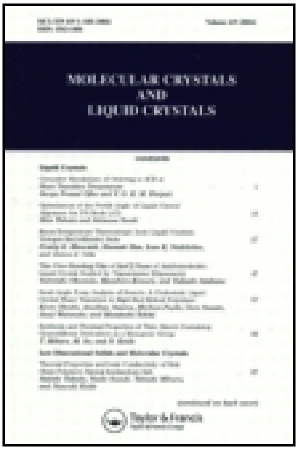

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Holographic Method and Electron Beam Lithography for Determining the Average Polymer Chain Length in Diacetylene Single Crystals

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HOLOGRAPHIC METHOD AND ELECTRON BEAM LITHOGRAPHY FOR DETERMINING THE AVERAGE POLYMER CHAIN LENGTH IN DIACETYLENE SINGLE CRYSTALS

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Abstract Microstructures of polymer in a TS - 6 diacetylene monomer matrix were produced using UV-holography at different wavelengths and electron beam lithography. The resolutions along the chain direction were 600 nm for UV-holography and 200 nm for electron beam irradiation. However, there is not sufficient evidence that these values are limited by the chain length and not by the experimental procedure. So the values of the resolution give upper limits of the average chain length of 600 nm (1200 repeat units) and 200 nm (400 repeat units), respectively, for these two methods of polymerization.

INTRODUCTION

The solid state polymerization of diacetylenes has grown into an interesting field of research because it provides the means of producing macroscopic single crystals of polymers with a conjugated backbone. The reaction scheme is given in fig. 1. The polymerization can be initiated

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by heat, UV, γ or electron beam irradiation.

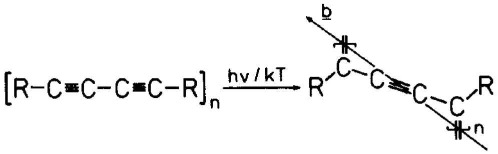


Fig. 1 Reaction scheme for the solid state polymerization of diacetylenes. For TS - 6: R = $CH_2 - O - SO_2 - \emptyset - CH_3$. The crystallographic b-axis is along the polymer backbone.

Since the pioneering work of Wegner[1], information on the chain length was lacking for a long time due to the insolubility of most of the poly(diacetylenes)[2]. It is only recently that data on chain length in these materials became available[3-7]. From the work on photopolymerization it is known that short chain oligomers are stable at temperatures below 100 K whereas long chains develop by irradiation at room temperature[8]. In this paper we intend to give values for the chain lengths at room temperature under UV and electron beam irradiation. For this purpose we tested the resolution of microstructures which were produced by UV-holography and by electron beam lithography. Furthermore, we also want to prove whether the chains are short enough to allow the generation of submicron structures in diacetylene crystals. Submicron structures have already been produced in Langmuir-Blodgett films of diacetylenes by Garito and Singer[9].

The first attempt to determine the chain length in diacetylenes was made by Mondong and Bässler[3] using UV-lithography i. e. generation of microstructures by UV exposure and subsequent etching. The distortions of the microcstructures were viewed under the electron microscope and yielded information about the chain length, l. A value of l = 0.4 µm in TS-6 single crystals was given by the authors. Albouy et. al. used diffuse X-ray scattering for the determination of chain lengths in TS-6[5]. The only measurements with standard methods of molecular weight determination were reported by Wenz and Wegner[6] on soluble poly(diacetylenes), which became available very recently. Preliminary results on our new holographic method for determining the chain length were given in the preceeding conference of this series[10]. In this paper we report on our progress in holography[4] and electron beam lithography[7] in TS - 6 single crystals and on latest results of the holographic method.

SAMPLE PREPARATION

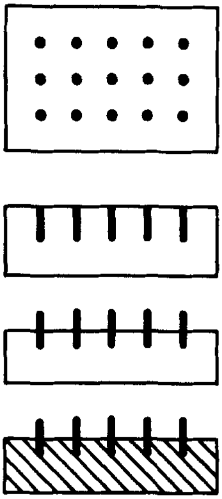
Our experiments were performed on TS-6 single crystals (2,4-hexadiynylene-bis-(p-toluene-sulfonate also named PTS or TS). Monomer crystals were grown from solution as described by Wegner[1]. They were cleaved along their (100) plane to give samples of some mm^2 in area and about 100 µm thick. The polymer content of fresh crystals was about 0.01 %.

ELECTON BEAM LITHOGRAPHY

Fig. 2 shows the schematics of the experimental procedure. A quadratic point lattice of polymer in TS-6 monomer was generated by irradation with 30 keV electrons in a scanning electron microscope (SEM). The electron beam diameter at the sample surface was about 5 nm. However, this increased inside the crystal by about one order of magnitude due to scattering. The penetration depth of 30 keV electrons is about 10 μm in this material.

After irradation the crystals were etched with methanol in order to remove the monomer within a layer between 1 and 5 μm in thickness. This yielded a surface structure having the irradiation pattern, which could be seen in the SEM.
To avoid polymerization during observation in the SEM, which can lead to a peeling-off of the surface, the remaining monomer was thermally polymerized. Before observation in the SEM the sample was coated with gold (less than 10 nm).

Fig. 3 shows a typical dot pattern as viewed in the SEM. From a series of dot patterns with varying dot-to-dot distances we concluded that it is possible to generate microstructures with a resolution of less than 200 nm parallel to the chain direction and of less than 40 nm perpendicular to it. However it seems possible that this anisotropy was introduced by the experimental procedure. Therefore the observed



(1) Generation of a regular dot pattern of polymer by electron beam polymerization (top view)

(cross section)

(2) Etching

(3) Thermal polymerization of the remaining monomer

(4) Coating with gold

(5) Observation under the scanning electron microscope

Fig. 2: Generation of a dot pattern on a diacetylene crystal by electron beam lithography

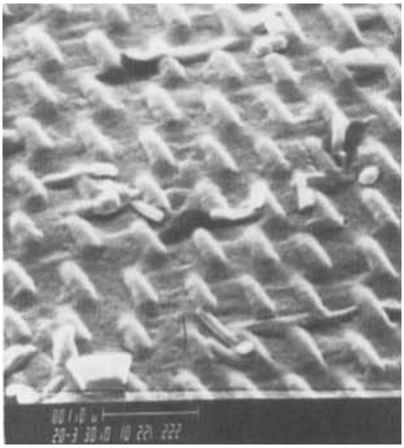


Fig. 3: Scanning electron micrograph of a dot pattern on a TS-6 single crystal surface (from ref.7). Do-to-dot distance is 560 nm in horizontal and vertical direction. The polymer chain direction is horizontal in the plane of the paper.

resolution gives an upper limit to the average chain length of 200 nm (400 repeat units) for electron beam polymerization.

UV-HOLOGRAPHIC GRATINGS

BASIC PROPERTIES

Microstructures on TS-6 were also produced by UV light. By interference of two laser beams a line pattern of polymer in monomer is created at the maxima of the interference fringes (fig. 4). We call this a holographic grating or, for short, a hologram. Readout was done by a He-Ne laser (633 nm, fig. 5). At this wavelength diacetylenes do not undergo photopolymerization. Furthermore, there is little absorption at 633 nm, but there is a drastic change in the refractive index in going from monomer to polymer so that we get almost pure phase holograms[4].

The polymer chain length is expected to have a remarkable effect on the resolution of the holograms if the chain direction is perpendicular to the grating stripes. It is evident that the grating will be smeared out if the chains grow longer than the grating spacing. But even if the chains are shorter, a considerable influence of chain propagation on the grating profile can be seen from theoretical calculations (fig. 6). This will lead to changes of the intensities of the different diffration orders as is known from diffraction theory.

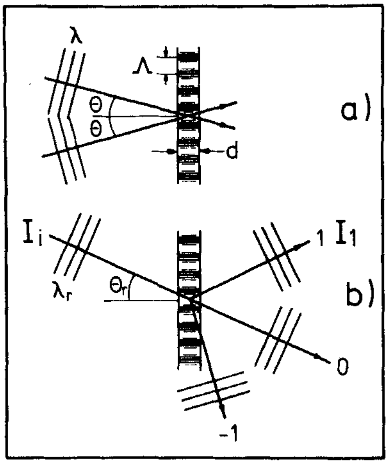


Fig. 4: a) Recording of a holographic grating by interference of two laser beams of wavelength λ. Λ: grating spacing, d: thickness of the holographic grating.
b) Readout by a laser of wavelength λ, and intensity I_i. Zero order and ± 1 st order diffracted beams are shown (from ref. 4c).

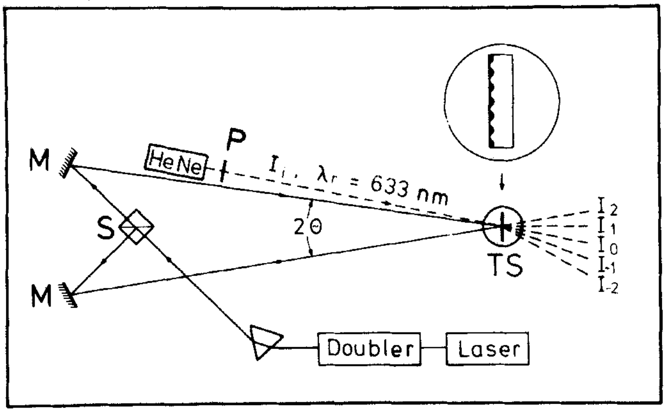


Fig. 5: Experimental setup for recording and reading holographic gratings on TS-6. S: beam splitter, M: mirror, P: polarizer. ± 2 diffracted orders are shown. Up to ± 5 diffracted orders were observed.

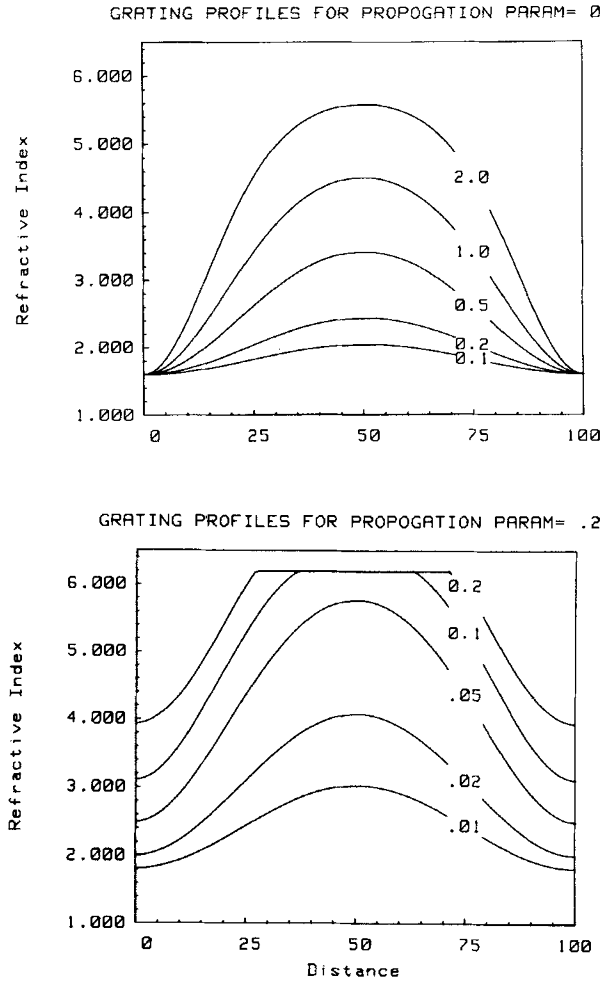


Fig. 6: Influence of chain propagation on the grating profile. The calculated refractive index between two minima of the grating is shown without propagation (upper part) and for a uniform chain length of 0.2(in units of the grating spacing, lower part). Curves are labeled by values of the reaction parameter kI_0t (k = rate constant, I_0 = light intensity at maximum, t = irradiation time)

EXPERIMENTAL

For most of the experiments reported here an argon ion laser with an ADP frequency doubler was used resulting in a wavelength of 257 nm[4]. In our latest experiments a pulsed dye laser (FL 2002 Lambda Physik) with KDP frequency doubler (300 nm) or an Xe-Cl - excimer Laser (EMG 500 Lambda Physik) operating at 308 nm was used for recording. This results in a deeper penetration of the exciting light.

RESULTS

The holographic efficiency is defined as the first order diffracted intensity divided by the incident intensity of the reading beam. It is dependent on the exposure during writing, reaches a maximum at an exposure of 100 - 150 mJ/cm^2 and decreases to very low values above 250 mJ/cm^2 [4b,c]. Fig. 7 shows the maximum holographic efficiency, η_{max}, for different spatial frequencies, $1/\Lambda$ (lines/mm). It can be seen that the maximum diffraction efficiency decreases sharply above a spatial frequency of 1500 lines/mm, which corresponds to a grating spacing, Λ, of 0.6 µm. It is possible to generate holograms with a spatial frequency of up to 3000 lines/mm and a holographic efficiency of about 1 %. We estimate an average chain length of less than 0.6 µm because the chain direction was perpendicular to the grating stripes.

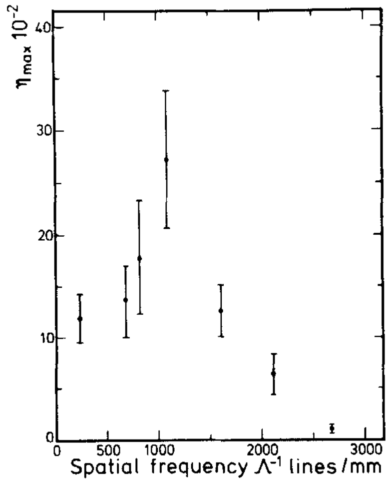


Fig. 7: Maximum holographic efficiency η_{max} for different spatial frequencies $1/\Lambda$. Chain direction was perpendicular to grating stripes (from ref. 4b.)

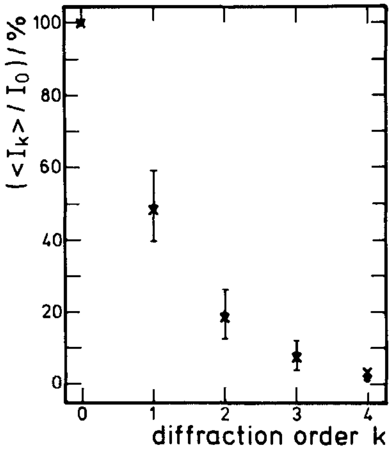


Fig. 8: Normalized higher-order diffraction intensities T_k/I_0 at normal incidence of the He-Ne laser beam (k = 0...4). Chain direction perpendicular to grating stripes (from ref. 4b).

We also recorded the higher-order diffractions (fig. 8). These yield the grating profile by evaluation of the Fraunhofer diffraction formula, which gives about the same value for the chain length as from fig. 7[4b]. This value of 0.6 microns has to be considered as an upper limit of the chain length, which is for the moment given by our experimental arrangement. The actual value of the average chain length may be shorter.

The gratings which were written at a wavelength of 300 nm[11] show a sharp Bragg-condition (FWHM about 1° for chain direction parallel to the grating stripes). This is much sharper than for the gratings reported above which were written at 257 nm, and is due to the deeper penetration of the writing beams at 300 nm. The Bragg-condition was found to be about one order of magnitude less sharp for the "perpendicular" orientation. (i. e. chain direction perpendicular to the grating stripes). There is no safe indication so far that this effect is related to chain propagation, but rather to the anisotropic absorption of the polarized laser beam. A method for analysis of our data on thick gratings will be presented in a forthcoming paper[12].

DISCUSSION

The most detailed investigation on chain lengths of poly(diacetylenes) was reported by Wenz and Wegner[6] on TS-12 (Dodeca-5,7-diyne-1,12-ylene-bis (p-toluene sulfonate)), which yields a soluble polymer. It was shown that the average chain length increases with conversion during polymerization by ^{60}Co γ-irradiation from about 50 repeat units in the beginning to 2000 at 10 % conversion, and then stays constant.

Given the polymer yield of $P = 0.068 \pm 0.010$ at 257 nm[4b,c] we can calculate that the average conversion was 8 % within the penetration depth of 0.5 µm for the UV light at an exposure of $E = 100$ mJ/cm^2. This was used for the data in figs. 7 and 8. Thus the conversion for our chain length data is near the autocatalytic regime and our estimate for the upper limit of the average chain length of 1200 repeat units (0.6 µm) is in reasonable agreement with the above cited values for TS-12 at this conversion. It should be pointed out that the method for polymerization and the side groups of the diacetylene were different in both cases. A comparsison with the results of Mondong and Bässler[3] is given in ref. 4b. The conversion for our experiments on electron beam polymerization is not known.

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REFERENCES

1. G. Wegner, Polymerization von Derivaten des 2.4-Hexadiin-1.6-diols im kristallinen Zustand. Z.Naturforsch. 24b (1969) 824
2. G. Wegner, IV. Polymerization of Bis-(p-toluene Sulfonate) of 2,4-Headiin-1,6-diol. Makromol. Chemie 145 (1971) 85
3. R. Mondong, H. Bässler, Determination of the Chain Length in Polydiacetylene by Scanning Electron Microscopy. Chem. Phys. Lett. 78 (1981) 371
4. a) K.H. Richter, W. Güttler, M. Schwoerer. Holographic Gratings on Diacetylene Single-Crystal Surfaces. Chem. Phys. Lett. 92 (1982) 4
   b) K.H. Richter, W. Güttler, M. Schwoerer. UV-Holographic Gratings in TS-Diacetylene Single-Crystals. SpatialResolution and Sensitivity Appl. Phys. A 32 (1983) 1
   c) K.H. Richter. Holographische Gitter auf Diacetylen-Einkristall-Oberflächen, Diplomarbeit, Universität Bayreuth 1983
5. P.A. Albouy, J.N. Patillon, J.P. Pouget. X-Ray Study of the Topochemical Polymerization of Two Diacetylenes. Mol. Cryst. Liq. Cryst. 93 (1983) 239
6. G. Wenz, G. Wegner. Kinetics of Radiation Induced Polymerization of a Diacetylene Studied by Analysis of the Molecular Weight Distribution. Mol. Cryst. Liq. Cryst. 96 (1983) 99
7. H. Niederwald, H. Seidel, W. Güttler, M. Schwoerer. Submicron Structures on Diacetylene Single-Crystal Surfaces by Electron Beam Irradiation. J. Phys. Chem. 88 (1984) 1933
8. M. Schwoerer, H. Niederwald. Photopolymerization of Diacetylene Single Crystals. (Review). Makromol. Chem., Suppl. 12 (1985) 61-82
9. A.F. Garito, K.D. Singer Laser focus 18 (1982) 59
10. H. Niederwald, K.H. Richter, W. Güttler, M. Schwoerer. Photopolymerization of Diacetylene Crystals: Reaction Kinetics and Holography. Mol. Cryst. Liq. Cryst. 93 (1983) 247

11. H.-D. Bauer. Holographie in der UV-Photopolymerisation von Diacetylen-Einkristallen: Parallele Orientierung von Interferenzstreifen und Polymerachse. Diplomarbeit, Universität Bayreuth (1985).
12. Bryan E. Kohler, H.D. Bauer, Bern E. Kohler, W. Güttler and M. Schwoerer. Holographic Method for Determining the Spatial Extent of Photochemistry: Room Temperature Polymerization of Diacetylen-PTS (in preparation)