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Macroscopic single crystals of polymers by solid-state polymerization: a study of the monomer to polymer phase transformation of 1,6-dicarbazolyl hexadiyne

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The solid-state polymerization of 1,6-di(*N*-carbazolyl-2,4-hexadiyne (DCH) giving rise to macroscopic single crystals of the corresponding polymer is described with regard to structural aspects. The crystal structures of the monomer and polymer are discussed with respect to the observed solid-state reactivity. An autocatalytic acceleration in the conversion–time characteristics of the radiation-induced polymerization is attributed to a non-destructive phase transition as indicated by a sudden change in the lattice parameters and the elastic constants of the polymerizing crystal. The same phase transition occurs with destruction of the parent lattice during thermal polymerization. The Young's modulus in the chain direction of radiation-polymerized crystals reaches the theoretical value expected for infinitely long polymer chains.

1. Introduction

The topochemical polymerization of substituted diacetylenes can be regarded as a typical example of a homogeneous solid-state reaction. The polymerization is initiated thermally by annealing or photochemically by exposure of the monomer crystals to ultraviolet or high-energy radiation. Each molecule joins with two neighbours adjacent along a particular crystallographic direction by a 1:4 addition reaction giving rise to extended, fully conjugated polymer chains. It has been demonstrated that a polymerizing diacetylene crystal can be considered as a solid solution of polymer chains growing independently from each other in a unique crystallographic direction in the monomer lattice [2–4]. This contrasts with the phase segregation observed in all other known solid-state polymerizations which leads to more or less disordered fibrous polymers [5–9]. In many cases large, nearly defect-free polymer single crystals can be obtained by the topochemical polymerization of diacetylenes. The packing of the monomer molecules plays a dominant role in the reactivity. The optimal packing geometry necessary to bring about reactivity has been derived from empirical data by Baughman [3]. The validity of this packing model has been confirmed by structure analyses of various diacetylene monomers [10]. However, it should be pointed out that this approach does not help to really predict reactivities since there is no theory available to predict all possible packing modes of organic molecules.

The polymerization of 1,6-di-(*N*-carbazolyl)-2,4-hexadiyne (DCH) [11, 12] is particularly interesting because, as a consequence of monomer packing, it represents a case of limited reactivity, where complete conversion to polymer is only achieved because a phase change is coupled to the reaction. We have therefore investigated the thermal and γ-ray induced polymerization of DCH by X-ray diffraction, morphological studies and by Brillouin scattering. Because of the large differences of the elastic constants of monomer and polymer, Brillouin scattering is a valuable method for the investigation of these polymerizations. It has been shown recently that crystal perfection, average chain length and spatial distribution of the grow-

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ing polymer chains can be determined by this method [13, 14].

2. Experimental procedure

DCH was synthesized according to the literature [11, 12]. By slow evaporation of a concentrated solution in DMF at room temperature, large single crystals in the form of needles elongated along **b** with principal faces {1 0 0}, {1 0 2}, and {$\bar{1}$ 0 2} were obtained. Polymerization was achieved by irradiation in a ^{60}Co-γ source with a dosage of 0.71 Mrad h^{-1}. The conversion was determined gravimetrically by leaching out the residual monomer with acetone. The lattice constants were determined from Straumanis-type double radius Weissenberg photographs ($R = 57.3$ mm) taken at room temperature with Cu$K\alpha$ radiation. Refractive index measurements were performed by the immersion method using an Abbe refractometer and a Jelley microrefractometer with a high refracting prism ($n = 1.116$ to 2.35). The immersion liquids were obtained from R. P. Cargille Laboratories Inc, Cedar Grove, N.J. The indicatrix was characterized at 546 nm on a polarizing microscope (Zeiss) using a 4 axes universal stage. Brillouin spectra were recorded at room temperature with the 514.5 nm line of an argon laser as the light source. The optical apparatus was as described by Sandercock [15]. The power of the laser beam was kept below 5 mW to prevent damage to the crystal. The back-scattered light was analysed by a four-pass Fabry–Perot interferometer which exhibited sufficient contrast to detect the relatively weak intensity of the scattered light. The time necessary to measure a spectrum varied from 10 to 100 min depending on the degree of conversion. The two scattering geometries used are shown in Figs. 1 and 2. Owing to the back-scattering configuration, phonons with wavevectors parallel to **a** and **b** were detected. In the latter configuration (Fig. 2) a clean surface inclined to the (0 1 0) plane by 4° was obtained by polishing the crystal with a soft paper wetted with DMF.

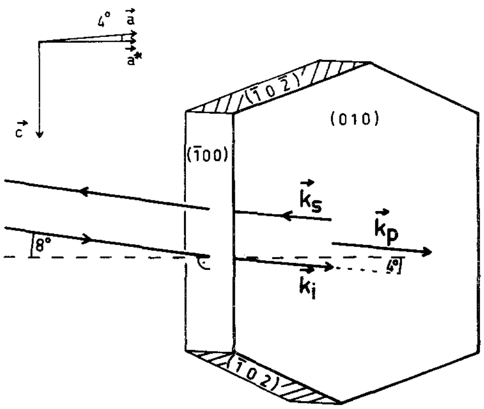

Figure 1 Scattering geometry for measuring the phonon frequency in the direction 4° inclined to **a***. k_i, k_s, k_p are the wavevectors of the incident beam, scattered beam and phonon, respectively.

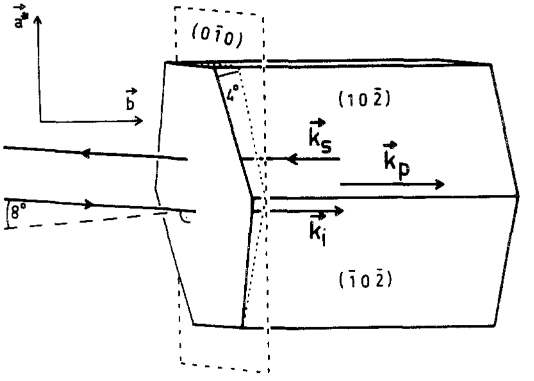

Figure 2 Scattering geometry for measuring the phonon frequency in the **b** direction. The polished surface is inclined 4° to (0 1 0).

3. Solid-state polymerization of DCH

DCH can be polymerized quantitatively thermally by annealing at temperatures between 120 and 240° C or by exposure to ^{60}Co-γ-radiation. At low conversions the crystals turn blue. At full conversion DCH polymer crystals show the typical metallic lustre known from other poly(diacetylenes). Unlike most other reactive diacetylenes, DCH is quite stable, e.g. the polymerization in the X-ray beam is sufficiently slow to allow a structure determination at room temperature [11]. In the γ-ray polymerization, a distinct induction period is observed before the polymerization rate is increased in an "autocatalytic period" which looks similar to that observed in the thermal polymerization of PTS. The dosage–conversion curve is shown in Fig. 3.

The structure analysis reveals the reason for the relatively low reactivity of the pure DCH monomer. Here neighbouring diacetylene groups are stacked with a distance of 4.55 Å forming an angle of 60° with the stacking axis. These values are well outside the range where optimal reactivity has been predicted. According to Baughman, a diacetylene crystal should exhibit optimal reactivity, if the stacking distance is approximately 4.9 Å and if the stacking angle approaches 42°. Appro-

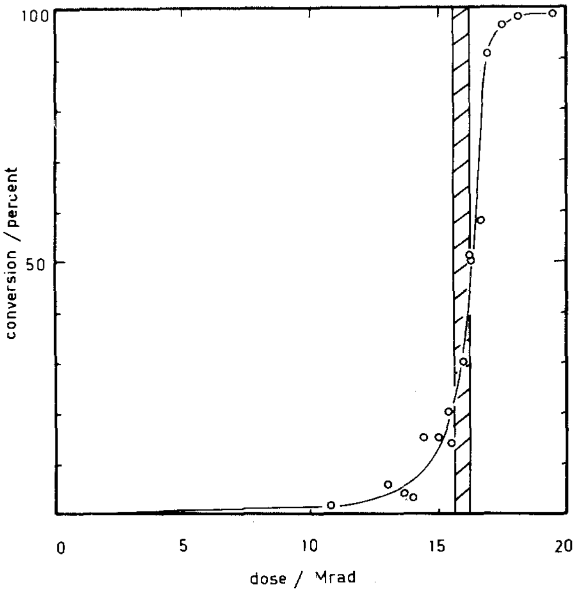

Figure 3 Dependence of conversion on the γ-ray dosage.

priate projections of the monomer and polymer structures are shown in Fig. 4.

At the beginning of the reaction the polymer chains dispersed randomly in the monomer crystal are contracted by 8%. In PTS, a similar mismatch is observed [17]. Here the autocatalytic effect can be explained by a simple mechanical model [14, 18]. With increasing conversion the monomer lattice is continuously deformed by the stress introduced by the polymer chains. In this way the chains can propagate for much longer distances at higher conversions when the monomer stacking approaches the polymer repeat of 4.91 Å. The behaviour of polymerizing DCH crystals is much more complex. Determinations of lattice parameters depending on conversion show unusually large changes in the region of increased reactivity. Here all parameters change abruptly and a phase change is observed (Fig. 5). It is characterized by a shearing of the monomer lattice. The monoclinic angle β which, within the experimental error, is constant in the monomer phase, changes its value by 12°. Pertinent crystallographic data for DCH monomer and polymer are given in Table I. The two structures are shown in Fig. 6. Below the critical conversion, the polymer forms a solid solution in the monomer crystal. After the transition, the situation is reversed and the residual monomer occupies lattice sites in the polymer structure. Here the packing is much more favourable for the polymerization and consequently, the reaction proceeds with large speed.

TABLE I Crystallographic data of DCH

	DCH monomer		DCH polymer [16] room temperature
	Room temperature	below 142 K	
a (Å)	13.60 [5]	13.38 [1]	12.87 [1]
b (Å)	4.55 [2]	4.20 [5]	4.91 [1]
c (Å)	17.60 [5]	18.44 [1]	17.40 [1]
β	94.0	92.0	108.3 [4]
Z	4	4	$4/n$
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
D_x (g cm^{-3})	1.25	1.31	1.30

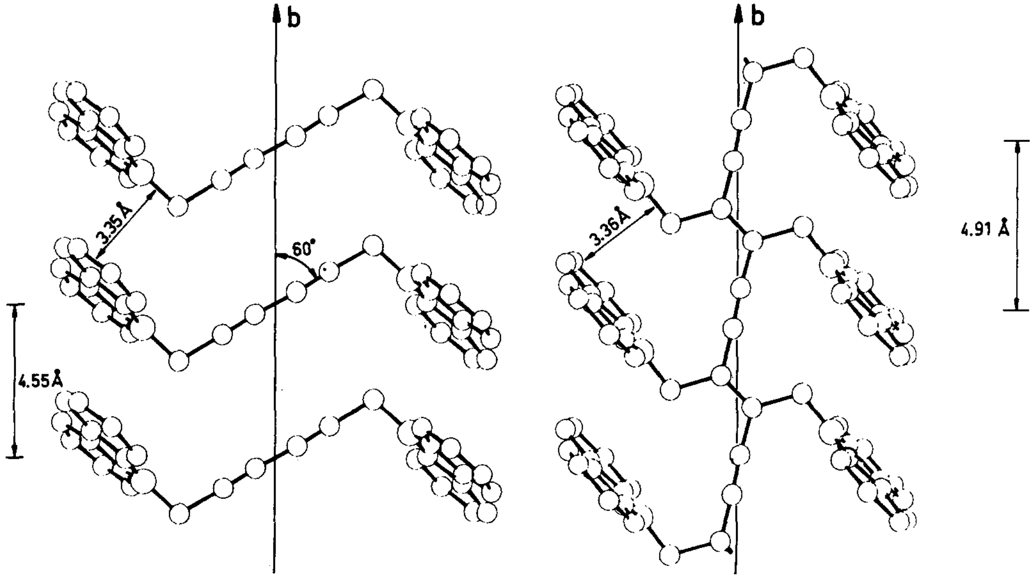

Figure 4 Projections of DCH monomer and polymer structure on a common plane.

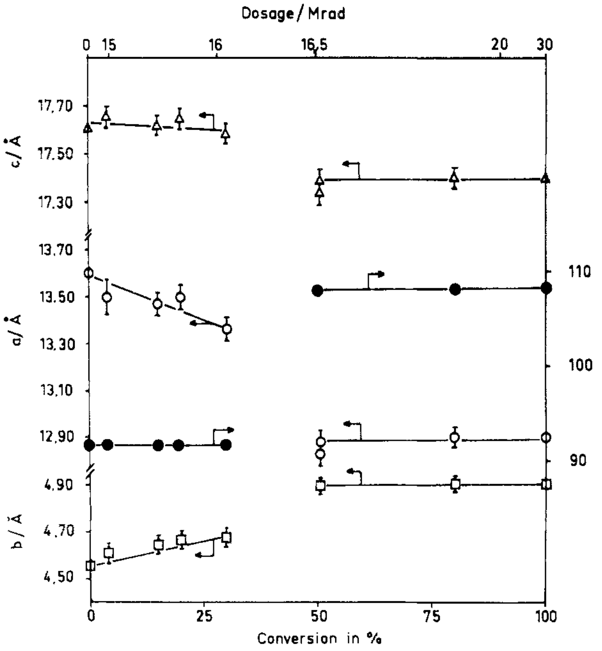

Figure 5 Dependence of lattice parameters on conversion.

DCH monomer crystals undergo a second phase transition at 142 K. The data of the low-temperature modification are also given in Table I. Here the stacking distance **b** is further decreased and consequently, the crystals are completely inactive. Most of the investigations of the luminescence of DCH crystals refer to this modification [11, 19]. A complete structure determination of the low-temperature structure is in progress. This phase transition cannot be observed in the polymer.

As in most other diacetylenes, the packing of the side groups is the dominant feature of the crystal structure. In DCH the carbazole groups are attached very close to the diyne system. This is why the side group rearrangements which have been shown to be necessary in the diacetylene polymerization [10, 17], especially when large lattice changes are observed, will strongly affect the reaction.

In Fig. 4 it can be seen that the carbazole groups retain their stacking distance of 3.35 Å during the polymerization. This is only possible by a large rotation of the carbazole rings. Consequently, the shape of the molecule stacks changes in the course of this side-group rearrangement. The large shearing of the monomer lattice results from the close packing of these stacks (see also Fig. 6). In many other diacetylene polymerizations, restrictions imposed by side-group packing requirements on the necessary mobility of the diyne system result in a limited reactivity or lead to phase separation [10]. In DCH, complete reaction is made possible by the phase transition. It should be emphasized that

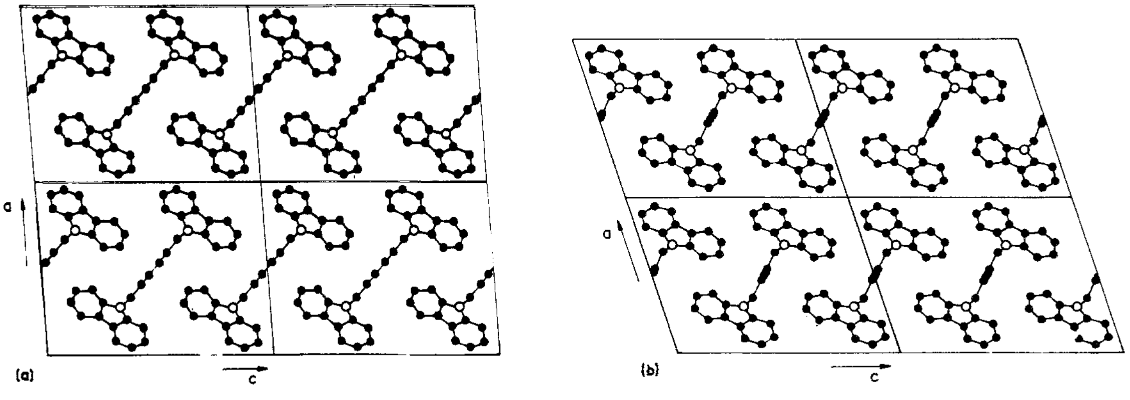

Figure 6 DCH monomer (a), and polymer (b), crystal structures.

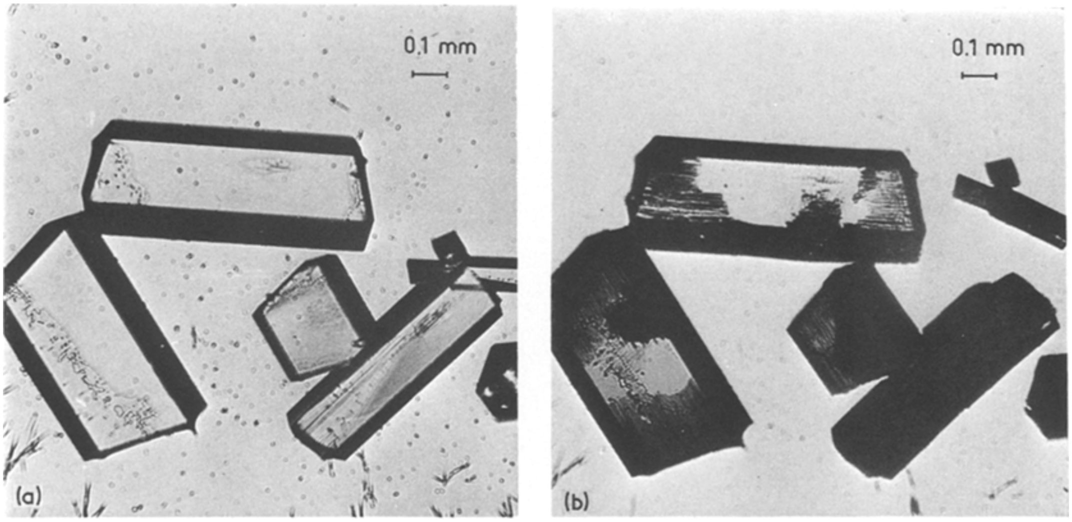

Figure 7 Thermal polymerization of DCH. (a) DCH monomer; (b) after 20 h at 120° C.

although we deal here with a displacive phase transition it proceeds homogeneously throughout the crystal in the γ-ray polymerization and introduces little disorder. We assume that the polymer chains already present at the transition prevent the fragmentation of the crystal which normally should be observed with such large lattice changes. During the polymerization the crystals change their shape accordingly to the microscopic changes of the unit cell dimensions, i.e. they expand by 8% along the **b** direction and are sheared according to the change of β.

Thermal polymerization of DCH always proceeds heterogeneously with nucleation of separate polymer domains. The thermal polymer is polycrystalline with a fibrous texture. Lattice parameters are identical to the γ-ray polymer. Observation of thermally polymerizing DCH crystals shows that the reaction starts from the crystal edges and other visible defects. Phase separation then continues by the growth of several separate daughter domains inside the monomer crystal. This eventually leads to the destruction of the single crystal. In Fig. 7, a DCH crystal before polymerization and at a medium conversion is shown. It is typical for the thermal polymerization of DCH that more perfect monomer crystals require longer reaction times than defect-rich crystals.

4. Brillouin spectroscopy

The measureed frequency shifts, $\Delta\nu$, are related to the sound velocity v of the phonon by

$$\Delta\nu = \frac{2nv}{\lambda}, \qquad (1)$$

where n is the refractive index for the incident light of wavelength, λ. In order to measure the sound velocities in different crystallographic directions, the indicatrix of DCH monomer crystals was determined. The results are summarized in Figs. 8 and 9 and in Table II.

The indicatrix is negative biaxial. The optical plane, OP, is inclined by 49° to the (1 0 0) plane.

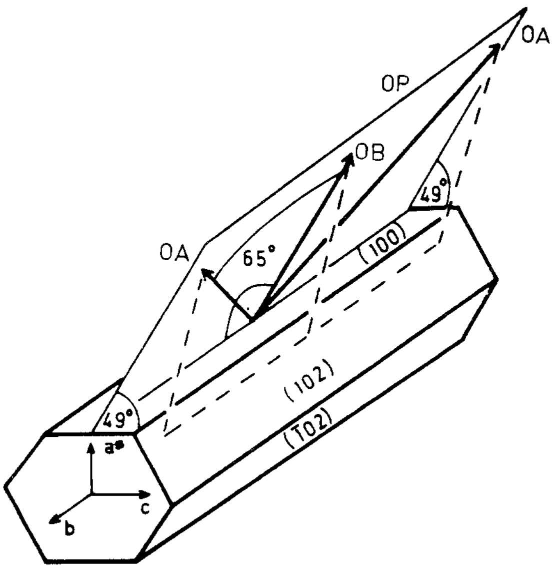

Figure 8 Orientation of optical plane, OP, optical axes, OA, and obtuse bisectrix, OB, in relation to the morphology of DCH monomer crystals.

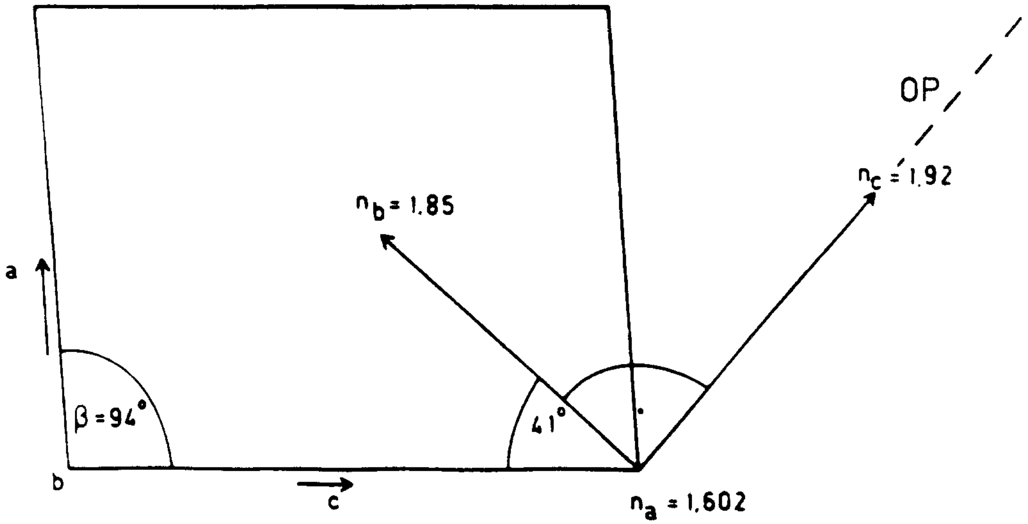

Figure 9 Orientation of the principal values n_a, n_b and n_c of the indicatrix in relation to the unit cell of monomer DCH.

The optical angle between the two optical axes, OA, is 50°. The dispersion with wavelength is low, e.g. at 633 nm the optical angle changed to 42°.

The values obtained at 546 nm were used for the evaluation of the Brillouin spectra taken with a wavelength of 514 nm. The obtuse bisectrix, OB, lies in the (0 1 0) plane forming an angle of 65° with the optical axes. The main section of the refractive index ellipsoid is shown in Fig. 9. n_c coincides with OB, n_b forms an angle of 41° with the (1 0 0) plane, and n_a is parallel to the **b** axis.

Owing to the low (monoclinic) symmetry it is not possible to determine all elastic tensor coefficients from the measured spectra. The two different scattering geometries were chosen because different information on the behaviour of polymerizing DCH crystals can be obtained by determination of the elastic constants in these lattice directions. With phonons travelling parallel to **b** (Fig. 2) the elastic constant c_{22} along the polymer chain direction can be determined as

$$c_{22} = \rho v_4^2, \qquad (2)$$

where ρ is the density of the crystal and c_{ik} are the elastic constants in the abbreviated index notation [20, 21]. The other configuration where the sound velocities of phonons with wavevectors parallel to the **a*** direction were determined, was used in order to characterize the phase change during the polymerization.

TABLE II Refractive indices of monomer DCH at 546 nm

n_a	1.602 [1]
n_b	1.85 [1]
n_c	1.92 [1]
$n_{c',m}$	1.88 [1]
$n_{c'p}$	1.82 [1]

$n_{c'm}$, $n_{c'p}$: refractive indices parallel to the crystallographic c-axis for monomer and polymer, respectively.

The Brillouin spectra obtained with the pure DCH monomer in the two scattering geometries are shown in Figs. 10 and 11. The phonon frequency also depends strongly on the polarization of the incident beam with regard to the indicatrix. In order to obtain the spectrum plotted in Fig. 10 the laser beam was polarized parallel to **c**. With the polarization changed to parallel to **b**, the frequency of the more intense phonon shifted from 19.9 GHz to 17.2 GHz. This decrease of 13.6% agrees well

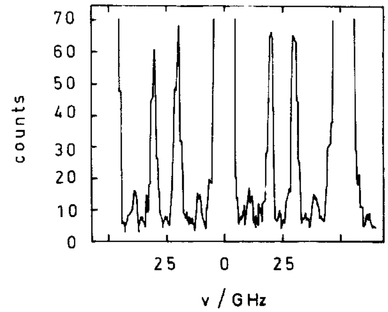

Figure 10 Brillouin spectrum obtained with the wavevector of the phonon in the (0 1 0) plane inclined 4° to **a***.

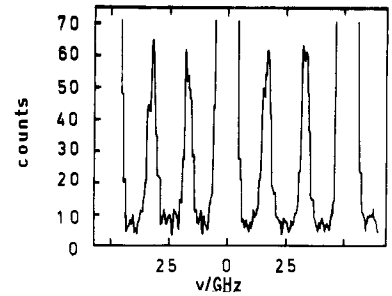

Figure 11 Brillouin spectrum obtained with the wave-vector of the phonon parallel to **b**.

with the difference of the refractive indices in the two directions of $n_{c,m} = 1.88$ and $n_a = 1.602$. In the following only experiments where the polarization was parallel to **c** will be discussed. In this configuration the birefringence did not cause any essential problems since the difference between n_b and n_c is small.

The elastic constant, c_{22}, in the polymer chain direction is strongly influenced by the degree of conversion. A partially polymerized DCH crystal can be considered as a composite material with large differences in the mechanical properties of the both components. The dependence of the phonon frequency parallel to **b** on γ-ray dosage is plotted in Fig. 12. It shows a behaviour similar to the dosage–conversion curve (Fig. 3) with a strong increase in the "autocatalytic" region. It should be noted that inside the shaded area phonons could not be detected at all. The elastic constant of a two component system such as a polymerizing diacetylene crystal, depends not only on the relative concentrations of the components but also very strongly on the geometrical arrangement of the structural elements. Two limiting cases have been considered: the first has been treated theoretically by Voigt [22] and consists of infinite rods of the high-modulus material (polymer) embedded randomly in the matrix of the soft component aligned in the direction of strain which is uniformly distributed in the sample. This model gives the highest possible value of c_{22} with a linear dependence of c_{22} on the volume fraction of the polymer, v_p, according to

$$c_{22} = (1 - v_p)c_{22}^m + c_{22}^p \tag{3}$$

where c_{22}^m and c_{22}^p are the elastic constants of the pure monomer and polymer, respectively.

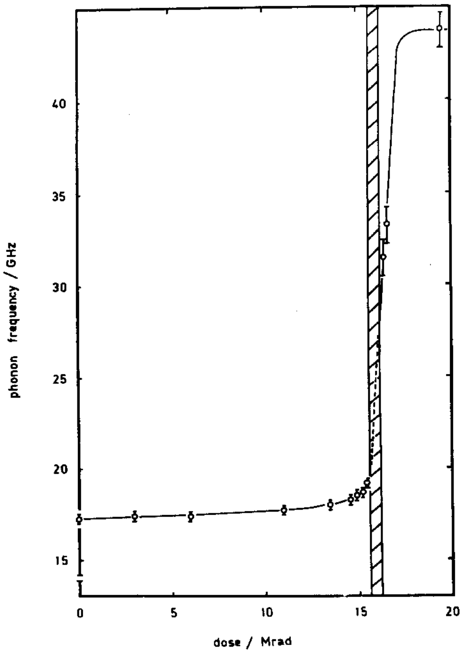

Figure 12 Dependence of phonon frequency of phonons travelling parallel to **b** on the irradiation dosage.

The other limiting case of a two component system is a sandwich structure of alternating layers of the high and low-modulus materials loaded perpendicular to the layer plane [23]. Here the stress is uniformly distributed in the sample. The resulting modulus is given by

$$\frac{1}{c_{22}} = \frac{1 - v_p}{c_{22}^m} + \frac{v_p}{c_{22}^p}. \tag{4}$$

The theoretical curves for the two models and the experimental values obtained for DCH are shown in Fig. 13. At low conversions below the transition, the experimental data are very close to the Reuss curve indicating that here only oligomers are formed. At medium conversions, the experimental values start to deviate from the Reuss curve and the elastic constant observed for the pure polymer meets the expected value which can be calculated from the known modulus of other poly(diacetylenes) [13, 25]. The high value of c_{22} in the pure polymer indicates that the average length of the polymer chains is comparable to other diacetylene polymers where degrees of polymerization of 1000 and above have been determined [14, 24]. Apparently, long chains of the polymer are formed only in the polymer structure. It is unclear, however, whether this increase of average chain length is due to a continuous growth of oligomers formed in the induction period or to an initiation of new polymer chains with a larger kinetic chain length per initiation step.

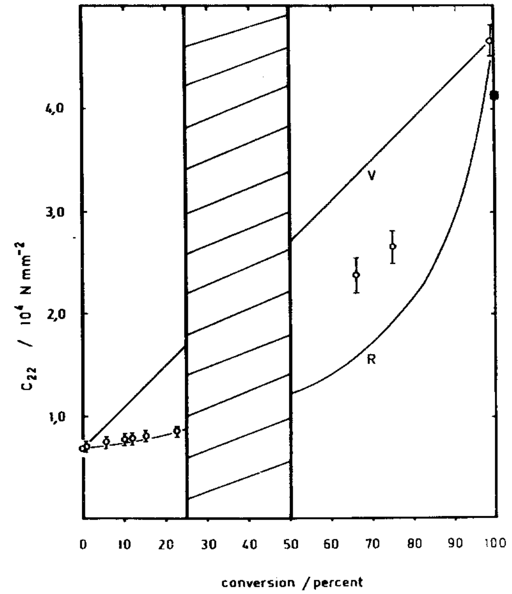

Figure 13 Elastic constant c_{22} for DCH single crystals depending on conversion. The black square is the calculated value for the pure polymer crystal. The curves marked (V) and (R) give upper and lower limits of expected behaviour according to the Voigt and Reuss model.

The dependence of the phonon frequency of phonons with wave-vectors parallel to the **a*** direction on dosage is shown in Fig. 14. Here below the critical conversion, a continuous decrease of phonon frequency with increasing γ-ray dosage is observed followed by an increase after the phase change. The continuous softening of the monomer lattice indicates fluctuations in the direction of the motions during the transition. Unfortunately, in the transition region no phonons could be detected so that the behaviour of the elastic constant in the vicinity of the critical conversion could not be determined.

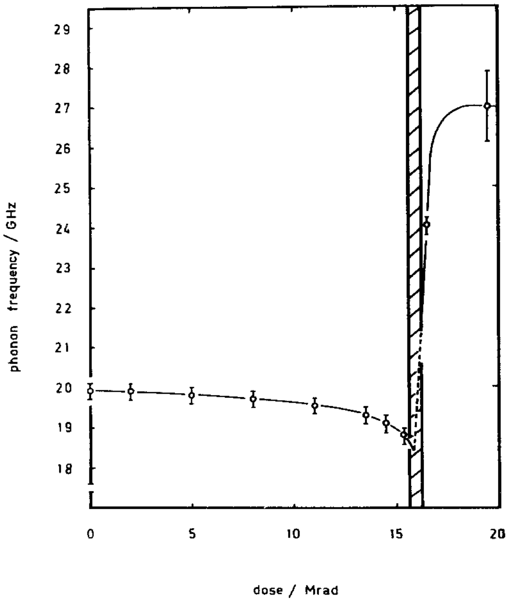

Figure 14 Dependence of phonon frequency of phonons with wavevectors inclined 4° to the **a*** direction on γ-ray dosage.

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