Thermal and X-ray measurements on *n*-hexatriacontane (C₃₆H₇₄)

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Abstract. The polymorphism of *n*-hexatriacontane (C₃₆H₇₄) was investigated by X-ray diffraction and DSC thermal analysis. C₃₆H₇₄ displays at least two stable monoclinic phases and a rotator phase. Starting from a solution-grown sample of very high purity the following phases are observed with increasing temperature: M011 < 345K < M101 < 346K < RIII < 348K < liquid. Depending on the thermal treatment also other forms may be observed. During these transitions, both the crystalline volume and the lamellar thickness increase. The higher order reflections of the layer structure was precisely measured by X-ray diffraction. Using a Fourier synthesis, electron density profiles of the three phases were analysed. The results show that the interlamellar structure is disturbed by increasing molecular motions with elevating temperatures. For some homologous alkanes also p(T) phase diagrams and binary systems have been studied.

1. INTRODUCTION

Paraffins (n-alkanes, C_nH_{2n+2}, abbreviated C_n) are of great technological and scientific interest, as they

Figure 1: Sequences of phases observed in C₃₆H₇₄ on heating [9].
 a) from a solution-grown sample b) through rapid crystallization from the melt c) slow crystallization from the melt

serve as model substances for polymers, lipids and liquid crystals. Their rich polymorphism has been studied by thermodynamic and spectroscopic methods. The rotational transition and melting is accompanied by an appreciable latent heat that makes them suitable for thermal protection and energy storage materials [1]. For these applications the study of binary or multi-components systems of n-alkanes is particularly interesting [2-4].

The polymorphism observed in n-alkanes has been reviewed in detail [5-8]. Various low-temperature modifications and disordered rotator phases have been found. Longer n-alkanes are interesting, as they are closer to polymers. In this work we present results of *n*-hexatriacontane (C₃₆H₇₄), for which thermodynamic and crystallographic data have been reported [8-16]. Binary systems of n-alkanes with longer carbon chains have been studied by Poirier [9] and Josefiak [14]. In the latter work high-pressure DTA was employed in order to establish p(T) phase diagrams. In all cases the rotator phase region is pressure-limited [17,18]. Small impurities, however, may shift the phase boundaries significantly [14].

2. RESULTS

Depending on the thermal treatment and the purity $C_{36}H_{74}$ displays monoclinic and orthorhombic phases at low temperatures [9,10]. Starting from a solution-grown sample of high purity the following phases are observed with increasing temperature: $M011 < 345K < M101 < 346K < R_{III} < 348K < \text{liquid}$, Fig. 1a. The feature of the transition was clearly observed by the X-ray diffraction results shown in Fig.2 [9].

However, when the sample is obtained through rapid or slow crystallization from the melt and reheated, the sequences (b) and (c) respectively in Fig.1 may be observed [9]. Various metastable phases appear (the sequences are classified according to the proportion) and coexist together at 293 K (two orthorhombic OI, OII and a monoclinic M201). On heating these phases transform to M101, except OI which passes first through M012. After very slow cooling from the melt a new phase X is observed, Fig.1(c), its X-rays pattern is very similar to the M011 one, but the transition temperature to M101 is lower [9].

Asano et al. [10] used samples of different purities for the X-ray measurements and found an orthorhombic modification for a less pure sample of $C_{36}H_{74}$. Using a single-crystal mat of $C_{36}H_{74}$, higher order intensities of the layer scattering (001, 002, 003, ...) of M011 were measured at room temperature. The layer scatterings of M101 and R were observed at 345 K and 347 K, respectively. The intensity of the layer scattering was carefully observed adjusting on the Bragg's condition. The M011 phase showed more than 18 orders, while the M101 and R_{III} phases disappeared at lower orders. During these transitions, both the crystalline volume and the lamellar thickness increase. Using a Fourier synthesis, electron density profiles of the three phases were analysed. The electron density profiles are compared in Fig.3. The M011

Figure 2: X-ray diffraction pattern of $C_{36}H_{74}$ [9]

Figure 3: Comparison of electron density profiles for $C_{36}H_{74}$

phase has a profile of fine oscillation in the layer, but disappears in the M101 and R phases. Due to inclination of the c-axis in the layer, the regular arrangement of the planar zigzag CH₂-CH₂ conformation makes periodic oscillation in the electron density. In the case of M011 having the inclination angle 29.1°, the period of the oscillation has a distance of 2.22 Å with 18 fine peaks. In the phases of M101 and R the regular packing is disturbed by molecular motions along the c-axis. During the phase transition, the valley of the electron density at the interlayer structure becomes shallow with increasing temperature. This fact strongly indicates that the molecules jump out from the layer surface by the thermal motion.

High pressure phase diagrams have been established for n-alkanes [14,15,17-22] and polymers [23-25]. Josefiak et al. performed DTA measurements under pressure for some n-alkanes in the range C₂₇ to C₃₈ [14]. The phase diagram of C₃₈H₇₈ is presented in Figure 4. The rotator phase region is rather narrow and ends at a triple point of 382 K and 125 MPa. The lower solid-solid transition could only be observed up to 20 MPa. Only few other high-pressure studies of this kind are reported in literature [19,20]. In this context we note the usefulness of pVT measurements [4,26-28].

Crystalline cell parameters of the three phases of C₃₆H₇₄ are presented in Table 1, showing a monoclinic group for the rotator phase R [11,12], whereas RIII is assigned a triclinic group [5,6].

Table 1: Crystallographic structures of the phases of C₃₆H₇₄ [11,12]

Structure	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	L(Å)
M ₀₁₁	7.42	5.57	48.35	119.1	90	90	41.79
M ₁₀₁	7.76	4.90	48.27	90	106	90	45.49
R	4.98	8.62	48.10	90	107	90	45.33

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