was only observed in monomer single crystals and in a wide temperature range between 206 K and 163 K, temperature at which a lock-in transition to the commensurate low temperature superstructure $2a \times b \times c$ takes place.[4] The incommensurate modulation of the structure has been confirmed, on a local scale, by the broadening of the ESR spectra of the triplet carbene on a partially polymerized crystal, between 160 K and 206 K.[5] In fully polymerized crystals, on the contrary, the transition from the high temperature phase (Phase I) to the commensurate superstructure $2a \times b \times c$ (Phase III)[6] proceeds directly at about 206 K.[2,3]

The aim of the present paper is to report the results of an X-ray study of the incommensurate modulated phase (Phase II) as a function of polymer conversion. Throughout this paper we shall always refer (as already done above) to the room temperature unit cell of PTS, with translation vectors **a**, **b**, **c**. The experimental conditions of the present investigation are given in Section II. The phase diagram and its saliant features will be described in Section III. In Section IV, disordering effects observed around the 50% conversion region will be presented. Finally some remarkable aspects of the phase diagram and of the incommensurate modulation will be discussed in Section V.

II EXPERIMENTAL CONDITIONS

The PTS single crystals were synthesized and grown according to well known procedures[7] and as described in an earlier paper.[2] The X-ray study was performed with a conventional precession camera and monochromatic CuKα radiation from reflection on a double curved pyrolytic graphite monochromator. In order to get both high intensity X-rays, and sufficient resolution for the determination of the modulation wave vector, a high intensity rotating anode source equipped with a 100 micron focus was used. The exposure durations were kept as short as possible (5 to 15 minutes) by limiting the amplitude of oscillation of the precession (5°) such as to explore only the useful portion of an $(hk0)$ plane around one set of satellite reflections ($h = 3.5, k = 1 \pm \delta, l = 0$), this, in order to minimize unwanted effects of polymerization during the X-ray irradiation. For the same reason, several crystals were used for each annealing time (or each polymer conversion), with experiments performed at overlapping temperature ranges, and were optically oriented on the precession camera. The crystals were cooled by a regulated nitrogen flow; thanks to the very short exposures, the temperature could be controlled within 0.5°K during each measurement. As in our previous report,[2] annealing of the crystals was performed at 60°C.

III THE PHASE DIAGRAM

Previously reported results on monomer crystals are summarized in Figure 1 which shows precession X-ray patterns of a portion of the (*hk*0) plane in the high temperature Phase I, in the incommensurate Phase II, and in the low temperature Phase III. Figure 2a shows the temperature dependence of the satellite position (wave vector component δ in b^* direction). From such data the upper transition temperature T_H is determined by the temperature at which the satellite reflection width starts to broaden beyond the experimental resolution, and the lower transition temperature T_L by the drop of δ to zero.

When the monomer crystals are annealed (at 60°C) for less than one hour, both transition temperatures begin to decrease. This is most pronounced for the incommensurate to commensurate lock-in transition T_L, which decreases by 10°K after only 15 minutes of annealing (Figure 2b).

For annealing of more than one hour and up to about 14 hours, the upper transition T_H continues to decrease linearly with annealing time, while T_L increases slowly (Figure 2c), after a minimum temperature at 151 K for a sample annealed one hour, which corresponds to about 0.5 percent of polymer conversion. It is at the upper end of this range that the satellites of the incommensurate "phase" start to broaden somewhat, giving rise to difficulties for the precise determination of the upper "transition temperature" T_H. This will be discussed in more details in Section IV below. In this range, T_L is determined, without ambiguities, by the temperature at which the twin satellites, separated by 2δ along b^*, merge into a single superstructure reflection (Figure 3).

After 14 hours of annealing (corresponding to about 15% of polymer conversion), that is to say when the incommensurate Phase II is only stable in a narrow temperature range of about 7.5°, T_H presents a broad minimum, and a change of slope in the rate of increase of T_L is observed. Both transitions merge at about 168 K just after 15 hours of annealing or 50% of polymer conversion, which constitutes thus the limit of existence of the incommensurate phase. For longer annealing times and up to about 18 hours, or 97% of polymer conversion, the single remaining transition temperature T_c (to the $2a \times b \times c$ low temperature superstructure) continues however to increase at the same rate as the former lock-in transition T_L. At about 18 hours of annealing a new change of slope is observed, and the rate of increase of T_c as a function of annealing or additional polymer conversion (above 97%) becomes very small.

The resulting phase diagram for annealing up to 1 month is shown in Figure 4, together with the previously measured lattice constant b in stacking direction (at room temperature), which relates directly the annealing time to the percentage of polymer conversion.[8] The overall features of this phase diagram are in fair agreement with those derived from recently obtained specific heat measurements in partially polymerized samples.[10]

In Figure 4 one can note that although at a slow rate, the transition temper-

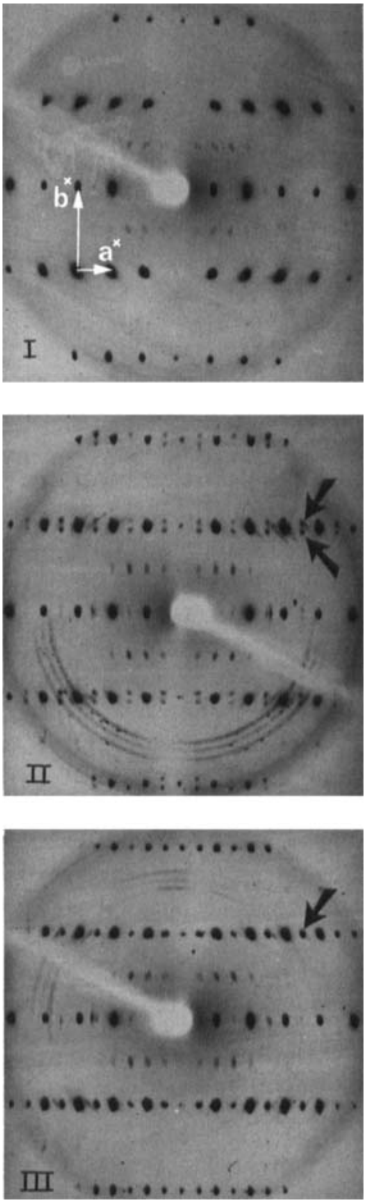

FIGURE 1 Typical X-ray patterns from monomer PTS: (a) in the reference high temperature Phase I, (b) in the incommensurate Phase II, with satellite reflections at the wave vectors $q_i = (0.5a^*, \pm \delta b^*, 0c^*)$, (c) in the low temperature commensurate Phase III, with superlattice reflections at the wave vector $q_c = (0.5a, 0b^*, 0c^*)$. (The satellites $(3.5a^*, 1 \pm \delta b^*, 0c^*)$ followed in this study are shown by arrows). (The extra layer lines of weak Bragg reflections at $b^*/2$ are artifacts due to the radiation at $\lambda/2$).

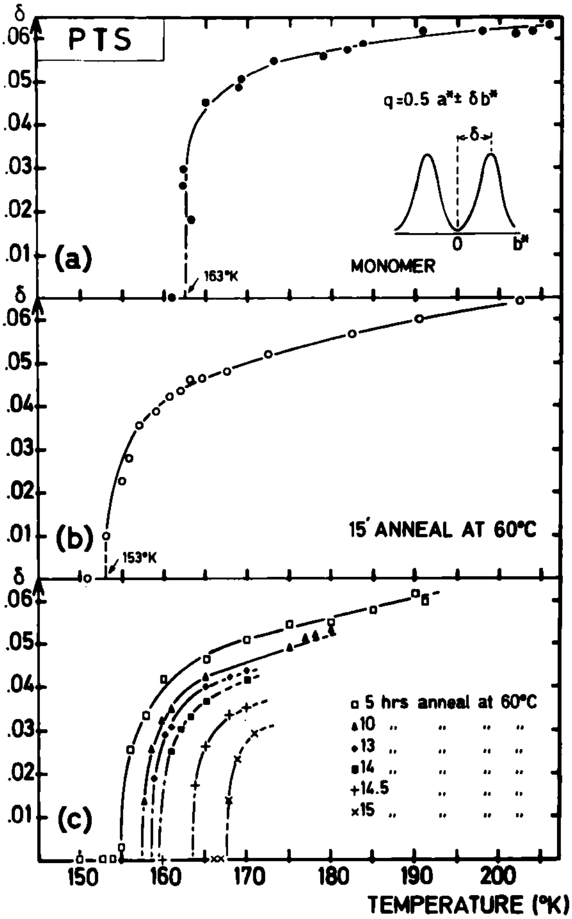

FIGURE 2 Temperature dependence of the satellite wave vector component, δ, along b^* in the incommensurate Phase II for different annealing times at 60°C. The dotted lines correspond to temperatures at which the satellites either broaden beyond resolution, or present a sharp increase of their linewidth (see Figure 5).

ature T_c continues to grow from 188 K to 206 K for samples annealed for more than 18 hours. The temperature of 206 K is only reached after about one week annealing, then stays constant for annealing up to one month. It can therefore be considered as the asymptotic limit for the fully polymerized crystals. It is probably this slow increase of T_c for such a large range of annealing, corresponding to extremely small changes (a few percent or less) of the polymer conversion, which explains the wide dispersion (between 185 and 206 K) found in the previous literature[2,3,9,10] for the transition temperature in samples considered as fully polymerized. In fact, recent X-ray diffuse scattering exper-

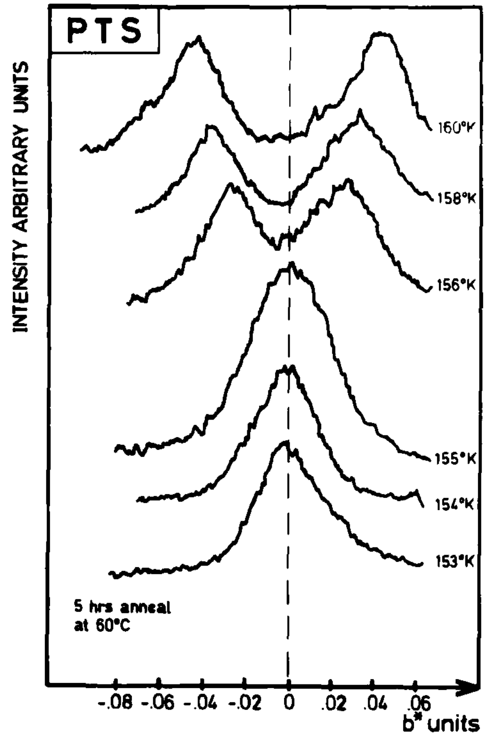

FIGURE 3 Typical microdensitometer scans along b^* through the satellites ($3.5a^*$, $1 \pm \delta b^*$, $0c^*$), showing the lock-in phase transition when the satellites merge. Here $T_L \simeq 155$ K for a sample annealed 5 hours at 60°C.

iments,[12] performed with nearly polymerized samples, have shown that the few remaining monomer chains disappear very slowly with increasing annealing time. This might be the cause of the slow rate of increase of T_c observed.

IV THE CRYSTALLINE PERFECTION

If one considers now the superstructure reflection widths, measured at 150 K in the low temperature Phase III, after about 13 hours of annealing a significant broadening becomes observable in a^* direction (as the experiments were performed, this direction corresponds to our best Q resolution of 0.028 Å^{-1}, there is no other meaning to this particular direction).[11] The full width at half maximum (FWHM) as a function of annealing time goes through a sharp maximum in the autocatalytic region as illustrated in Figure 4c. The maximum FWHM of $(\Delta a^*)_M = 0.032$ Å^{-1} (after resolution correction) yields a minimum correlation length of $\xi_a = 2/(\Delta a^*)_M$ of about 60 Å assuming lor-

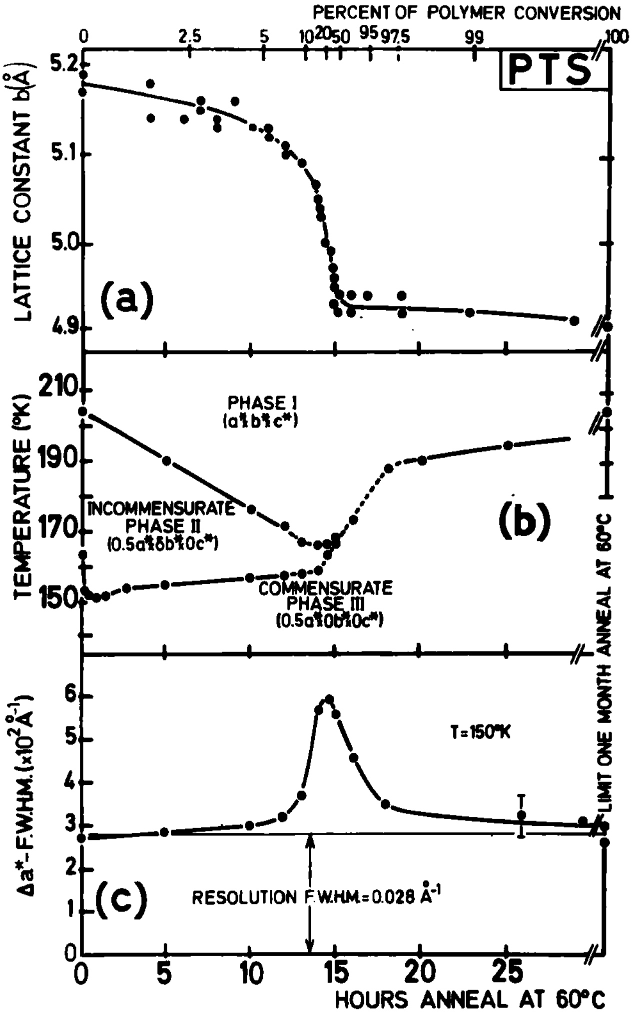

FIGURE 4 Lattice constant, *b*, in chain direction, at room temperature (a), phase diagram (b), and satellite width along a^* (c) as a function of annealing time at 60°C, i.e. polymer conversion. In the phase diagram the dotted lines correspond to "phase" boundaries in the cases where the satellites are at all temperatures broader than the experimental resolution (see text in Section IV).

For the evaluation of the polymer conversion, the fractional change of the lattice constant was, versus annealing time, normalized to the data reported by Baughman[8] by putting in coincidence the autocatalytic region. This procedure was already used by Baughman to compare conversion rates for different annealing temperatures.

entzian line shapes. A similar behavior is observed for the width of the superstructure reflections in b^* direction with a corresponding minimum correlation length of about 150 Å (or 30 lattice spacings in polymer chain direction). This distance is appreciably shorter than the average length of a polymer chain for a 50% polymer conversion (>1000 Å).[12]

In contrast with this broadening of the satellite reflections, we have not observed a significant broadening of the main Bragg reflections from the reference substructure in the autocatalytic region. This shows that the average lattice remains fairly perfectly 3D ordered throughout the whole process of polymerization and that the disorder affects only the extent of the modulation for the incommensurate and commensurate superstructures.

The width of the superstructure reflections is remarkably constant in the two low temperatures phases. In particular no noticeable change can be observed at the incommensurate—commensurate transition at T_L. This is illustrated in Figure 5 which gives the temperature dependence of the FWHM after 13 hours of annealing. Figure 5 further shows how the higher transition temperature was determined in the autocatalytic region. In this range T_H was determined from the break, as observed at 167 K in Figure 5, of the temperature dependence of the satellite width. The rapid increase of the reflection width above this break, indeed corresponds to a rapidly decreasing correlation length as expected from fluctuations above a transition temperature.

Beside the broadening of the satellite reflections themselves, another feature could be noticed in the autocatalytic region. While intensity profiles

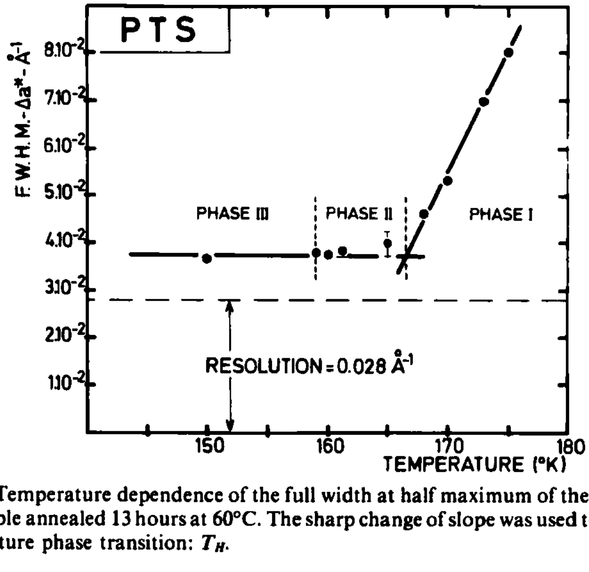

FIGURE 5 Temperature dependence of the full width at half maximum of the satellite reflections for a sample annealed 13 hours at 60°C. The sharp change of slope was used to determine the upper temperature phase transition: T_H.

through the twin satellites ($3.5\ a^*,\ 1 \pm \delta b^*,\ 0c^*$) after 5 hours of annealing clearly show well separated peaks at $T = 160$ K (Figure 3), after 14 hours of annealing a ridge with about half the peak intensity joins the two satellites at 170 K. (This temperature was chosen in order to keep the same separation between the two satellites). As can be seen from Figure 6 this is by far more than expected from the satellite broadening which can be estimated from the outer half profile of the satellites. Such an effect may be the consequence of a distribution of modulation wave vectors (from 0 to δb^*) induced by strains. Such an explanation was already put forward from similar observations in one of the modulated phases of TTF-TCNQ.[13] Here there is an obvious intrinsic source of important strains in the region where about half of the sample is still in the monomer state and the other half has polymerized. We can further notice that in none of the investigated samples could we observe a three peaked profile ($-\delta$, 0, $+\delta$).

Let us now briefly consider the possible nature of the lattice modulation. The structural determinations performed in the low temperature superstruc-

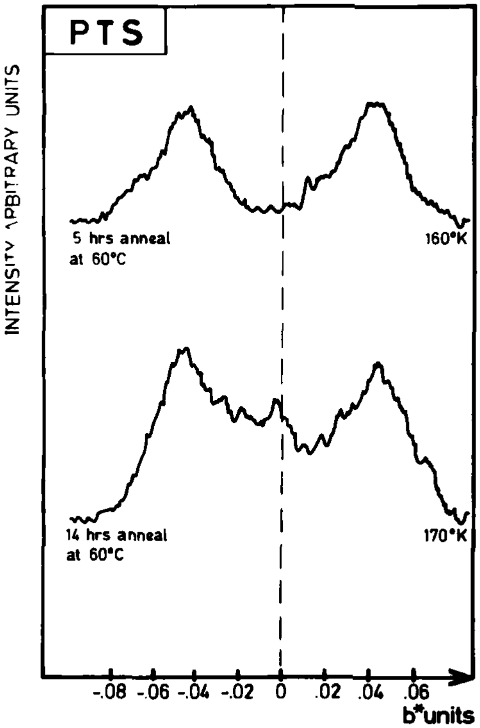

FIGURE 6 Typical scans along b^* through the satellites ($3.5a^*,\ 1 \pm \delta\, b^*,\ 0c^*$), showing the intensity ridge between the satellites in the autocatalytic region (sample annealed 14 hours at 60°C). This is not observed with a sample annealed 5 hours at 60°C.

ture phase (Phase III) have shown that the superstructure is caused by torsions of the side groups attached to the diacetylene backbone.[4,6] By analogy, it is natural to think that the incommensurate modulation of Phase II arises either from an orientation wave of the side groups or from an occupation probability wave involving the two different configurations observed in the commensurate superstructure. As considerable displacements and rotations take place in the transformation from the monomer to the polymer, it is not clear, in Phase II, that the monomer matrix and the polymer chains experience locally the same modulation. This can introduce an inhomogeneous distribution of modulation wave vectors and account for the intensity ridge shown in Figure 6 between the $-\delta$ and $+\delta$ satellites. Since as noted above we never observed a three peaked structure even for samples around the 50% conversion range, we can however conclude that the polymer chains must also present the incommensurate modulation in the first half of the phase diagram.

This last observation and the sharp, but finally very limited increase of width of the satellites in the autocatalytic region, confirm independently that the polymerization proceeds fairly homogeneously, as earlier concluded from various investigations.[1,2]

V DISCUSSION

These are several additional observations which can be made from the present investigation.

Concerning the stability of the incommensurate phase of PTS, one of the surprising results is that the largest stability range is observed for about 15 minutes of annealing. This is due to the very rapid decrease of the T_L transition in the first stages of polymerization (Figures 2 and 4). Taking into account the difficulty to estimate very precisely the amount of polymer conversion, for the very small changes in the early stages of conversion, one might first think that this observation could be due to an experimental artifact (independent specific heat[10] measurements did not reveal this effect, only the minimum value of T_L for partially polymerized crystals has been confirmed by independent elastic neutron scattering measurements.)[14] We have however very carefully verified this evolution. If a newly grown monomer single crystals is immediately cooled to 158 K, a first exposure to X-ray yields a pattern similar to Figure 1c with the commensurate superstructure $2a \times b \times c$. Since the PTS crystals also polymerized under irradiation, after several successive similar exposures at the same temperature, one expects from the phase diagram of Figure 4 that the resulting X-ray pattern converts to the type shown in Figure 1b, that is to say to the incommensurate modulated structure. This is indeed observed and gives a non ambiguous confirmation of the variation of T_L in the early stages of conversion.

The almost vertical phase separation line between Phase II and Phase III, in the early conversion stages, then raises a second question: does the incommensurate modulated phase exist in the pure monomer, or is it an effect of the polymerization itself? This question is more difficult to answer since it is almost impossible to guarantee 0% polymer conversion. Taking all imaginable precautions such as crystals just grown at low temperature in the dark, mounted in the dark on the X-ray camera on prealigned sample holders, patterns taken between 206°K and 163°K always revealed the incommensurate Phase II. One eventual conclusion could be that Phase II is well present in the pure monomer, but is further stabilized by small amounts of polymer chains until the length of the chains, for instance, reaches a critical value after about 15 minutes of annealing at 60°C; such a possibility is under present investigation.[12] Additional clarifications concerning the behavior of T_L deduced from the temperature dependence of δ will be considered below.

Figure 2 shows clearly that the modulation wave vector component in b^* direction, δ, in Phase II, has a monotonous temperature dependence with no evidence of sharp steps when δ crosses a rational fraction of the reciprocal lattice constant, in contrast with other systems like TTF-TCNQ for variable temperature[13] and pressure[15] or thiourea.[16] This may either indicate that the present example belongs to the continuous lattice modulations, as first described by McMillan for phase modulations of the distorsion wave, or perhaps more simply that the commensurability effects are negligible for such small wave vector components (here $\delta \leqslant 0.06\ b^*$, yielding modulation periods longer than 16 lattice units), with the exception of course of the lock-in at $\delta = 0$, below T_L.

In the pure monomer, Figure 2a shows that δ decrease slowly with temperature until about 165 K, temperature below which the wave vector starts to decrease so rapidly that it has been impossible to determine whether δ reaches zero continuously or discontinuously. This general behavior indeed recalls that predicted by McMillan's theory of phase modulation of the distorsion wave. In McMillan's approach, the rapid but continuous drop to zero corresponds to a rapid growth of phase defects (discommensurations), and $1/\delta$ gives the density of such defects. Here, however, δ presents a more contrasted temperature variation than predicted by McMillan. This particular behavior could arise from the fact that the satellites move here along a Brillouin zone boundary, toward a lock-in wave vector of type II, as considered by Bruce *et al.*[18]

Another very surprising behavior is presented by samples annealed for less than about 5 hours. Above 165 K, δ is independent of the polymer conversion, while below this temperature the decrease is progressively smoothened with higher polymer conversion. The nonmonotonic variation of T_L with the annealing (Figures 2 and 4) reflects the changes in the rate of decrease of δ below 165 K. In the picture where the rapid drop of the modulation wave vector is due to the development of equidistant defects, it means that the first polymer chains could slow down the rate of defect growth as a function of temperature. In summary up to 5 hours of annealing, the change in the temperature dependence of the wave vector component δ is obviously related to the variation of the lock-in transition temperature T_L, and corresponds to change in the process of lock-in of the wave vector at a commensurate value.

In contrast, annealing for more than 5 hours, does not change further the type of temperature dependence of the wave vector component δ. Besides of the very slow variation of T_L, increasing annealing seems now to reduce the stability range of the incommensurate phase from above (Figure 2), without changing the nature of the lock-in.

Finally two additional points may be raised. Concerning the upper transition, in the whole range where the satellites are resolution limited, their intensity drops continuously to zero, yielding a 2nd order transition; this drop is of course somewhat washed out when the satellites are broadened for the higher polymer conversions. Concerning the satellites themselves, no higher order harmonics could be detected.

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