MICROWAVE DIELECTRIC PROPERTIES OF DISUBSTITUTED DIACETYLENE DNP SINGLE CRYSTALS

M. DRESSEL^{*} and H.W. HELBERG Drittes Physikalisches Institut der Universität Göttingen, Göttingen (F.R.G.)

ABSTRACT

The dielectric properties of disubstituted diacetylene DNP single crystals were measured by microwaves in order to study the ferroelectric phase transition as a function of solid state polymerization. The high frequency properties of the permittivity were studied in DNP monomer and also in DNP crystals that were partially polymerized at a temperature of 130°C for different periods of time. At $T_c = 46.5$ K the dielectric constant of the monomer shows a sharp peak. No change of this behaviour was found by cooling down for several times. The peak of ε' is getting flat and shifted to lower temperatures with advanced duration of thermal polymerization. The monomer crystals show a small peak of dielectric losses $\varepsilon'' \approx 1$ at T_c . At the beginning of polymerization the peak height is getting larger and dielectric losses were measured down to 4 K. For polymerizing more than 3 h the maximum is reduced and flat; no losses at all are found after full polymerization.

INTRODUCTION

It is well known that disubstituted diacetylenes can be converted via solid state polymerization into polymere single crystals [1, 2]. The monomer crystals of symmetric 1.6-bis (2.4 dinitrophenoxy)-2,4-hexadiyne (DNP) undergo a phase transition at $T_c = 46.5$ K, where the permittivity and spontaneous electric polarization shows a large anomaly in the \vec{b} -direction [3, 4]. This ferroelectric transition is not clearly understood; X-ray datas show a structural change from the group P2₁/n to P2₁ in the low temperature phase of DNP monomer, i.e. a loss of the molecular centrosymmetry [5]. In order to study the phase transition as a function of increasing solid state polymerization we measured the dielectric properties of disubstituted diacetylene DNP single crystals in the microwave region.

EXPERIMENTAL

The flat plate-like crystals of the DNA monomer were grown similar to the method described in Ref. 4 and 6. Small rectangular samples (e.g.: 0.2 mm × 0.9 mm × 0.3 mm) were placed in the centre of a cylindrical microwave cavity (TE_{111} -mode, resonance frequency $f_0 =$ 10.3 GHz) with the electrical field *E* directed parallel to the **b**-axis of the monomer crystal. We measured frequency shift and change of quality factor as a function of temperature from

Present address: Laser-Laboratorium Göttingen, Im Hassel 21, D-3400 Göttingen, F.R.G.

300 K down to 2 K and determined real and imaginary part of the relative dielectric permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ by the usual microwave cavity perturbation technique [7]. The rate of cooling did not exceed 3 K per minute and was only 0.2 K in temperature range between 30 K and 70 K. Some crystals of DNP were isothermally polymerized at a temperature of 130°C ± 1°C for different periods of time. Partially polymerized samples could be produced by stopping the polymerization process at times t_P shorter than that necessary for full polymerization (i.e. about 15 h [6]). The contactless method of microwave investigations enables to measure the same sample for many times and after each period of polymerization.

RESULTS AND DISCUSSION

The real part of the relative permittivity of a single sample is plotted in Fig. 1a as a function of temperature for different times of thermal polymerization. The dielectric constant of the DNA monomer ($\varepsilon' \approx 4$) is uniform in the temperature range of 100 K - 300 K. After a gradual rise below 100 K it shows a fairly sharp peak at $T_c = 46.5$ K ± 2 K with $\varepsilon'(T_c) = 12...20$ varying with different samples. Below the peak the dielectric constant falls off very rapidly to its room temperature value.

In partially polymerized DNP the nature of the anomaly in the permittivity depends on the extent of polymerization, while the time of polymerization is related to the amount of polymer present [3]. Figure 1 shows the temperature dependence of the microwave dielectric constant for the same DNP sample polymerized for different periods of time $t_{\rm P}$ The peak heights of ε' (Fig. 1a) and of ε'' (Fig. 1b) decrease and and the peak position shift to lower temperatures with increasing polymerization time. In Fig. 2 the transition temperature $T_{\rm c}$ -defined as temperature of the maximum of ε' is plotted as a function of polymerization time $t_{\rm P}$ the corresponding ε' -maximum and ε'' -maximum is shown in Fig. 3. After 15 h tempering at 130°C the anomaly in the permittivity has completely disappeared. The polymerization can be interrupted at every time and continued after cooling down for measurements, but it takes about 20%



Fig. 1. Temperature dependence of (a) the real part ε and (b) the imaginary part ε " of the relative permittivity of a single DNP crystal measured in a microwave cavity at 10.3 GHz with the electrical field *E* parallel to the \overline{b} -axis of the monomer. The variation with duration of thermal polymerization at 130°C is shown for different periods of time: 0 h (monomer crystal) (x), 3 h (\diamond), 3+7 h (+) and 3+7+3 h (\Box).





50

40

<u>2</u> 30

_⁰ 20

Fig. 2. Variation of transition temperature T_c with the duration of thermal polymerization t_P



Fig. 3. Variation of ε' -maximum (×) and ε'' -maximum (\diamond) with the duration of polymerization t_P

longer to reach the same stage of polymerization compared to the uninterrupted procedure. \oplus

No change of the permittivity of DNP monomer as well as partially polymerized crystals was found for up to 8 cycles cooling down from room temperature to 4 K. In opposite to quasi-dc measurements [4] the high-frequency behaviour of the dielectric properties of the crystals is completely reversible for every stage of the solid state polymerization process. The phase transition can be passed through for many times without any change in the peak of the permittivity or the absolute values.

The ferroelectric phase transition in DNP monomer seems to be weakly first order [3, 4]. The ε '-anomaly can be analysed by splitting the dielectric constant ε ' in a part of the electrical susceptibility χ_F due to the transition and the suceptibility χ_0 from all other processes except that of the transition: $\varepsilon' = 1 + \chi_0 + \chi_F$. In a Devonshire ferroelectric [8] Curie-Weiß behaviour

 $(\chi_{P})^{-1} = \beta(T - T_{0})$

is expected both below and above the transition. Fig. 4 is a plot of the inverse susceptibility $(\chi_P)^{-1}$ due to the transition versus temperature. Curie-Weiß behaviour is observed in the region above and below the transition temperature T_c for DNP monomer crystals as well as for partially polymerized samples. The Curie-Weiß temperature T_0 (for the region $T > T_c$) is about 42 K, respectively 35 K, and not equal to the transition temperature T_c . For unpolymerized crystals values of the slope

$$\beta_{I}^{0h} = \left(d\chi_{F}^{-1} / dT \right)_{T < T_{c}} = -0.488 \text{ K}^{-1} \text{ for } T < T_{c} \text{ and} \\ \beta_{2}^{0h} = \left(d\chi_{F}^{-1} / dT \right)_{T > T_{c}} = 0.0286 \text{ K}^{-1} \text{ for } T > T_{c}$$



Fig. 4. Temperature dependence of the reciprocal susceptibility $(\chi_F)^{-1}$ due to the ferroelectric transiton for DNP monomer (×) and partially (10 h) polymerized (+) crystals

were measured and show a considerable difference: $\beta_1^{0h}/\beta_2^{0h} = -17$. The low-frequency measurements show a ratio of $\beta_1^{0h}/\beta_2^{0h} = 0.11$ [4]. If the ratio of the slope below and above T_c is an indicator for the order of the transition, as proposed [9], the ferroelectric phase transition of the DNP monomer is a first order transition [10]. After polymerizing the sample for 10 h the slopes above and below the transition are equal in the absolute value ($\beta^{10h} \approx 0.018 \text{ K}^{-1}$), as reported in Ref. [4]. Nevertheless these datas are not sufficient for a final interpretation of the phase transition.

The temperature dependence of the imaginary part of the relative permittivity is plotted in Figure 1b. Above 60 K there are no dielectric losses ε ". The DNP monomer crystals show a small peak of the imaginary part of the relative permittivity $\varepsilon^* \approx 1$ at $T_c = 46.5$ K. At the beginning of the polymerization process ($t_P \le 3$) the peak is getting larger (up to $\varepsilon^* = 20$) and dielectric losses of $\varepsilon^* = 1$ were measured down to 4 K. For a polymerization time $t_P > 3$ h the maximum is reduced and flat (Fig. 3); after complete polymerization there were found no losses at all. Due to the randomly distributed starting points of the homogeneous growth of diacetylene solid state polymerization [11], these results can be interpreted as a lattice softening in the boundary between the monomer and the polymer part of the crystal. In the beginning the polymerization starts at many points, which causes a large amount of grain boundaries. The advance of thermal treatment leeds to a mostly polymerized sample, at last to a polymer single crystal of high perfection. No dielectric losses could be measured then. Temperature dependent ultrasonic absorption experiments should be carried out for verification.

CONCLUSIONS

The microwave investigations of the ferroelectric phase transition of DNP crystals show in principle the same behaviour of the dielectric properties as quasi-dc measurements, i.e., there is no significant frequency dependence. At $T_c = 46.5$ K there is a large anomaly of the dielectric constant of the monomer, which is sign of a weak first order ferroelectric phase transition. This transition is suppressed by the solid state polymerization at a temperature of 130° C. The sharp peak of the dielectric losses near the transiton temperature may point to a lattice softening in the grain boundery between polymerized part of the DNP crystal and the still remaining monomer. Ultrasonic investigations are necessary for a better description and understanding of the phase transition.

ACKNOWLEDGEMENTS

We would like to thank Professor E. Dormann, P. Gruner-Bauer and I. Müller (University Bayreuth) for the crystals and their careful preparation.

REFERENCES

- 1 G. Wegner, <u>Z. Naturforschung</u> **24b** (1969) 824
- 2 A.R. McGhie, G.F. Lipscomb, A.F. Garito, K.N.Desai, P.S. Kalyanaraman, <u>Makromol.</u> Chemie 182 (1981) 965
- 3 G.F. Lipscomb, A.F. Garito, T.S. Wei, Ferroelectrics 23 (1980) 161
- 4 H. Schultes, P. Strohriegl, E. Dormann, Ferroelectrics 70 (1986) 161
- 5 M. Bertault, L. Toupet, Material Science 13 (1987) 23 and unpublished datas
- 6 P.S. Kalyanaraman, A.F. Garito, A.R. McGhie, K.N. Desai, <u>Makromol. Chemie 180</u> (1979) 1393
- 7 H.W. Helberg, B. Wartenberg, Z. angew. Physik 20 (1966) 505
- 8 A.F. Devonshire, Advances in Physics 3 (1954) 87
- 9 D.A. Draegert, S. Singh, Solid State Commun. 9 (1971) 595
- 10 M.E. Lines, A.M. Glass, <u>Principles and Applications of Ferroelectrics and Related Materi-</u> als, Clarendon Press, Oxford 1977
- 11 G. Wegner, in: <u>Chemistry and Physics of One-Dimensional Metals</u>, p. 297, ed. by H.J. Keller, Pienum Press, New York/London 1977