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1994 J. Phys.: Condens. Matter 6 1417

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# The ferroelectric phase transition of the disubstituted diacetylene 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne (DNP): analysis by heat capacity measurements

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Received 4 October 1993

**Abstract.** The ferroelectric phase transition of 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne (DNP) is characterized by specific heat measurements for monomer and thermally polymerized polymer single crystals. The data support a tricritical phase transition of monomer crystals, with the transition enthalpy clearly lower than that corresponding to an order-disorder transition. A lowering of the transition temperature and the transition enthalpy with increasing polymer content is observed, in agreement with the known dielectric data.

## 1. Introduction

Diacetylenes are unique in that monomer single crystals of appropriately disubstituted diacetylenes ( $R_1-C\equiv C-C\equiv C-R_2$ ,  $R_1 \neq R_2$ ) can be converted into polymer single crystals of high perfection via solid state polymerization [1, 2]. The symmetrically substituted diacetylene 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne (DNP) is the only ferroelectric diacetylene known up to now [3-5]. Each of its substituent groups carries a permanent electric dipole moment of about  $1 \times 10^{-29}$  C m. DNP monomer crystals undergo a phase transition from a centrosymmetric high-temperature phase of space group  $P2_1/n$  to a polar low-temperature phase of space group  $P2_1$  at about 46 K [4-7]. Poling experiments with a static electric field strength of up to  $3.3 \text{ MV m}^{-1}$  proved that the direction of the spontaneous polarization of DNP monomer crystals can be reversed at least for parts of the crystals [5], the low-temperature phase thus being ferroelectric and not just pyroelectric, as is observed more frequently for diacetylenes [8]. The maximum polarization measured at 10 K amounts to  $2.4 \times 10^{-3}$  C m $^{-2}$ , which is in good agreement with the structural reorientation revealed by x-ray studies [5, 7]. At the transition temperature,  $\epsilon_r$  reaches values of up to 150, which are relatively high for organic materials [5].

DNP monomer single crystals can be converted to polymer single crystals only by thermal solid state polymerization (SSP). At 130°C, the induction period of SSP (leading to about 10% polymer content), lasts for about  $t_p = 12$  h. The autocatalytic region of the SSP starts at about 12 h and leads to more than 95% polymer content after about  $t_p = 15$  h [9, 10]. Above 97% polymer content, an order-disorder transition was reported to occur, leaving a fibrillar structure for the solid polymer [2, 9]. With increasing polymer content, the transition temperature to the polar low-temperature phase is lowered, accompanied by a reduction of the maximum values for the electric permittivity at the transition temperature and the low-temperature limiting value for the spontaneous polarization [4]. A combination of x-ray and  $^1\text{H}$  nuclear magnetic resonance studies showed that both the phenyl rings of DNP are slanted against each other at an angle of  $5.1^\circ$  and the molecule is twisted

around its diacetylene backbone in the polar phase of the monomer crystal [6, 7]. Since the polymerization prevents torsion of the monomer units, the suppression of the phase transition with increasing polymer content could be understood [3, 4, 7]. The sensitivity of the transition temperature to the polymer content and presumably also to crystal defects explained that generally a distribution of transition temperatures was observed even for nominally monomeric crystals [5].

Important details for the phase transition of DNP are at present not finally settled. Only negligible thermal hysteresis was observed in the dielectric properties [4, 5]. The temperature dependence of the spontaneous polarization was compared with the empirical relation

$$P = P_0(1 - T/T_c)^\beta \quad (1)$$

with  $\beta = 0.21$  [11] or with the variation

$$P(T) = \pm P_0[1 - T/T_c + \alpha(1 - T/T_c)^3]^{1/4} \quad (2)$$

with  $\alpha = -0.55 \pm 0.10$  [5]. In a more restricted temperature range, equation (2) with  $\alpha = 0$  gave a reasonable fit to the data too [5]. This led to the conclusion that the polarization of DNP might support a tricritical phase transition in the framework of a Landau theory of phase transitions for ferroelectric materials, thus we have a borderline case between a first-order and a second-order phase transition. But unfortunately, the domain structure, sample defects and distribution of transition temperatures prevented the use of the temperature dependence of the dielectric permittivity for a proof of the nature of the phase transition [5]. Therefore we investigate here the heat capacity of DNP single crystals in order to obtain additional information on the phase transition. After a short summary of experimental details in section 2, we present results for the heat capacity in monomer and partially polymerized DNP crystals in sections 3.1 and 3.2, which are discussed in detail in sections 4.1 and 4.2, respectively.

## 2. Experimental details

The synthesis and crystal growth of DNP single crystals are described in the literature [4, 12]. For specific heat measurements, single crystals of up to 7 mm length and approximately quadratic cross section ( $1 \times 2 \text{ mm}^2$ ) and weights of up to 30 mg were used. The  $a$  axis (the polymer chain direction) is parallel to the long crystal axis. Partially or fully polymerized DNP crystals were obtained by thermal polymerization at  $T = 129^\circ\text{C}$  for selected periods of time under an inert atmosphere [13], with the constant temperature realized by means of an oil-bath thermostat.

The heat capacity was measured in a standard  $^4\text{He}$ -bath cryostat in the temperature range between 20 and 100 K. The crystals were carefully attached to a sapphire plate using a thermally conductive vacuum grease (Apiezon) in order to guarantee a good thermal contact between the sapphire plate and the crystal. The sample and sapphire plate were surrounded by two copper cups whose temperatures were regulated to follow the sample temperature with PI regulation. The samples were cooled slowly through the transition region ( $0.5 \text{ K min}^{-1}$ ). The specific heat was measured by the continuous heating method suggested by Junod [14] in the whole temperature range; the sample is heated with a constant heating power ( $RI^2$ ) by means of a manganin resistor that is evaporated on the sapphire plate. The experimental technique adopted allows measurements only for increasing temperatures.

For heat capacity measurements at varied polymer content the respective DNP crystal was cleaned after each specific-heat run with toluene and then kept under technical vacuum

for about 6 h prior to the thermal polymerization. As has been mentioned previously [4], crack formation is frequently observed after crossing the phase transition temperature for DNP monomer crystals. Thus the crystals have to be handled with due care in order that they are not broken into small pieces in the successive measurement–cleaning–polymerization ... steps.

### 3. Experimental results

#### 3.1. Heat capacity of monomer crystals

The temperature dependence of the molar heat capacity is shown in figure 1 for two individual DNP monomer single crystals. In both sets of data a pronounced anomaly is seen at the known phase-transition temperature of about 46 K. The behaviour marked A is typical for the results obtained for most DNP monomer crystals studied here whereas B was rather an exception. The crystals of type A with the secondary maximum at lower temperature have a lower 'visual' quality compared with crystals of type B. The type A crystals had some cracks which were observed under a microscope and their colour was slightly orange. The type B crystal, whose heat capacity shows only the main anomaly, was of 'good' visual quality, even when under a microscope no cracks in this crystal could be identified and its colour was homogeneously at most very slightly orange but nearly colourless. The weight of the first crystal was about 37 mg and that of the second 10 mg.

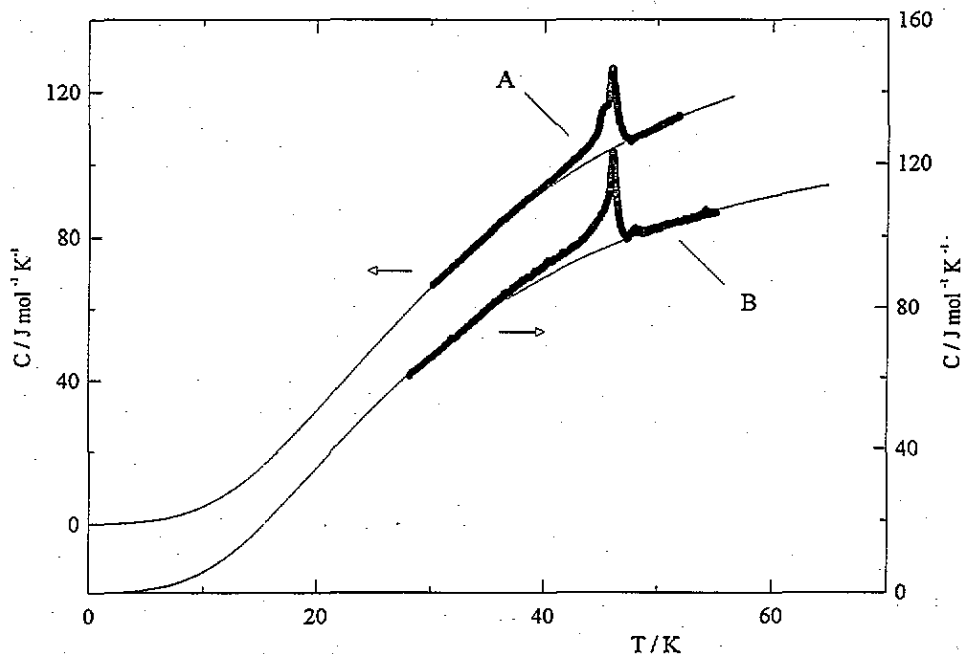


Figure 1. The temperature dependence of the molar heat capacity for two individual DNP monomer single crystals A and B. The full curve shows a Debye fit (equation (3)). For details see the text.

In order to analyse the character of the phase transition, the measured molar heat capacity was corrected for the contribution of those lattice vibrations which are unrelated to the phase

transition. This contribution was approximated by the Debye model. The respective molar heat capacity was thus calculated by the formula [15]

$$C_D = 9RZ(T/\Theta)^3 \int_0^{\Theta/T} x^4 e^x / (e^x - 1)^2 dx \quad (3)$$

with the molar gas constant  $R$  and the two free parameters  $\Theta$  and  $Z$ .

In figure 1 the full curve shows the fit of equation (3), with the parameters  $\Theta = 139$  K and 132 K and  $Z = 5.6$  and 5.4 for A and B, respectively. In spite of the neglect of the optical vibrations in the Debye model, a reasonable agreement is observed. Therefore, in figure 2, the difference

$$\Delta C = C - C_D \quad (4)$$

is plotted, representing that part of the molar heat capacity that is related to the phase transition for type A and type B DNP monomer crystals.

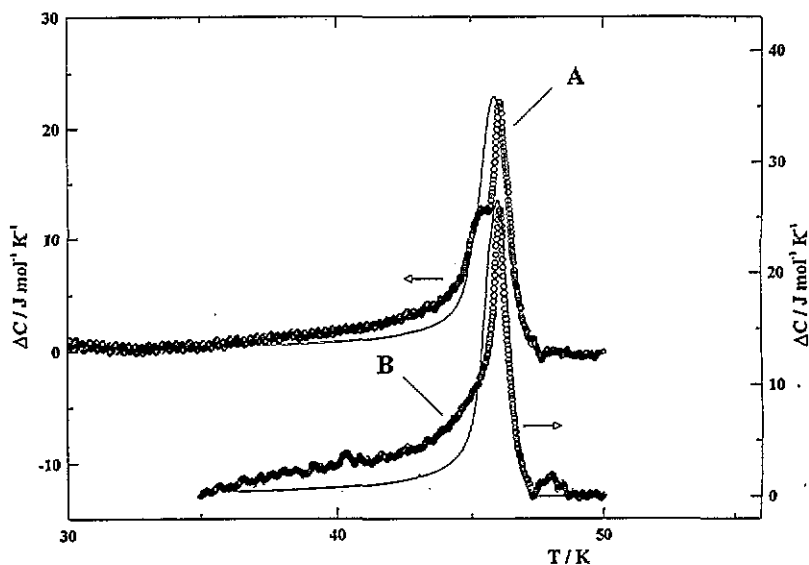


Figure 2. The temperature dependence of the 'ferroelectric' contribution to the molar heat capacity for the two individual DNP monomer single crystals A and B of figure 1. The full curve fit assumes a critical phase transition (with  $h = 0.23$  (0.21)  $\text{J mol}^{-1} \text{K}^{-3/2}$  and  $\sigma = 0.42$  (0.32) K, for A (B)). For details see the text.

### 3.2. Heat capacity of polymer crystals

The molar heat capacity of partially or fully polymerized DNP crystals was measured in the temperature range between 20 and 100 K. The data, converted using equations (3) and (4) are shown in figure 3. These results were obtained for the two crystals used already for figure 1. The secondary maximum disappears or is smeared out with increasing polymer content.

For one crystal the molar heat capacity was measured after time intervals of 2 h + 4 h + 3 h + 3.5 h spent at 129 °C for thermal polymerization. For control of reproducibility the second crystal, which spent 4 h in the thermal bath, was investigated. The shift of the

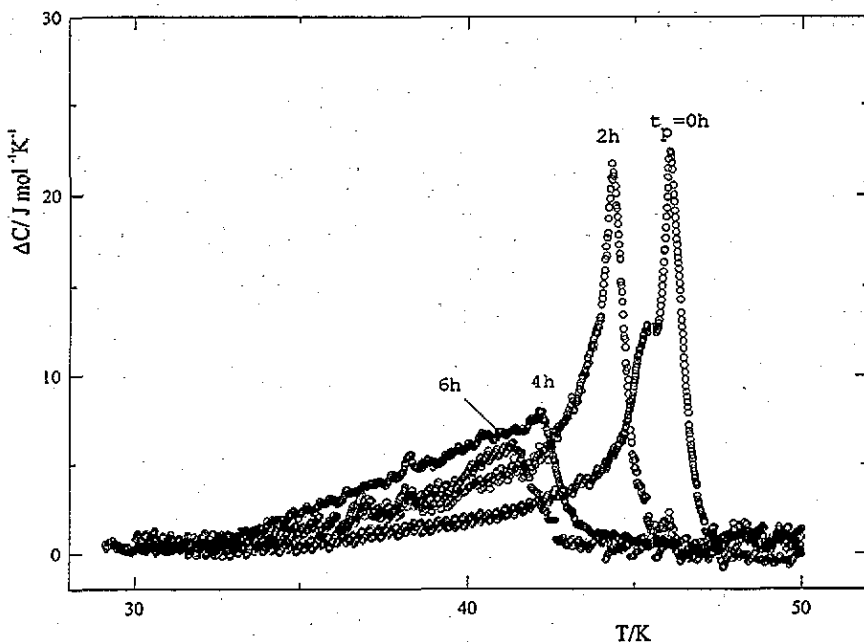


Figure 3. The variation of the 'ferroelectric' contribution to the molar heat capacity with annealing time  $t_p$  at 129°C for solid state polymerized DNP single crystals.

transition temperature with polymer content known from dielectric investigations is clearly visible in figure 3. Evidently the transition entropy also decreases with increasing polymer content (see figure 4).

#### 4. Discussion of the results

##### 4.1. Monomer crystals

Measurements of the spontaneous electric polarization [5] led to the supposition that the ferroelectric phase transition of DNP monomer single crystals is a tricritical phase transition. The simplest approach to a theoretical description of a ferroelectric phase transition is Landau's theory of ferroelectrics [16]. In the absence of an external electric field the free enthalpy  $G$  is developed in a power series of even powers of the order parameter, in this case the spontaneous polarization  $P$ :

$$G = G_0 + (\alpha/2)P^2 + (\beta/4)P^4 + (\gamma/6)P^6 \quad (5)$$

where  $G_0$  is the free enthalpy at zero polarization. The coefficients  $\beta$  and  $\gamma$  are assumed independent of the temperature.  $\alpha$  is taken as a linear function of  $T - T_c$ . The equilibrium value for  $P$  can be determined by demanding it to be stable, i.e.

$$\partial G / \partial P = 0 \quad \text{and} \quad \partial^2 G / \partial P^2 > 0. \quad (6)$$

The coefficient  $\beta$  is decisive for the classification of the order of the phase transitions. Generally, a phase transition of  $n$ th order is accompanied by a discontinuity of the  $n$ th derivative of  $G$ . For  $\beta > 0$  the phase transition is of second order and if  $\beta < 0$  the phase transition is of first order. A borderline case is when  $\beta$  is tending to zero. This is

called a tricritical phase transition. In a tricritical phase transition the molar heat capacity is described by the equations:

$$\Delta C = \begin{cases} hT/\sqrt{T_c - T} & \text{for } T \leq T_c \\ 0 & \text{for } T > T_c. \end{cases} \quad (7a)$$

$$(7b)$$

The observed variation of the heat capacity  $\Delta C$  in figure 2 compares favourably with the expectation for a tricritical phase transition, especially the curve labelled B. The appearance of the secondary maximum in curve A can be explained using an area of the crystal which has been already partially polymerized, with the transition temperature shifted to lower temperature in accordance with figure 4.

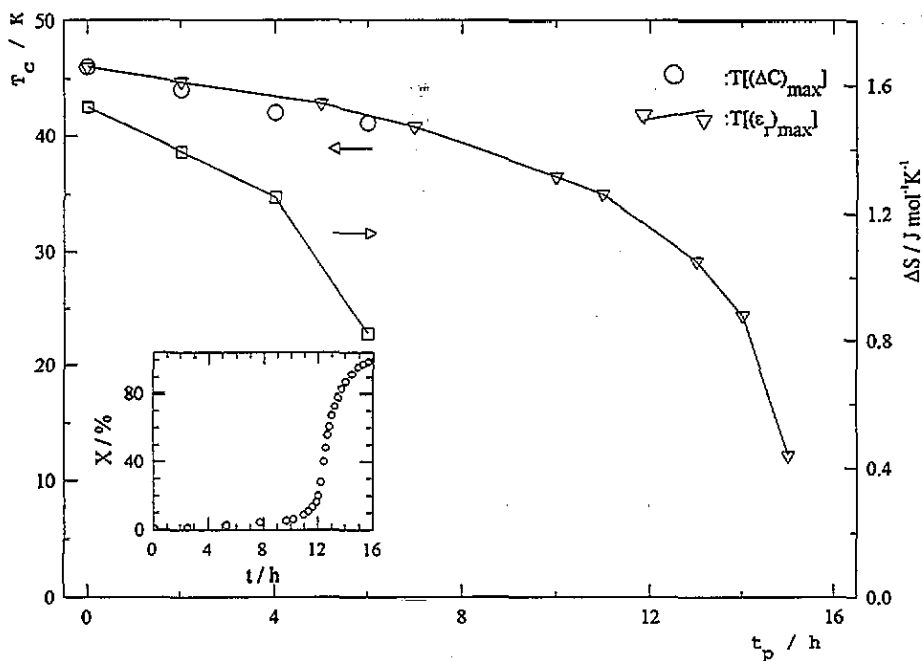


Figure 4. The transition temperature  $T_c$  and the conversion entropy (transition entropy change)  $\Delta S$  as functions of the annealing time  $t_p$  at 129°C for DNP single crystals. The  $T[(\epsilon_r)_{\max}]$  data are taken from [4]. The lines are guides to the eye. A typical variation of the polymer content  $X$  with annealing time  $t_p$  is shown in the inset for comparison [3, 4, 10, 13].

For a more detailed analysis of the phase transition the separated heat capacity (figure 2) was fitted to the behaviour characteristics for a tricritical phase transition. As real monomer crystals already have a small and non-uniform polymer content, and the transition temperature  $T_c$  depends on polymer content, a distribution of transition temperatures must be considered. For a Gaussian distribution of transition temperatures

$$\Delta C_P(T) = \int f(T_P) \Delta C_P^{(T_P)}(T) dT_P \quad (8)$$

with

$$f(T_P) = (1/\sqrt{2\pi})(1/\sigma) \exp[-(T_P - T_c)^2/2\sigma^2] \quad (9)$$

and

$$\Delta C_P^{(T_P)}(T) = \begin{cases} hT/\sqrt{T_P - T} & \text{for } T \leq T_P \\ 0 & \text{for } T > T_P \end{cases} \quad (7c)$$

$$(7d)$$

The fits and the measured curves in figure 2 show reasonable agreement, in spite of disregarding the systematic errors which occur by subtracting the measured curves from the Debye fit (figure 1). Also, the influence of the cracks which appear due to crossing the transition temperature is not taken into account. For a first-order phase transition the molar heat capacity should increase discontinuously towards infinity at the transition temperature. In spite of the distribution of transition temperatures such a behaviour can be excluded. In the case of a second-order phase transition the heat capacity should increase linearly with the temperature up to the transition temperature  $T_c$ . Such behaviour is also in disagreement with the experiment. The results of these fits thus support the conclusion from polarization measurements [5] that the phase transition of DNP monomer crystals from the centrosymmetric high-temperature phase to the non-centrosymmetric low-temperature phase is a tricritical phase transition which is the borderline case between a first-order and a second-order phase transition.

The conversion entropy  $\Delta S$  (transition entropy change) derived from figure 2 amounts to  $(1.53 \pm 0.25) \text{ J mol}^{-1} \text{ K}^{-1}$ . This is clearly lower than the value expected for an order-disorder transition estimated as

$$\Delta S = R \ln 2 = 5.76 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (10)$$

#### 4.2. Polymer crystals

The values for the Debye-temperature  $\Theta$  obtained by the fit to the total molar heat capacity (equation 3) hardly change with increasing annealing time. By the polymerization the torsion of the central diacetylene unit of the monomer molecules is prevented and thus the phase transition is suppressed with increasing polymer content [4, 7]. In agreement with this, the 'ferroelectric' part of the molar heat capacity measured after different annealing times  $t_p$  at 129 °C, and shown in figure 3, decreases with  $t_p$ . The temperature dependence of the molar heat capacity after an annealing time of 4 h or above corresponds rather to the expectation of a second-order phase transition. The values for the transition temperature derived from the permittivity maximum [4] and from the anomaly of the molar heat capacity show reasonable agreement (figure 4). The values for the conversion entropy  $\Delta S$  (figure 4) are also plotted as a function of the annealing time. The decrease of  $\Delta S$  with increasing polymer content is correlated with the reduced portion of DNP molecules amenable to the non-centrosymmetric molecular distortion.

#### 5. Summary

The ferroelectric phase transition of DNP monomer single crystals has been characterized by measurements of the molar heat capacity. The heat capacity of all monomer crystals shows a pronounced anomaly at about 46 K. The temperature dependence of the molar heat capacity related to the phase transition could be best described by a tricritical phase transition within Landau's theory of ferroelectrics, that means a borderline case between a first-order and second-order phase transition. This could be confirmed with a fit of the theoretical prediction to the data considering a distribution of transition temperatures. In addition to the pronounced anomaly at 46 K a secondary maximum of the heat capacity was



usually detected at a 0.4–0.8 K lower temperature. This anomaly might be interpreted as the phase transition (possibly of weakly first order) caused by small areas of the monomer crystals with non-negligible polymer content or sample defects. This secondary anomaly was not observed in a crystal with good 'visual' quality (no cracks or colouring). This result agrees with the earlier observation that monomer crystals could only be partially poled with a small external field strength [5]. The value  $\Delta S = (1.53 \pm 0.25) \text{ J mol}^{-1} \text{ K}^{-1}$  was derived from the conversion entropy of the phase transition for DNP monomer crystals. This is only about one third of the theoretical value for an order–disorder transition, i.e.  $\Delta S = R \ln 2 = 5.76 \text{ J mol}^{-1} \text{ K}^{-1}$ . This is in keeping with results obtained by Bertault in a Raman spectroscopical analysis of DNP monomer crystals that proved the importance of displacive contributions to the phase transition [17].

Also, partially or fully polymerized DNP crystals were investigated. For partially polymerized crystals the transition temperature and the maximum of the heat capacity anomaly decreases with the increasing amount of polymerization. The variation of the transition temperatures derived from the heat capacity measurements was in agreement with permittivity measurements reported previously [4]. Also the conversion entropy is reduced with the increasing polymer content of the DNP crystals. All these results are consistent with the twisting of the DNP monomer molecules in the ferroelectric low-temperature phase of the DNP monomer crystals which is prohibited for diacetylene molecules that are part of the polymer backbone of partially or fully polymerized crystals.

### Acknowledgments

We would like to thank Irene Bauer for growing the DNP crystals. We are indebted to Petra Gruner-Bauer and M Bertault for valuable discussions.

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A soft mode behaviour was observed in the temperature range 6–47.5 K with an order parameter varying as  $(1 - T/T_c)^{0.2}$ .