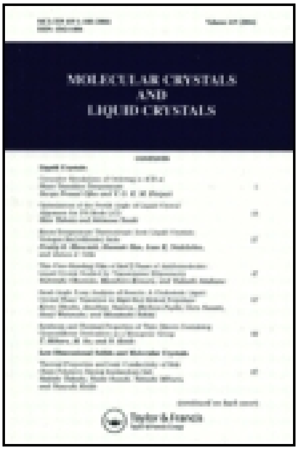

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X-ray Study of the Topochemical Polymerization of Two Diacetylenes

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X-RAY STUDY OF THE TOPOCHEMICAL POLYMERIZATION OF TWO DIACETYLENES

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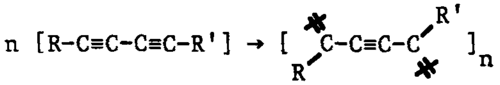
Abstract The thermal polymerization of two diacetylenes has been investigated by X-ray scattering. We report here on the evolution of the polymer chain parameter and of the polymer chain length during the reaction. The identity of behaviour for both compounds is shown.

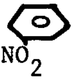
INTRODUCTION

Many diacetylenes are known to yield perfect polymer single-crystals by annealing or exposure to ionizing radiations, according to[1] :



$$n\,[\mathrm{R{-}C{\equiv}C{-}C{\equiv}C{-}R'}] \rightarrow [\,\underset{\mathrm{R}}{\overset{*}{\mathrm{C}}}\mathrm{{-}C{\equiv}C{-}}\underset{*}{\overset{\mathrm{R'}}{\mathrm{C}}}\,]_n$$

The reaction proceeds by formation of polymer chains along the monomer stacking axis [1].

In many cases the thermal polymerization is characterized by autocatalytic acceleration of the reaction. This kinetics is best illustrated by Figure 1, obtained with one of the two studied compounds, DNP (R = R' = $-CH_2-O-$$-NO_2$). An induction period is followed at to by an autocatalytic period after about 15 percent conversion. Both periods follow first-order kinetics (see insert of Figure 1). The other studied compound, PTS (R = R' = $-CH_2-O-SO_2-\Phi-CH_3$) displays the same kinetics[1,2].

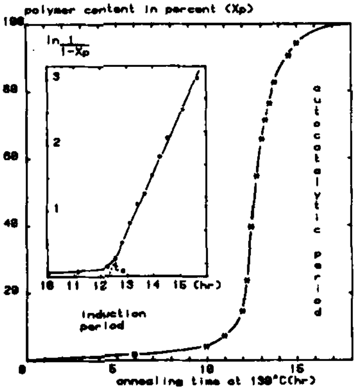


FIGURE 1. Conversion curve of D.N.P. Dots represent calorimetric measures[2]. (t_o = 12hrs at 130°C)

This behaviour has been explained in the case of PTS by the mismatch existing between the lattice constant of the pure monomer (about 5.16Å) and that of the pure polymer (about 4.9 Å) along the chain direction[3]. First polymer chains are thus extended and the polymer growth very slow. As the reaction proceeds, the monomer matrix is more and more stressed by the chains. The beginning of the autocatalytic period is determined by the moment where the monomer lattice yields and releases strain on the chains. A very rapid growth of polymer is then possible.

The conservation of the crystalline state during all the reaction[4] allowed an investigation of the polymerization mechanism with X-ray scattering techniques.

EXPERIMENTAL

PTS and DNP crystals were grown according to published procedures[5]. The rapid polymerization of PTS under the X ray beam at room temperature obliged us to work at low temperature (20 K) [6]. No such problem is encountered with DNP. We have used conventional X-ray sources and the synchrotron radiation at station D16 of LURE for higher resolution and intensity.

DISCUSSION OF AN X-RAY PATTERN

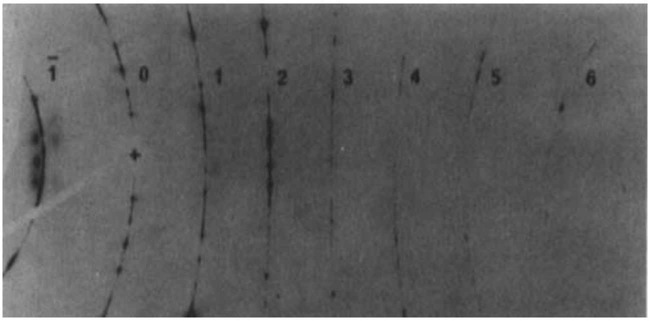


FIGURE 2. X-ray pattern of a partially polymerized DNP crystal (X_p = 50 percent) taken with the synchrotron radiation of LURE. The chain axis is horizontal.

This diffraction pattern (Figure 2) has been obtained by the fixed-film fixed-crystal method. It shows Bragg spots which are in reflection position on the Ewald sphere. They are the direct consequence of the conservation of an average periodic lattice through out the reaction. Furthermore there are diffuse lines perpendicular to the polymerization axis and passing through the Bragg spots. This aspect of the pattern is unchanged by turning the crystal around the polymerization direction, showing that diffuse lines are produced by the intersection of the Ewald sphere with diffuse sheets perpendicular to the chain axis. This diffuse intensity comes from the difference between the real crystal and the average lattice. The formation of diffuse sheets reflects the one-dimensional character of the polymer growth.

A first conclusion can be drawn : there is no nucleation phenomena. In case of nucleation, one should observe two lattices : one lattice for the monomer and one lattice for the polymer clusters. Polymer and monomer form thus a solid-solution. If one now considers a chain of parameter d and length N.d, it is easy to show[7] that the associated reciprocal space consists of equidistant sheets (spacing $2\pi/d$) perpendicular to the chain axis and having a finite width related to the chain length by the Scherrer formula :

Half Width at Half Maximum (HW HM) = $0.888\pi/Nd$

In a weakly polymerized crystal (i.e. in the induction period) polymer chains growing at random are practically independent one from each other so that X ray intensities scattered by each chain just add, giving the observed diffuse sheets.

As diffuse lines pass exactly through the Bragg spots, there is only one periodicity along the polymerization axis ; polymer and monomer accommodate a common parameter, d. Thus, the lattice constant deduced from the Bragg spots correctly accounts for the chain parameter.

The third information that can be drawn from the width and profile of diffuse sheets concerns the polymer chain length. It will be given below.

CHAIN PARAMETER BEHAVIOUR

We see on Figure 3 that the elongation of polymer chains, i.e. the stress exercized upon them by the monomer matrix

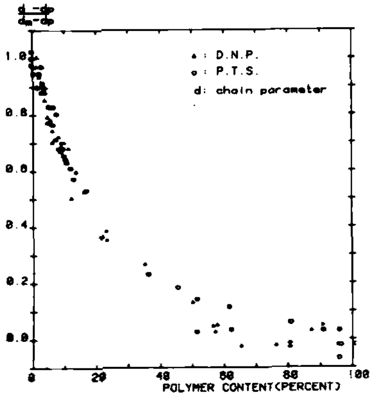


FIGURE 3. Relative change of the chain parameter as a function of conversion for PTS and DNP

relaxes in the same way with conversion for both compounds. Thus Baughman's elastic theory[3] of PTS kinetics remains valid for DNP. In both cases, the relative variation of the chain parameter during the reaction is 5 percent :

For PTS : $d_m = 5.165$ Å $d_p = 4.904$ Å
For DNP : $d_m = 5.199$ Å $d_p = 4.930$ Å

POLYMER CHAIN LENGTH

It is easy to show, using the Scherrer formula, that when the length of a chain increases, the corresponding diffuse sheets become thinner, up to the experimental resolution. The HWHM plotted Figure 4-a-b versus annealing time is a measure of the thickness of the diffuse sheets. At the beginning of the induction period, the HWHM decreases showing an increase of the chain average length, up to the autocatalytic period where it reaches the experimental resolution: polymer chains have become too long to be measured with our apparatus.

The determination of the corresponding chain length

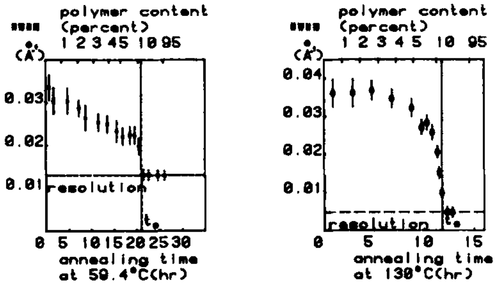


Figure 4-a-b. Half width at half maximum of diffuse lines plotted as a function of annealing time for both compounds. t_o : beginning of the autocatalytic period

has been made in two steps.

First Step

In order to get a rough estimation of the average chain length, we assumed that all the chains had the same length, ℓ. It is thus possible to use directly the Scherrer formula. The results are presented Figure 5-a-b.

First polymer chains are short : about 100 Å (20 units) for PTS and 75 Å (15 units) for DNP. The "average" length then slowly increases up to the autocatalytic period where it becomes very long. A lower limit of 700 Å can be given for both compounds.

Second Step

In the case of DNP, which is a more manageable compound, it has been possible to work out the exact profile of the diffuse sheets in the induction period from high resolution

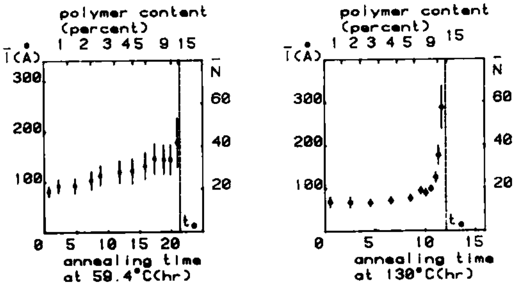


FIGURE 5-a-b. "Average" polymer chain length ℓ deduced from the HWHM by the Scherrer formula, as a function of annealing time

experiments performed at LURE. It is then possible to extract from the data the chain length distribution function P(N), i.e. the number of chains having N units[8-9].

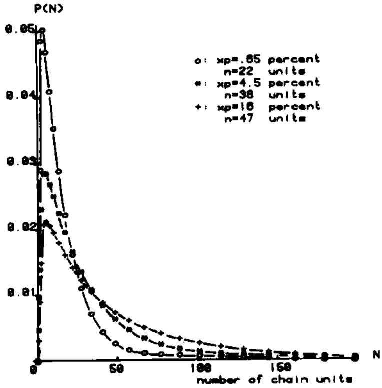


FIGURE 6. Chain length distribution function P(N) for different conversions. "n" is the corresponding average value. P (N) has been normalized

As the reaction proceeds, we see that P(N) broadens towards longer chain lengths, but its maximum practically does not move in the induction period. It should also be noted that the average value "n" agrees well with the rough estimation given Figure 5.

CONCLUSION

In this paper, we have tried to exemplify the kind of information that X ray diffuse scattering can bring to the study of solid-state polymerization, in connection with pure crystallography. The polymerization mechanism appears to be the same in the two investigated compounds : growth of short extended polymer chains in the induction period and of very long relaxed polymer chains in the autocatalytic period.

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