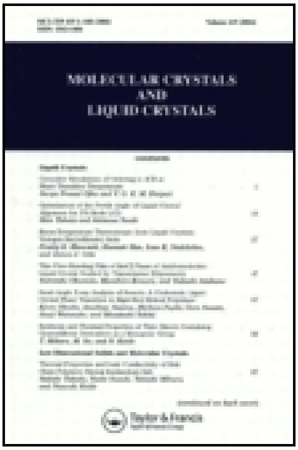


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Photopolymerization of Diacetylene Crystals: Reaction Kinetics and Holography

Hansjörg Niederwald [a], Karl-Hermann Richter [a], Wilfried Güttler [a] & Markus Schwoerer [a]
[a] Physikalisches Institut, Universität Bayreuth, 8580, Bayreuth, W.-Germany

Version of record first published: 17 Oct 2011.

To cite this article: Hansjörg Niederwald, Karl-Hermann Richter, Wilfried Güttler & Markus Schwoerer (1983): Photopolymerization of Diacetylene Crystals: Reaction Kinetics and Holography, Molecular Crystals and Liquid Crystals, 93:1, 247-260

To link to this article: http://dx.doi.org/10.1080/00268948308073532

Mol. Cryst. Liq. Cryst., 1983, Vol. 93, pp. 247–260
0026-8941/83/9304–0247/$18.50/0

Printed in the United States of America

PHOTOPOLYMERIZATION OF DIACETYLENE CRYSTALS: REACTION KINETICS AND HOLOGRAPHY

HANSJÖRG NIEDERWALD, KARL-HERMANN RICHTER, WILFRIED GÜTTLER AND MARKUS SCHWOERER
Physikalisches Institut, Universität Bayreuth,
8580 Bayreuth, W.-Germany

Abstract The intermediate products during the solid state photopolymerization of TS (2,4-hexadiynylene-bis-(p-toluene-sulfonate)) are investigated by time resolved optical absorption spectroscopy. The absorption transients after the initiating UV laser flash unambiguously confirm the most simple kinetic model: the intermediate products are short oligomers which react in a direct sequence. The fit between the calculated and the experimental optical transients is almost perfect. The temperature dependencies of the rate constants yield activation energies ΔE (0.25 eV $\le \Delta E \le 0.30$ eV) and frequency factors (10^{11} s^{-1}) which give a hint to the vibration which is driving the reaction.

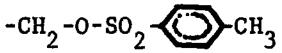
Holographic gratings on the surface of TS-crystals, generated by coherent UV-light, show TS to be a photographic material with high spatial resolution which needs no developing process.

1. INTRODUCTION

The solid state polymerization of macroscopic diacetylene crystals, discovered by G. Wegner[1], was investigated extensively in the past ten years. An actual review is given by D. Bloor[2].

By far the most experiments were done with TS:

$R-C\equiv C-C\equiv C-R$ -R:



$-CH_2-O-SO_2-C_6H_4-CH_3$

After the initiation of the reaction by UV-irradiation at low temperatures several intermediate products could be detected to be stable at low temperatures (Sixl et al.[3]). At higher temperatures the intermediate products are not stable[7] and had not been investigated in detail so far.

In this paper we report our investigations on the high temperature intermediates, being transients after an initiating UV-laser flash, their kinetics and energetics by time resolved optical absorption spectroscopy.

The holographic experiment, presented in the second part of this paper, was planned to give information on the spatial resolution of a UV-hologram, produced by interference of two coherent UV-laser beams on the surface of a TS crystal.

2. SINGLE FLASH IRRADIATION AT LOW TEMPERATURES

From the experiments of Sixl and Hersel we know that at temperatures below 80 K UV-irradiation produces optical absorption bands due to stable photoproducts which, when the crystal is annealed, vanish while the absorption of the stable polymer appears. Before we started our time resolved studies of reaction kinetics at higher temperatures, we performed a UV-flash-experiment at low temperatures which showed the important fact that from all these photoproducts only one (photoproduct A) is generated directly by UV light in the photoreaction in a fresh monomer crystal:

Figure 1a shows the result of irradiating a TS-crystal at 80 K with only one single UV-flash of an excimer laser (λ = 308 nm, τ = 15 ns, E = 0,1 mJ). The spectra shown are difference spectra, i.e. the difference in the optical densities of the crystal before and after irradiation. Therefore the crystal absorption due to the initial polymer content is

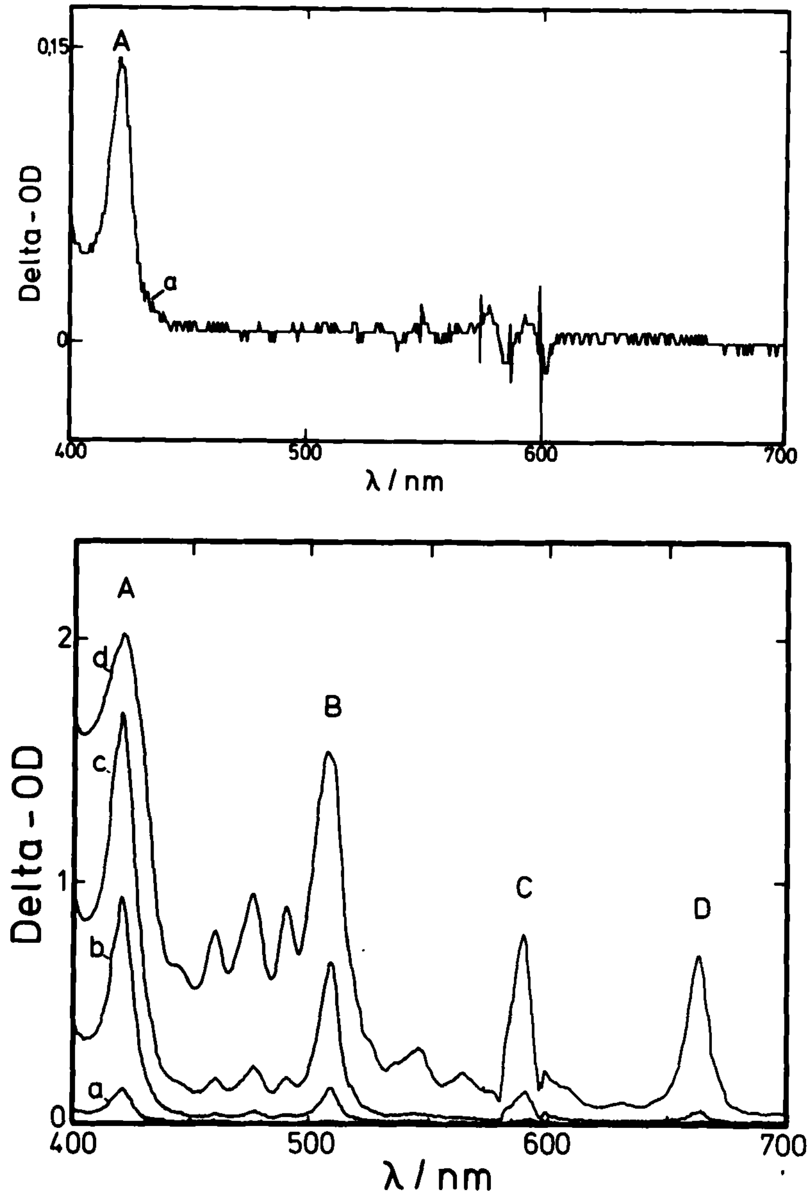


FIGURE 1. Difference spectra, i.e. the difference in the optical spectra of a TS-crystal at T = 80 K before and after irradiation. (a): Single UV-flash (τ=15 ns, λ =308 nm, E = 0.1 mJ); only photoproduct A is generated. The secondary photoproducts B,C,D (and E) are generated by multi flash exposures: (b): 10, (c): 50, (d): 100 UV flashes

discriminated. If the crystal is further irradiated with UV, also the secondary photoproducts B,C,D and E are generated as shown in figure 1b - 1d.

3. POLYCHROMATIC TRANSIENT ABSORPTION EXPERIMENT

To find out which intermediate products appear during the thermal polymerization reaction at temperatures above 180 K, we performed a polychromatic transient absorption experiment. It showed us the transient spectra during the thermal reaction after a single initiating UV-flash at temperatures above 180 K at which no intermediate products are stable.

In fig. 2 schematically the experimental setup is shown.

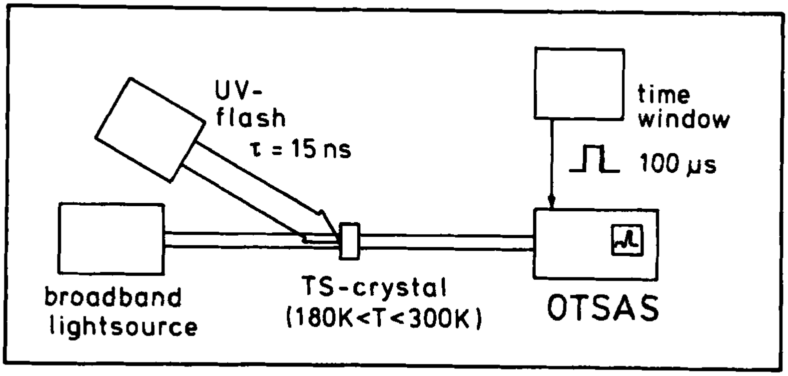


Figure 2. Experimental setup of the polychromatic transient absorption experiment. The optical transient spectrum analyzer system (OTSAS) consists of a polychromator and of a gated optical spectrum analyzer system[7].

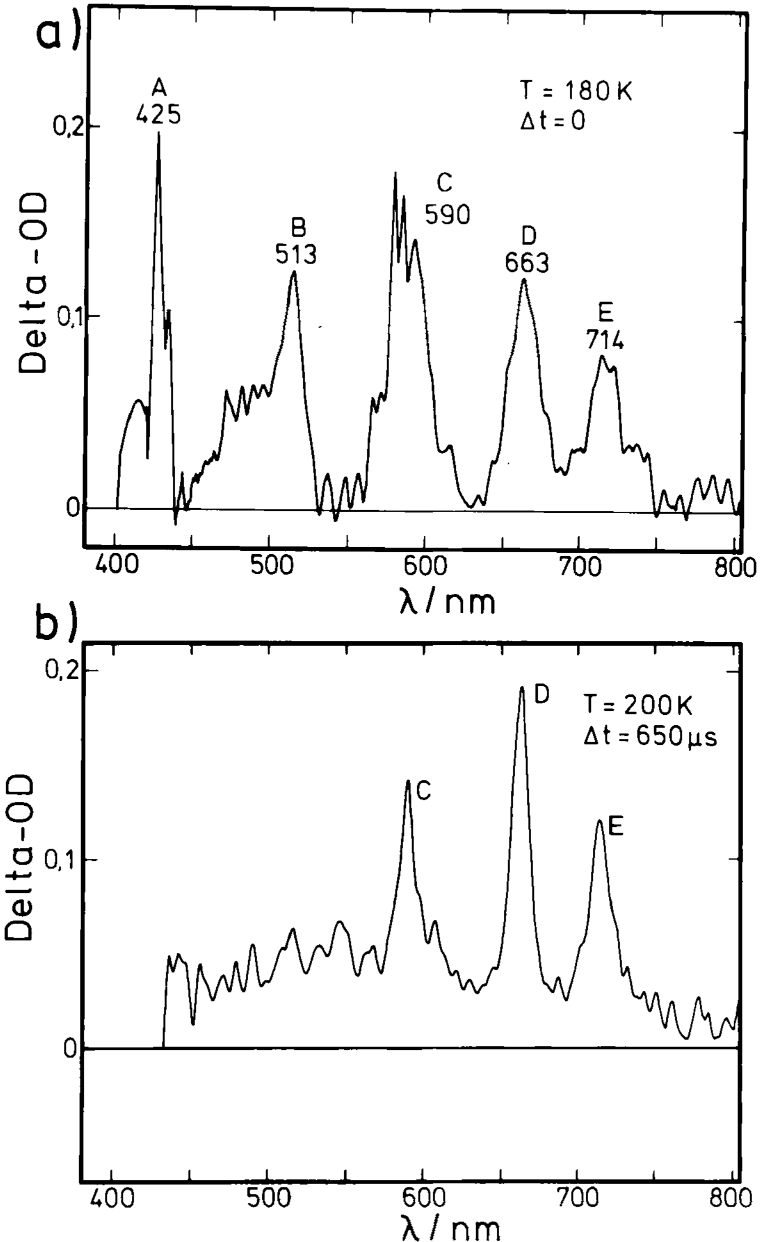


FIGURE 3. Transient difference spectra of a TS crystal (a): at 180 K within the first 100 μs after the UV-flash and (b) at 200 K within in a time window of 100 μs, delayed by 650μs relative to the UV-flash. In the reaction state of fig.3a the intermediate products A,B,C,D,E are still present, in that of fig. 3b A and B have already disappeared.

The sample is held at temperatures between 180 K and 300 K. The reaction is initiated by the excimer-laser-flash (τ = 15 ns, λ = 308 nm, E = 0,1 mJ). The monitor system consists of a broad band light source and an optical transient spectrum analyzer system (OTSAS) which is able to record spectra of the whole visible region from 400 nm to 800 nm within a time window of 100 µs[7]. This time window is shifted over the range between the time of the UV-flash and the time at which the final polymer is stable.

Examples of results of this experiment are presented in fig. 3 as difference spectra. Figure 3a shows that at 180 K within the first 100 µs, again the photoproducts A,B,C,D and E are present. Figure 3b shows at 200 K with 650 µs delay a later reaction state where A and B have already disappeared.

As a result this experiment shows that at temperatures above 180 K during the UV-initiated thermal polymerization the reaction intermediates are the products A,B,C,D and E which were known from the low temperature spectra as stable photoproducts.

4. MONOCHROMATIC TRANSIENT ABSORPTION EXPERIMENT

To study the kinetics of these intermediate products, we performed a monochromatic transient absorption experiment with which we measured the time dependence of the different absorption bands with a tunable cw-laser and a photodiode[7]. The result for the first photoproducts is presented in fig. 4. These four graphs show the time dependence of the optical density after the UV-flash at the peak-wavelengths of the absorption of photoproducts A (425 nm), B (514 nm), C (587 nm) and D (664 nm). The sample temperature was 270 K.

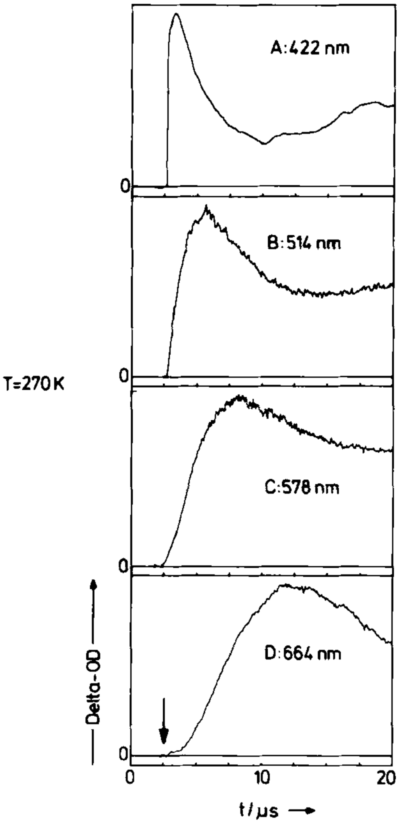


FIGURE 4. The absorption transients of the intermediates A,B,C,D at 270 K. The time of the UV-flash is indicated by an arrow.

Figure 4 makes it obvious how the intermediates follow one another after the UV-flash, which is indicated by an arrow. They appear and disappear on a microsecond time scale.

5. KINETIC MODEL

The transients in figure 4 indicate that the intermediate products follow one another in a direct sequence.

We express this by the following set of rate equations:

$$\frac{dn_i}{dt} = k_{i1}\, n_{i-1} - k_{i2}\, n_i$$

where the index i stands for different products A, B, C, D and E. Each photoproduct rises from its precursor with the rate k_{i1} and reacts to the next intermediate with the rate k_{i2}, i.e. $k_{i1} = k_{(i-1)2}$:

$$\text{Monomer} \rightarrow ? \xrightarrow[k_{A1}]{} A \xrightarrow[k_{A2}]{} B \xrightarrow[k_{B2}]{} C \xrightarrow[k_{C2}]{} D \xrightarrow[k_{D2}]{} E \rightarrow \ldots \rightarrow \text{Polymer}$$

Following this model, in the time behaviour of product A two rate constants are involved, in that of B three, in C four and in D five. Because the rise of A is much faster than the further reactions, k_{A1} is omitted for the later products.

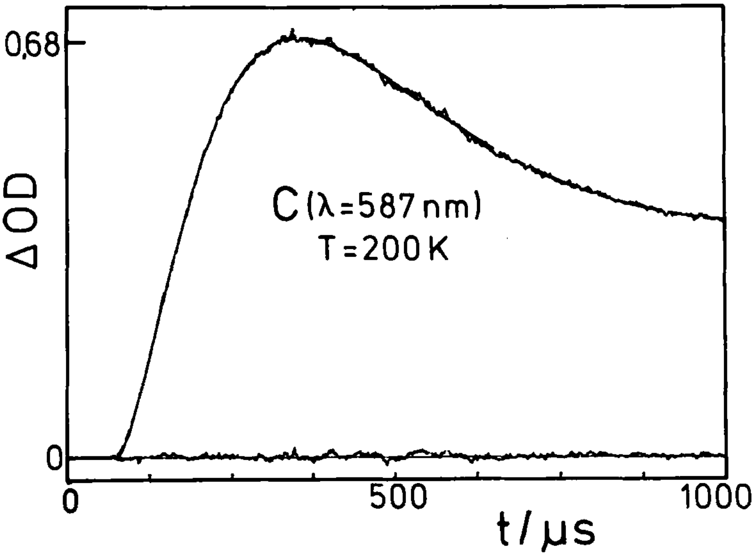


FIGURE 5. Absorption transient and model fit of product C at 200 K. As can be seen from the residuum (difference between transient and fit) which is plotted around the zero line, there is no systematic deviation.

From this model the time dependence of each intermediate product has been calculated. Fig. 5 shows as an example the transient of product C. The least squares fit to the experimental curve is perfect. (The residuum shows no systematic deviation). This fit yields the three relevant time constants (inverse rate constants) for the intermediate product C. The numerical values of rate constants for all intermediate products show unambiguously[7],

- that the model of a direct sequence is valid

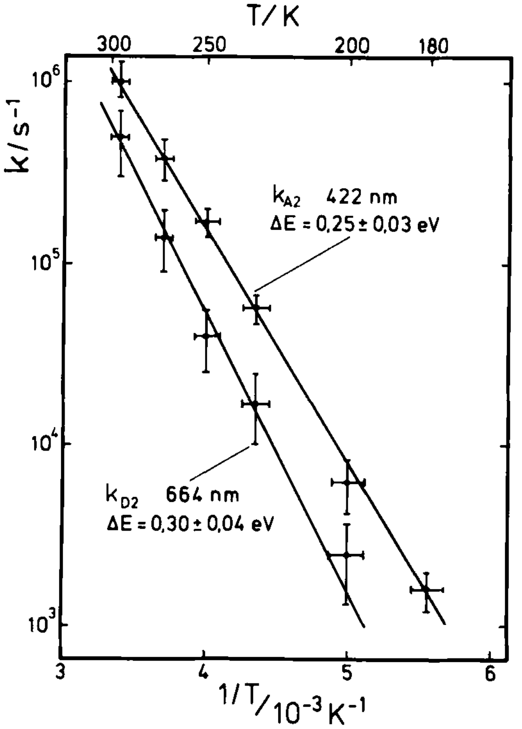


FIGURE 6. Arrhenius plot for the rate constants k_{A2} and k_{D2}

and

- that the different reaction steps (A→B, B→C ...) are very similar.

Fig. 6 shows the Arrhenius plots of some of the rate constants in the temperature range between 180 K and 300 K. The reactions are thermally activated:

$$k_i(T) = k_{io} \exp(-\Delta E_i/KT).$$

The values of k_{A2} and k_{D2} are very similar, those of k_{B2} and k_{C2} are in between them. For the activation energies we find E = 0.25 eV for the first step and a slight increase (some 2 % for one step) for the further ones. For each reaction step we find about the same frequency factor $k_{io} = 10^{11\pm1}\ s^{-1}$.

6. DISCUSSION

Our interpretation of the experiments described above is the following:

- A, B, C, D, E are oligomers of different length
- Each reaction step is the thermally activated addition of one monomer unit
- A is the dimer, D the pentamer
- The slight increase of the activation energies can be interpreted as follows: The parameter of the crystalline unit cell (in the direction of the polymer chains) is some 4 % shorter for the polymer than for the monomer[4]. So the distance between the oligomer-head and the next nearest monomer increases with increasing oligomer length. This might result in a higher amount of activation energy for the next reaction step.

The frequency factor of 10^{11} s^{-1} for each reaction step should give a hint on the involved vibration. It could be an optical phonon in which neighbouring molecules vibrate or librate against one another. For this type of lattice vibration the energy corresponding to 10^{11} s^{-1} seems too low. By inelastic neutron scattering with TS, Schott etal.[5] however detected a low energy optical phonon branch at 10^{11} s^{-1}. This phonon branch could drive the reaction.

7. HOLOGRAPHY

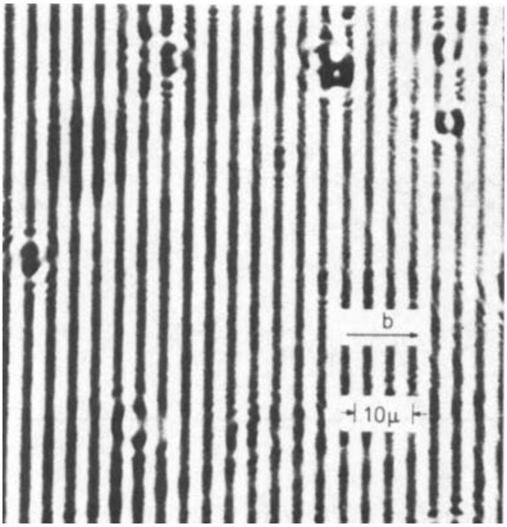


FIGURE 7. Photography of a holographic grating on a TS-crystal surface, taken in a light transmission microscope[6]

Fig. 7 shows the photography of a holographic grating on the surface of a TS-crystal. The distance of the interference fringes is 4 μm in this case, the interference stripes are perpendicular to the crystalline b-axis, the direction of the polymer chains. To our knowledge this is the first hologram on the surface of an organic single crystal. This experiment was planned to give information about the chain-length of the diacetylene polymer; it has some additional interesting aspects: so TS can be regarded as a photographic recording system which needs no processing. The growing polymer with its strong absorption immediately forms an image of the UV-illumination-pattern with - as shown below - very good spatial resolution.

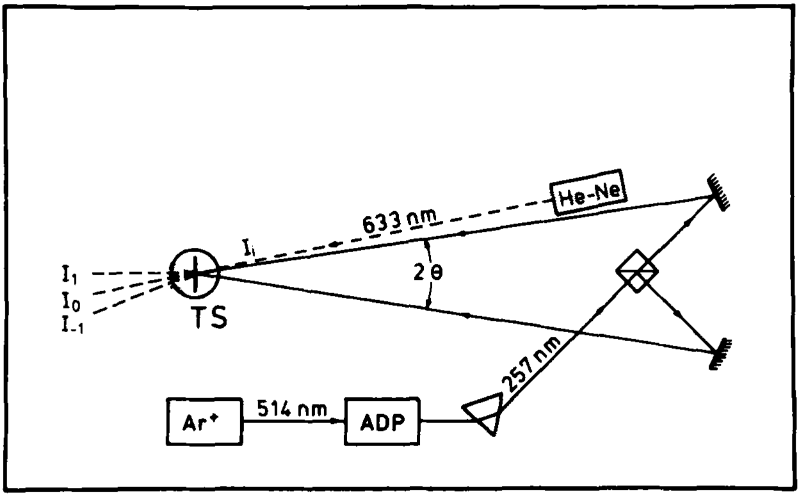


FIGURE 8. Experimental setup for the production of holographic gratings on TS-crystal surfaces[6] .

Figure 8 shows the experimental setup. The UV-light of a frequency doubled Ar^+-laser is split into two beams of equal intensity which coincide on the (100)-surface of a TS crystal. Due to the angle 2 θ between the two beams the spacing of two interference fringes is

$$\Lambda = \frac{\lambda}{2\sin\theta}$$

The penetration depth of 257 nm light is of the order of one µm. The crystal surface polymerizes in the regions of constructive interference, thus a thin grating is produced.

The grating is read out with a He-Ne-Laser at 632.7 nm. As the polymer absorption is very weak at this wavelength a mixture of amplitude- and phase-hologram is observed. The intensities of the reading laser beam and its diffraction maxima of first and second order is monitored by a photomultiplier.

The resolution of the holograms on TS should be limited by the length of the growing polymer chains. So, when the interference stripes are perpendicular to b and the polymer chains are longer than about half the distance between two interference stripes, the grating should be smeared out and a significant decrease in diffraction efficiency should be observed.

So far the grating constant was varied from 5 µm down to 0,4 µm. Even at the grating constant of 0.4 µm diffraction has been observed; however the efficiency decreased from its maximum value of about 25 % to about 2 %.

So far the polymer chain length could not be determined.

REFERENCES

1. G. Wegner, Z. Naturforsch. 24b (1969) 824
2. D. Bloor, "Developments in Crystalline Polymers", edited by D.C. Basset, Applied Science Publishers, London 1982
3. H. Sixl, W. Hersel, H.C. Wolf, Chem. Phys. Lett. 53,1 (1978) 39
   C. Bubeck, H. Sixl, W. Neumann, Chem. Phys. 48 (1980)269
4. V. Enkelmann, G. Wegner, Angew. Chemie 89,6 (1977) 432
5. M. Schott, private communication
6. K.H. Richter, W. Güttler, M. Schwoerer, Chem. Phys. Lett. accepted for publication

7. H. Niederwald, thesis 1982;
H. Niederwald, H. Eichele, M. Schwoerer, Chem. Phys. Lett. 72,2 (1980) 242;
H. Niederwald, M. Schwoerer, Z. Naturforsch., in preparation