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SHORT COMMUNICATION

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Structural and calorimetric investigations on nonaqueous liquid crystals and gel phases in the binary system K-stearate/glycerol

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Abstract The K-stearate/glycerol (KC_{18}/Gl) binary system was studied at mole fractions of stearate of $x_{KC_{18}} = 0.10$, 0.25, 0.30 and 0.50. Small- and wide-angle X-ray diffraction (XRD) measurements were combined with differential scanning calorimetry (DSC) measurements at different temperatures. The investigations were intended to verify the previously published phase diagram and were targeted at the confirmation of the gel-like (G_1) phase and the isotropic (I) phase. The XRD and DSC measurements lead to the conclusion that the G_1 phase as well as the I phase, the existence of which had been proposed from texture observations, do in fact not exist. Consequently, a correction of the preliminary phase diagram is given. This corrected phase diagram reveals the crystalline phase (C) ↔ gel phase (G) ↔ hexagonal phase (H_α) ↔ isotropic, micellar phase phase transitions for low KC_{18} concentrations of $x_{KC_{18}} = 0.15$–0.3 and the C ↔ G ↔ lamellar phase (L_α) phase transitions for concentrations about or higher than $x_{KC_{18}} = 0.35$. The C, G, L_α and H_α phases have been further characterized by structural parameters (characteristic *d* values) as a function of temperature. The phase transitions C ↔ G, G ↔ L_α and G ↔ H_α correlate with sharp shifts in the *d* value of the first small-angle reflections.

Key words Nonaqueous liquid crystals · Gel phase · X-ray diffraction · Calorimetry · K-stearate

Introduction

As a continuation of previously reported investigations on gel structures and lyotropic mesophases in connection with the verification of the phase diagrams of K-soap/glycerol (Gl) systems [1–4] we describe measurements on K-stearate (KC_{18})/(Gl). Samples with concentrations (mole fractions of stearate) of $x_{KC_{18}} = 0.10$, 0.25, 0.30 and 0.50 were examined.

The preliminary phase diagram (Fig. 1a), based on polarized microscopy texture observations, showed a gel-like (G_1) phase followed by an isotropic (I) phase, presumably a cubic phase [5]. However, these G_1 and I phases could not clearly be confirmed as unitary phase regions by polarized microscopy texture observations alone. Consequently, further structural investigation using X-ray diffraction (XRD) and differential scanning calorimetry (DSC) measurements were necessary to reveal the true nature of these structures. Details of the methods were previously described [1, 2]. For all XRD measurements Cu K_α radiation ($\lambda = 1.5$ Å) was used.

Results

Investigations at the composition $x_{KC_{18}} = 0.10$

At this concentration the crystalline (C) phase passes directly into the isotropic phase S. In Fig. 2 the small- and wide-angle diffractograms are displayed and compared with the DSC curve at rising temperature. A weak shoulder of the 0 0 1 reflection at approximately

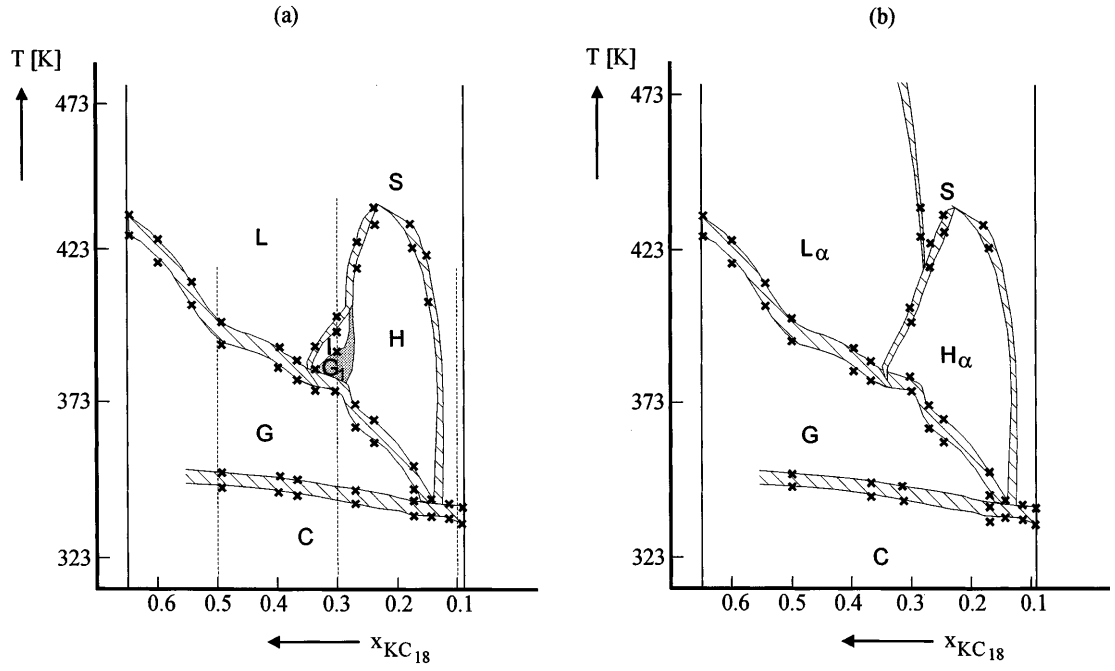


Fig. 1a, b Phase diagram of the K-stearate/glycerol (KC_{18}/Gl) binary system. **a** Preliminary phase diagram based on polarized microscopy texture observations [5]. **b** Revised phase diagram based on X-ray diffraction (*XRD*) and differential scanning calorimetry (*DSC*) measurements. The different phases are as follows: Crystalline phase (*C*), gel phase (*G*), hexagonal phase, chains fluid (H_α), lamellar phase, chains fluid (L_α), isotropic, micellar solution (*S*), second gel phase (G_l), isotropic phase (*I*)

$2\Theta = 1.7°$ is found within the C phase which only transforms into the small-angle reflection after the C ↔ S transition. Within the S phase this single reflection slightly broadens with rising temperature indicating a reduced molecular order. In Fig. 3 the *d* values (for definition see Ref. [2]) of the first small-angle reflections and the DSC curves for heating and cooling are shown. The perpendicular distance $(c^*)^{-1}$ between the (0 0 1) planes of $d = 4.25$ nm in the C phase is approximately $\Delta d = 0.8$ nm smaller than the average molecular distance within the S phase.

Investigations at the composition $x_{KC_{18}} = 0.25$

The phase diagram in Fig. 1a shows the polymorphous transitions C ↔ G ↔ hexagonal phase (H_α) ↔ S. The

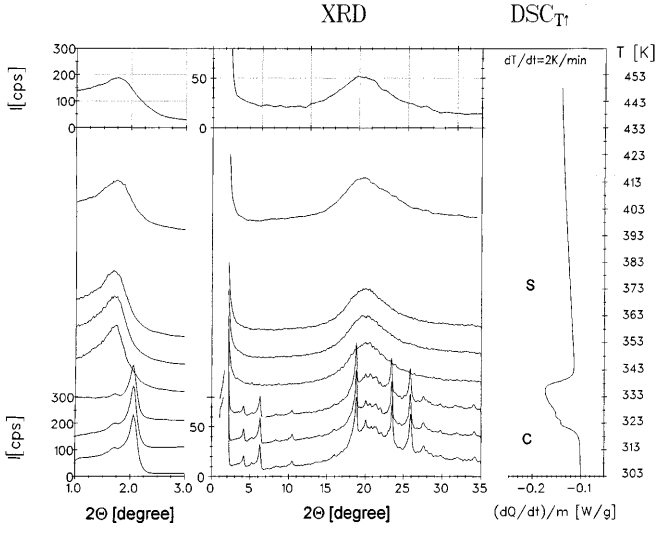


Fig. 2 Small- and wide-angle X-ray diffractograms and DSC curve at rising temperature for KC_{18}/Gl at $x_{KC_{18}} = 0.10$

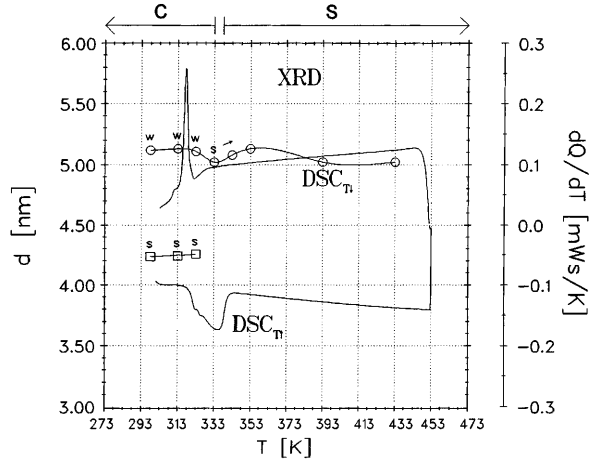


Fig. 3 *d* values of the first small-angle reflections and DSC curve at rising and falling temperatures for KC_{18}/Gl at $x_{KC_{18}} = 0.10$. Reflections of the C phase (□), reflections of the S phase (○). Reflection intensity: weak (*w*), strong (*s*)

phase-transition temperatures obtained from the XRD and DSC measurements are in good agreement with the values from texture observations [5].

The wide-angle angle diffractograms and the DSC curve for rising temperature are displayed in Fig. 4. In the C phase a pre-transition-like structural change occurs at about T = 323 K. This is mainly indicated by the reduced intensity and modified shape of the wide-angle XRD reflections. Furthermore, the small-angle background increases at angles smaller than that of the 0 0 1 reflection (Fig. 5). This pretransition phenomenon has already been observed [4] in the K-palmitate/Gl system at $x_{KC_{16}} = 0.30$.

The C $\leftrightarrow$ G phase transition is characterized by the distinct regrouping and intensity loss of the wide-angle reflections as well as a splitting of the small-angle reflections. As expected, the thermal effects of the G $\leftrightarrow$ H_α and H_α $\leftrightarrow$ S phase transitions are about 1 order of magnitude smaller than the C $\leftrightarrow$ G phase transition. The X-ray diffractograms recorded from samples in the H_α phase exhibit a remarkably high intensity of the 1 0 0 reflection, approximately 3 times stronger than the 0 0 1 reflections of the C phase. Also, the 1 1 0 and 2 0 0 reflections are detected, clearly confirming the H_α structure. With the transition to the S phase all wide-angle reflections disappear and only one small-angle reflection remains. The equivalent *d* values of the first small-angle reflections and the DSC curves for heating and cooling are compared in Fig. 6. The C $\leftrightarrow$ G transition correlates with a sharp shift in the *d* value of the small-angle 0 0 1 reflection by about $\Delta d \approx +0.35$ nm immediately followed by the known split of the small-angle reflections. The DSC curve at falling temperatures (upper portion of Fig. 6) shows that the phase transitions can be undercooled by about $\Delta T \approx 10$–15 K.

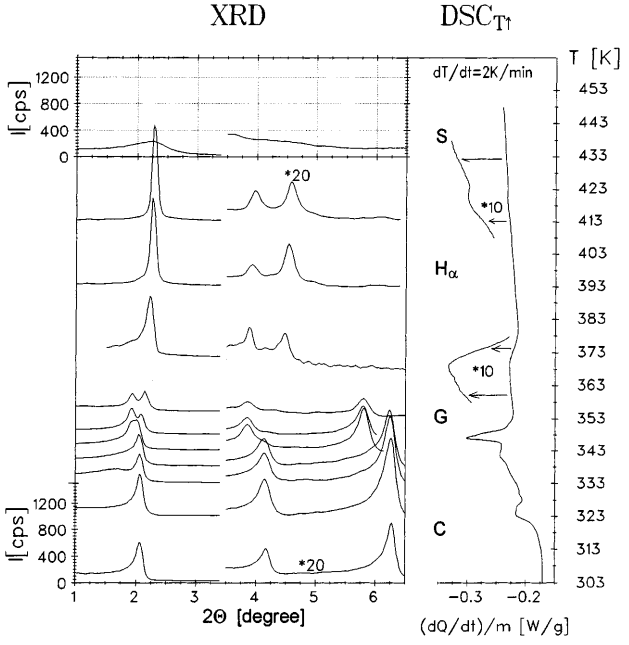


Fig. 5 Small-angle X-ray diffractograms and DSC curve at rising temperature for KC_{18}/Gl at $x_{KC_{18}} = 0.25$

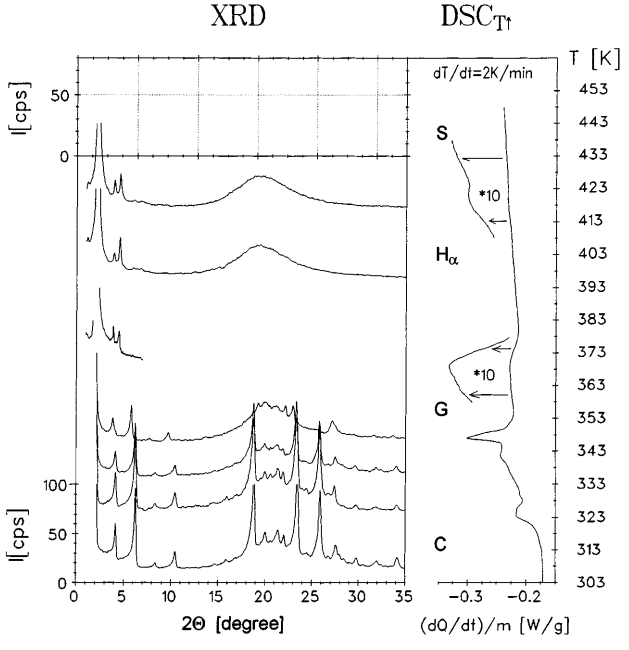


Fig. 4 Wide-angle X-ray diffractograms and DSC curve at rising temperature for KC_{18}/Gl at $x_{KC_{18}} = 0.25$

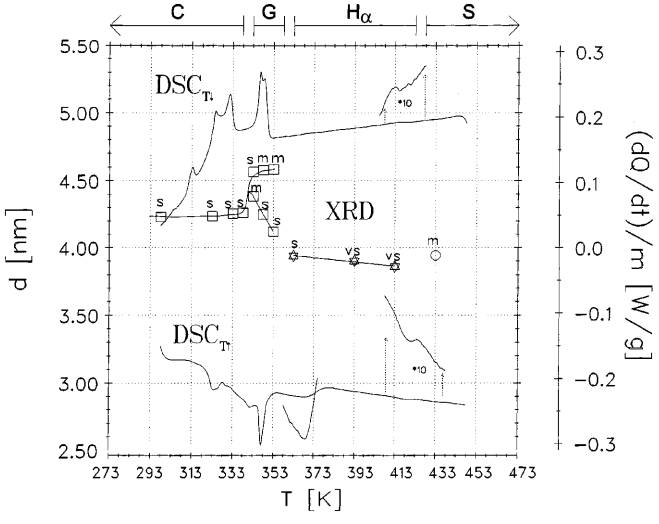


Fig. 6 *d* values of the first small-angle reflections and DSC curve at rising and falling temperatures for KC_{18}/Gl at $x_{KC_{18}} = 0.25$. Reflections of the C and G phases (□), reflections of the H_α phase (✡), reflections of the S phase (○). Reflection intensity: weak (*w*), medium (*m*), strong (*s*), very strong (*vs*)

Investigations at the composition $x_{KC_{18}} = 0.30$

The wide-angle X-ray diffractograms and the DSC data for rising temperature are summarized in Fig. 7. The polymorphism C $\leftrightarrow$ G $\leftrightarrow$ H_α $\leftrightarrow$ L_α occurs at this concentration. Again, the X-ray diffractograms and DSC data indicate a pretransition within the crystalline region. The diffractograms exhibit corresponding changes in the small-angle background on the left shoulder of the 0 0 1 reflection; however, neither small- nor wide-angle peaks regroup or change position. Within the temperature range between T = 348 and T = 353 K [5] the transition to the G phase is accompanied by the characteristic regrouping and intensity loss of the wide-angle reflections as well as the small-angle split (Figs. 7, 8).

The phase transition from the G phase to the H_α phase appears between T = 383 and T = 388 K. The reflections recorded within the H_α phase have comparably low intensity and broadened half-widths. With increased temperature the intensities of the reflections decrease further. Both the 1 1 0 reflection (1:$\sqrt{3}$) and the 2 0 0 reflection (1:$\sqrt{4}$) are detected at T = 393 K. At T = 403 K both reflections, while further reduced in intensity, are still clearly identified in the diffractogram (Fig. 9).

At $x_{KC_{18}} = 0.30$ the L_α region of the binary phase diagram, characterized by still smaller *d* values, again shows reduced crystallographic order as indicated by the relatively weak reflection intensity and the lack of measurable higher-order reflections. This reduced crystallinity causes the inadequate image formation encoun-

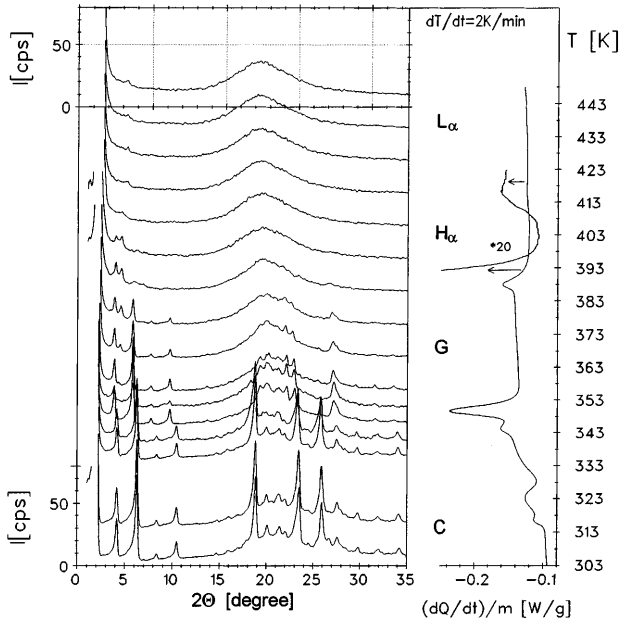


Fig. 7 Wide-angle X-ray diffractograms and DSC curve at rising temperature for KC_{18}/Gl at $x_{KC_{18}} = 0.30$

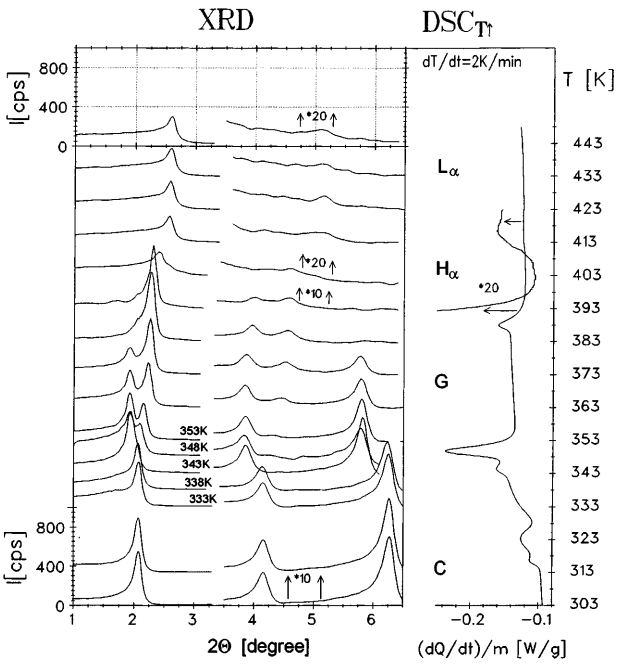


Fig. 8 Small-angle X-ray diffractograms and DSC curve at rising temperature for KC_{18}/Gl at $x_{KC_{18}} = 0.30$

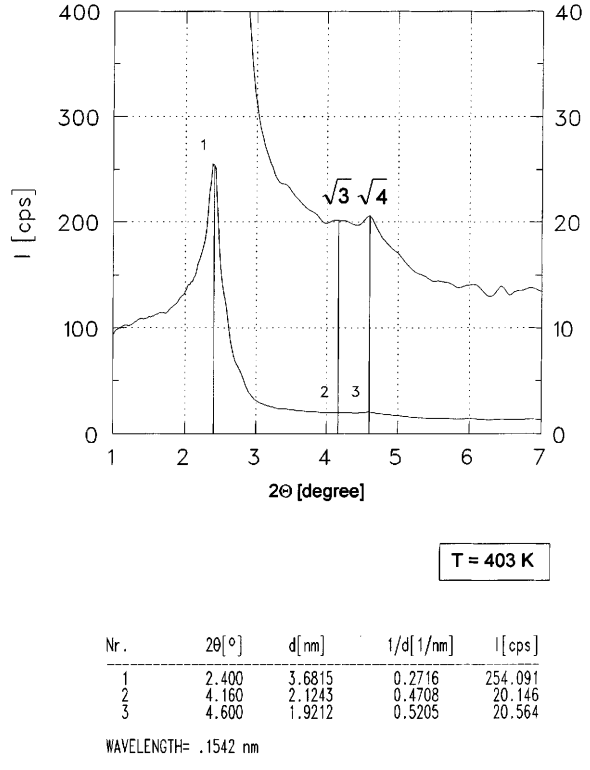


Fig. 9 Small-angle X-ray diffractograms for KC_{18}/Gl at $x_{KC_{18}} = 0.30$, $T = 403$ K

tered by polarized microscopy texture observations in this specific temperature–concentration area of the phase diagram. It led to the interpretation that these regions belong to the G_I phase and the I phase; however, they undoubtedly belong to the H_α phase as confirmed by the XRD measurements.

The *d* values of the first small-angle reflections and the DSC curves for heating and cooling are compared in Fig. 10. The data reveal that the C ↔ G transition correlates with a sharp shift in the *d* value ($\Delta d \approx +0.35$ nm) of the small-angle 0 0 1 reflection. The *d* values of the split small-angle reflections approach the corresponding values of the H_α structure; thus, between T = 383 and T = 403 K the *d* values decreased by $\Delta d \approx -0.15$ nm. A further shift by $\Delta d \approx -0.30$ nm appears at the transition into the L_α phase, and the *d* values form a shallow minimum at T ≈ 433 K.

Investigations at the composition $x_{KC_{18}} = 0.50$

The wide-angle angle diffractograms and the DSC curve at rising temperature are displayed in Fig. 11. Again, a pretransition is noticed within the C phase. Between the second and third diffractogram curve at T = 313 and 333 K in Fig. 11 the first and second wide-angle reflections are superimposed (see markings). It was shown [2, 6], that maximal four heads of the bands beginning with the peaks of the reflection (1 0 0), (0 1 0), (1 $\bar{1}$ 0), (1 1 0) can be extracted from diffractograms in the measurable 2Θ range for the long-spacing triclinic unit cells; however, if the unit-cell parameters *a* and *b* approach the same value, the two bands beginning with the 1 0 0 and 0 1 0 reflections become identical. Thus, the usually observed characteristic group of bands

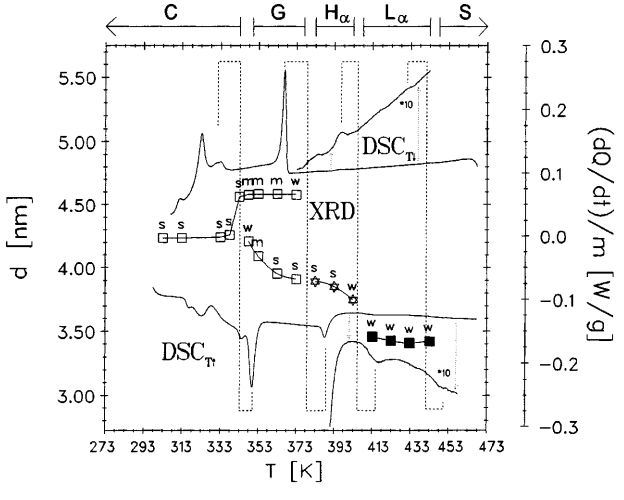


Fig. 10 *d* values of the first small-angle reflections and DSC curve at rising and falling temperatures for KC_{18}/Gl at $x_{KC_{18}} = 0.30$. Reflections of the L_α phase (■); other symbols as in Fig. 6

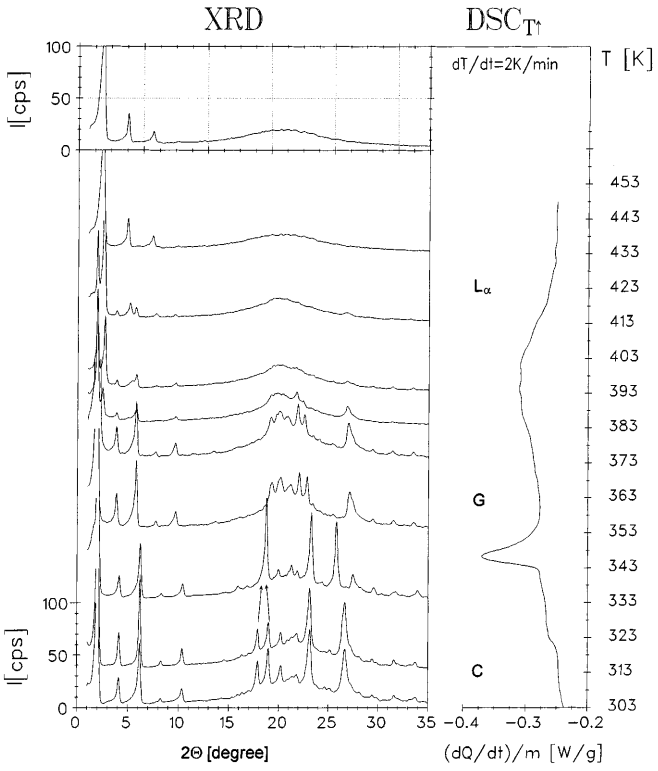


Fig. 11 Wide-angle X-ray diffractograms and DSC curve at rising temperature for KC_{18}/Gl at $x_{KC_{18}} = 0.50$

starting with three intense reflections is generated. The system discussed here exhibits this phenomenon only at temperatures above 333 K.

The transition into the G phase at T = 348 K causes the well-known split of the small-angle reflections. Furthermore, the characteristic wide-angle reflections with reduced intensity and a higher amorphous background are found. However, after the phase transition the formation of the G phase occurs slowly as can be seen from the successive buildup of the characteristic groups of reflection groups known from our previous observations. The wide G ↔ L_α phase transition which starts at T = 393 K and ends at approximately T = 413 K according to the DSC and XRD measurements (Fig. 12) is also remarkable. The restructuring of the reflections occurs very gradually. With rising temperature the molecular layers of the L_α phase gain structural order as indicated by the increased reflection intensity. Up to four orders of the small-angle 0 0 *l* reflection are identified at T = 463 K (Fig. 13).

The *d* values of the first small-angle reflections are compared with DSC curves at rising and falling temperatures in Fig. 14. The C ↔ G phase transition correlates with the characteristic split of the first small-angle reflection and a sharp shift of the *d* value of $\Delta d \approx +0.35$ nm. In the temperature range T = 413–463 K the *d* values of the reflections of the L_α phase increase by $\Delta d = 0.15$ nm.

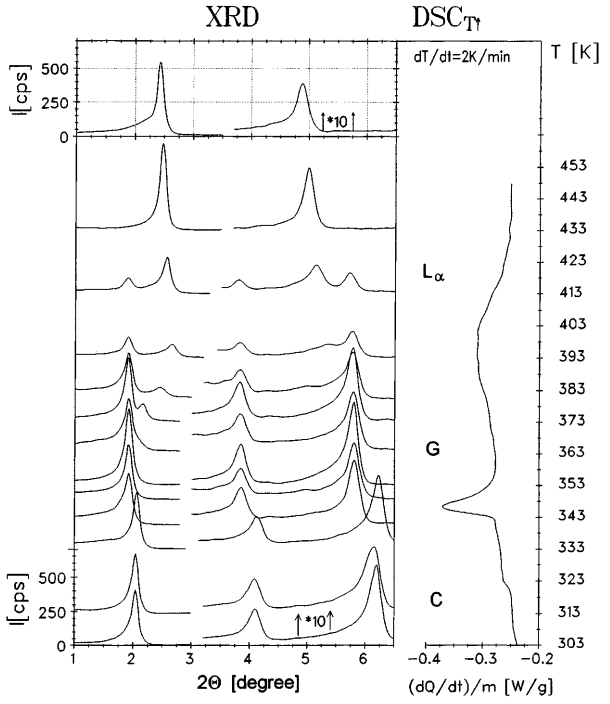
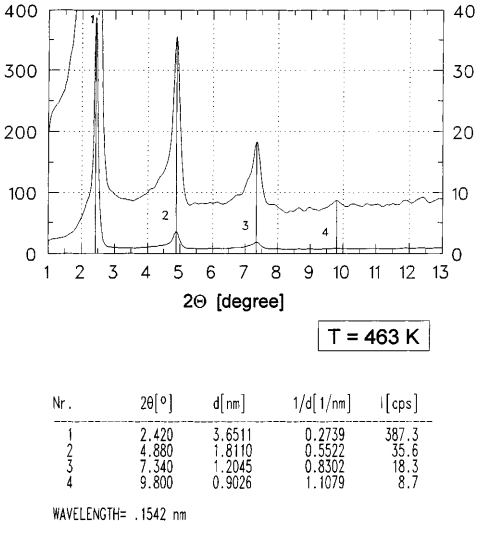


Fig. 12 Small-angle X-ray diffractograms and DSC curve at rising temperature for KC_{18}/Gl at $x_{KC_{18}} = 0.50$



Nr.	2θ[°]	d[nm]	1/d[1/nm]	I[cps]
1	2.420	3.6511	0.2739	387.3
2	4.880	1.8110	0.5522	35.6
3	7.340	1.2045	0.8302	18.3
4	9.800	0.9026	1.1079	8.7

WAVELENGTH= .1542 nm

Fig. 13 Small-angle X-ray diffractograms for KC_{18}/Gl at $x_{KC_{18}} = 0.50$, $T = 463$ K

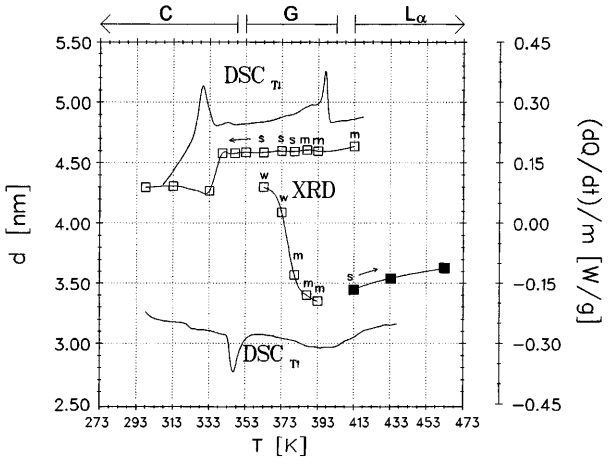


Fig. 14 *d* values of the first small-angle reflections and DSC curve at rising and falling temperatures for KC_{18}/Gl at $x_{KC_{18}} = 0.50$; symbols as in Fig. 10

Conclusions

Based on the XRD and DSC measurements on the KC_{18}/Gl system the conclusion has been reached that the G_I phase and the I phase indicated in the preliminary phase diagram [5] do in fact not exist and have to be understood as misinterpretations of the polarized microscopy texture observations. Consequently, a correction of the preliminary phase diagram becomes necessary (Fig. 1b). In the region of low KC_{18} concentrations, $x_{KC_{18}} = 0.15$–0.3, the phase transitions $C \leftrightarrow G \leftrightarrow H_\alpha \leftrightarrow S$ occur. At concentrations about or higher than $x_{KC_{18}} = 0.35$ the $C \leftrightarrow G \leftrightarrow L_\alpha$ polymorphisms were observed.

XRD and DSC measurements provided concordant results with respect to the determination of the phase-transition points. Differences in phase-transition points from DSC data obtained at raising and falling temperatures have been noticed. The phase transitions $C \leftrightarrow G$, $G \leftrightarrow L_\alpha$ and $G \leftrightarrow H_\alpha$ correlate with jumps in the *d* values of the first small-angle reflections.

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