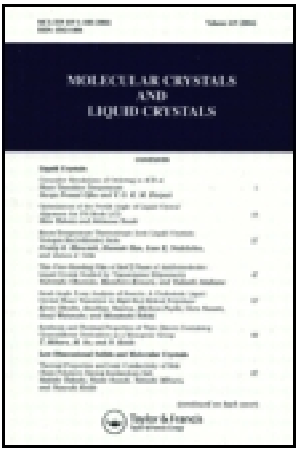

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Local Properties in Disordered Mixed $M_{1-x}P_x$ Monomer Polymer Crystal : A D-NMR Study

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LOCAL PROPERTIES IN DISORDERED MIXED $M_{1-x}P_x$ MONOMER POLYMER CRYSTAL : A D-NMR STUDY

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Abstract : The influence of the polymerization on the structural phase transition in a mixed monomer-polymer pTS-D system is studied by D-NMR. Results are compared with previous neutron and Raman scattering results.

INTRODUCTION

An important topics in disordered mixed compound concerns the structural instabilities they may present [1]. Some diacetylenes may enter such group of compounds by having the quasi-unique property to polymerize in the crystalline state [2]. In the case of pTS a large size (~1 cm^3) monocrystal of monomer can be converted into fully polymerized one, by irradiation (X, γ...) or by thermal annealing. When this solid state reaction is made by heating it leads to mixed monomer-polymer $M_{1-x}P_x$ crystals [3] with randomly distributed polymer chains [4-5]. The symmetrical diacetylene 2.4-hexadiynilene bis (p-toluenesulfonate) referred as pTS (figure 1) presents an antiferroelectric phase transition at almost the same temperature in the monomer and the polymer crystalline states. In the pure monomer, an intermediate incommensurate phase [6] occurs ; it extends in the [155 K - 195 K] temperature interval between the high symmetrical phase (HS) P $2_1/c$ (Z = 2) and the low symmetrical phase (LS) P $2_1/n$ (Z = 4) in pTS-D [7]. The cell of the LS phase is obtained by the doubling of **a** parameter of the HS phase. In the pure pTS-D polymer crystal, no incommensurate phase takes place and the HS to LS phase transition occurs at $T_c \approx 190$ K [8]. The HS and LS phases of the pure monomer and polymer crystals are isomorphous [7, 9, 10]. In the mixed $M_{1-x}P_x$ monomer-polymer crystals, the observed effects of the polymerization on the structural phase transitions give rise to a large controversy. Calorimetric study [11] indicates the progressively smearing and disappearing of the specific heat anomalies when going from the pure to the mixed crystals. Whereas X-rays diffraction measurements in pTS-H [12] and neutron scattering measurements in pTS-D [13] indicate that the phase diagram presents a phase transition at all the polymer contents, the authors observed a broadening of the low temperature superstructure peaks. In fact it is rather difficult to get experimental results in the $x = 0.2$ to $x \approx 0.8$ region due to the inhomogeneity of the polymerization kinetics [14]. Indeed in the "autocatalytic" region, the polymerization occurs in less than an hour when going from $x \approx 0.2$ to $x \approx 0.8$ in the pTS-D crystals, whereas it requires, at 60°C, more than 7 hours to go from $x \approx 0$ up to $x \approx 0.2$. Furthermore X-rays induce polymerization and consequently the polymer content is not unambiguously determined in the X-rays study.

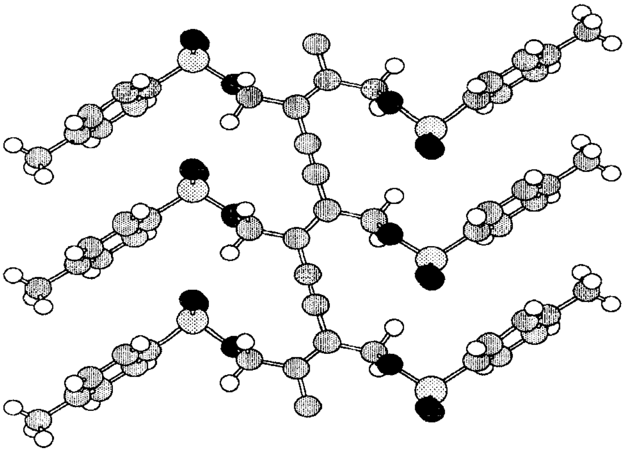

FIGURE 1 Molecular structure of pTS polymer.

We study the mixed $M_{1-x}P_x$ crystals in the polymer range where no specific heat anomaly occurs by using local (NMR, NQR...), collective (light and neutron scatterings...) and bulk (calorimetry...) approaches. Indeed several neutron studies show heterogeneous or homogeneous behavior as a function of the characteristic scale of experimental method. A particular example is the behavior of the longitudinal acoustic phonon branch along the polymerization axis as a function of the scale. Indeed, when the wavelength of the phonon is of the order of the defects (ie : the polymer chains) two branches are observed (by inelastic neutron scattering) whereas only one is observed when the wavelength of the phonons are much longer than the characteristic scale of the defects (by inelastic neutron scattering) [16]. Another topics conserns the evolution of the structural instabilities in the mixed monomer-polymer $M_{1-x}P_x$ crystals as a function of x. Previous results report a Raman scattering study of an internal mode of the polymer chains coupled to the order parameter ; it is then possible to observe the local ordering near the polymer chains [15]. The results given by elastic neutron scattering provide valuable informations on the correlation of the ordering in the low symmetry phase [13] ; they reveal that the order is preserved at all polymer contents but with limited spatial extension and below a temperature T^{MRO} (MRO : Medium Range Order). T^{MRO} is much more lower than the transition temperature observed in the pure monomer and polymer crystals. For $T > T^{MRO}$, the characteristic scale of the cluster decreases up to the disappearing of the diffuse neutron scattering associated to the antiferroelectric order. Two points will be clarified in this paper by D-NMR studies : first, it is important to obtain the integrated response of the entire crystal by summation of the local responses (ie. of the polymer molecule plus monomer "chains") and to compare it to the response of the polymer chains, given by Raman scattering (for a given temperature as a function of x) ; second it is to obtain the critical signature associated to the structural instabilities as a function of the temperature for different polymer contents x.

DISORDER IN THE HIGH TEMPERATURE PHASE AS A FUNCTION OF THE POLYMER STATE :

The quadrupolar nuclear coupling leads to the splitting of the deuterium (I=1) resonance peak in two resonance lines. It is well known that this splitting is a function of the angle θ of the C-D bond to the static applied field B_0 [17]. For the C-D bond, the electric field gradient is almost of axial symmetry and the splitting Δ is given by

$$\Delta \approx \frac{\nu_Q}{2}\left(3\cos^2\theta - 1\right)$$

$$\text{with } \nu_Q = \frac{3\,e^2 qQ}{h}$$

e^2qQ is the quadrupole coupling constant.

The values of ν_Q are about 75 kHz for a CD_3 bond and 155 kHz for a C-D_2 bond.

One can calculate the evolution of Δ for each deuterium bond of the unit cell from the cristallographic analysis. In the HS phase, there are two inequivalent molecules (1) and

(2) in the unit cell. The presence of an inversion center on the molecule in both monomer and polymer leads to consider two half molecules deduced from each other by the 2_1 fold axis. The methyl group of the end of the lateral group rotating fast, they will give average signature of their median axis, three times more intense than deuterium in CD or CD_2 groups. Further more their associated spin lattice relaxation rate is consequently much shorter, experimentally we just study these CD_3 groups.

Using the structures of the pure monomer [7] and the pure polymer [18] crystals at almost the same temperature, we calculate the evolution of the Δ^i ($i = 1, 2$ for the two inequivalent CD_3) as a function of θ for a static field $\mathbf{B_0}$ perpendicular to $\mathbf{c}$ (figure 2). It shows that the CD_3 orientations of the monomer and the polymer are different. Depending on the value of the angle θ, the disorder is observed on the line (1) or (2). For example, for $\theta \approx 30°$ the line (1) is strongly affected whereas the (2) is only a little disturbed. For $\theta \approx 60°$ the line (2) doesn't seem at all to be affected (figure 2). For inhomogeneous domain like structure, that is for structure with separated domains of polymer and monomer one should observe two distinct lines. If the polymer chains are randomly distributed in the monomer matrix (as it is observed by X-Ray scattering[4-5]) and if the interactions between the local structures are strong then one should observe a distribution of the θ angles corresponding to a distribution of the lateral group orientations. Figure 3 shows the high field D-NMR spectra (B_0 = 7

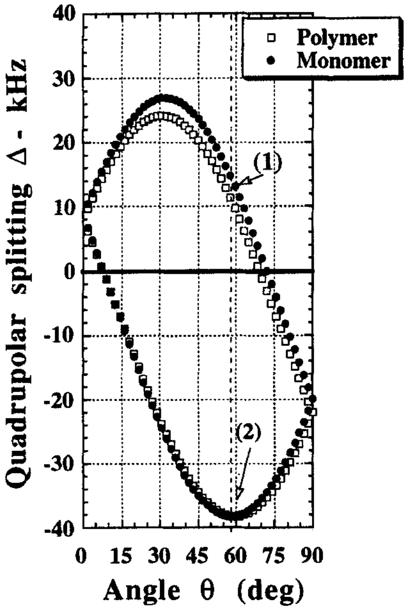

FIGURE 2 Calculated splitting Δ for CD_3 lines. θ is defined by the direction of B_0 with respect to the C-D bond for monomer (x = 0.015) and polymer (x = 0.95) structures at T = 250 K.

T ; $\nu_0 = 46$ MHz ; $\theta = 60°$) for $x \approx 0.95$ and $x \approx 0.60$ at $T \approx 250$ K. As it could be expected from attempted of the calculations and from the previous X-rays results, the doublet (2) is not affected by the disorder (the spectrometer resolution is about 1.5 kHz) but the doublet (1) clearly shows a broadening due to distribution of the CD_3 orientations. In spite of low signal to noise ratio, the distribution appears to be almost symmetrical. This results are in agreement with the X-rays scattering ones [4, 5] : the local structure is homogeneous, the polymer chains are randomly distributed.

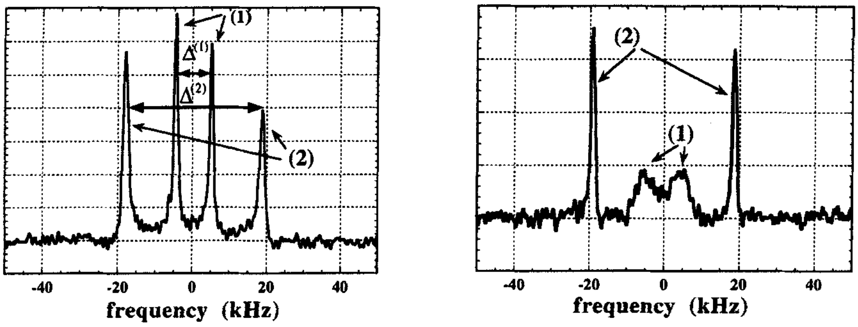

FIGURE 3 : D-NMR line shapes ($\theta = 60°$, $T = 270$ K) recording in two different PTS crystals, (a) $x = 0.95$ and (b) $x = 0.62$. The doublets (1) and (2) correspond to the two non equivalent CD_3 responses in the HS cell.

EVOLUTION AS A FUNCTION OF THE TEMPERATURE : A LOCAL OBSERVATION OF THE STRUCTURAL PHASE TRANSITION FOR A GIVEN POLYMER CONTENTS :

As it was mentionned above, a structural antiferroelectric phase transition occurs in both pure monomer and polymer pTS-D crystals. These structural instabilities are associated to lateral group rotation angle α around V_{11} axis (figure 1) with preservation of the inversion center of the molecules. So that the two inequivalent CD_3 orientations of the high temperature phase split in four orientations for $T < T_c$. The angle is zero in the HS phase and become $\pm\,\alpha$ different of zero in LS so that it could be the order parameter η ; and if it is not the case one can reasonnably postulate a linear coupling between α and η :

Consequently, following the formula (1), we can write for the splittings of (1) and (2) in LS phase :

$$\Delta^{(1)} \approx \frac{\nu_Q}{2}\left(3\cos^2\left(\theta+\tilde{\alpha}\right)-1\right)$$

$$\Delta^{(2)} \approx \frac{\nu_Q}{2}\left(3\cos^2\left(\theta-\tilde{\alpha}\right)-1\right)$$

$\tilde{\alpha}$ is the projection of the angle α in the **a*b** plan (for $\mathbf{B_0} \perp \mathbf{c}$)

if one calls δ the splitting of the two lines, we have

$$\delta = \Delta^{(1)} - \Delta^{(2)}$$

then $\delta = \dfrac{3\nu_Q}{2}\sin 2\theta \sin 2\tilde{\alpha}$

$\tilde{\alpha}$ is small ($\alpha \approx$ 6-7°)[7] and therefore

$$\delta = 3\nu_Q \sin 2\theta\tilde{\alpha}$$

So that $\delta \sim \tilde{\alpha} \sim \eta$ and finally $\delta \sim \left(T_c - T\right)^{\beta}$

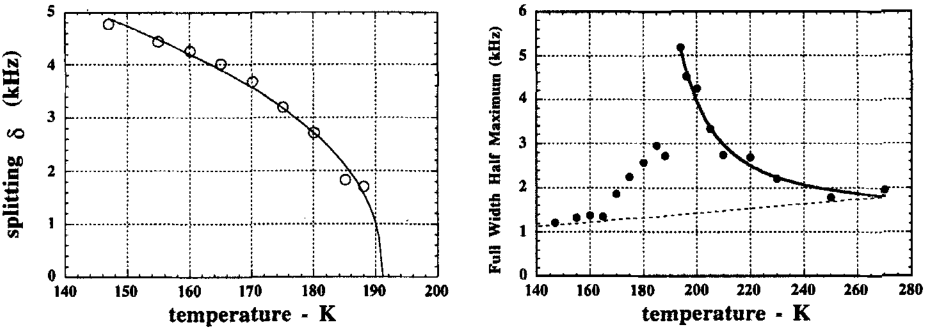

FIGURE 4 :Temperature evolutions of the parameters δ (a) and FWHM (b) in x = 0.62 crystal. The solid straight lines show the fitting laws (see text).

β is the critical exponent associated to the order parameter. Characteristic evolution of the parameter δ as a function of the temperature for the (1) line of the HS cell is shown in figure 4(a). For crystal of $x \approx 0.9$, the extrapolation of the $\delta \sim (T_C - T)^{\beta}$ curve leads to $\beta \approx 0.41 \pm 0.05$ and $T_C = 191 \pm 2$ K. The transition temperatue T_C is almost the same as observed in pure polymer pTS-D [8]. The evolution of the of the full width half maximum (FWHM) of the line (1) in the HS and the LS phases as a function of the temperature are shown in figure 4 (b). The critical exponent β and the transition temperature T_C are almost polymer contents independant : this shows that the local ordering is almost independant of x (within the experimental uncertainty). When looking by elastic neutron scattering at the intensity of the superstructure peak associated to the antiferroelectric ordering, one can observe a large interval of temperatures where fluctuations occur. From the temperature T^{MRO} below which the width of the superstructure peak are almost constant to the diseappearing of the diffuse scattering, we have more than 150 K in the most disordered compounds. The FWHM of the (1) line in the HS phase increases far above T_c ($T_C + 50$ K) in figure 4 (b). In the low temperature LS phase, far below T_C, the FWHM is almost identical as the one at T > 240K. The pretransitionnal fluctuations observed by inelastic neutron scattering are characterized by the softening of a phonon accompagnied by the growing of a central component, the central peak : these two signatures are observed by elastic neutron scattering at $\mathbf{q_C} = 3.5\ \mathbf{a^*+b^*}$. The frequency of the central peak is lower than the resolution fonction (in neutron experiments, the resolution of a triple axis spectrometer is a few ten Gigahertz) [8]. An interesting point is to study the physical origin of this neutron scattering signature : it leads to much controversy [see for example 19 and references therein]. At T ≈ 220 K the soft mode frequency is almost 250 GHz : consequently the soft mode could not induce the broadening of the D-NMR lines. At this temperature (T=220 K) the central peak is still observable : the physical origin of this signature and the broadening of the NMR lines could be of the same nature.

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