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Phase behaviour of amphiphilic side-chain polymers

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Phase behaviour of amphiphilic side-chain polymers

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The present study describes the phase behaviour of a low-molar-mass 1,3-diol with a linear alkyl chain in aqueous solution. From the combined results of differential scanning calorimetry and optical polarizing microscopy a phase diagram was constructed. The low-molar-mass diol forms a lamellar mesophase only in the presence of water. The influence of the linkage of the amphiphilic molecule to different polymer backbones on the stability of the mesophase was investigated. It is evident that amphiphilic side-chain polymers show a distinct stabilization of the mesophase. Moreover, comparison between the polyacrylate, polymethacrylate and polysiloxane indicates a strong influence of the main-chain flexibility on the stability of the liquid-crystalline phase. The type of the liquid-crystalline phase of the side-chain polyacrylate in the water-saturated state was identified by X-ray investigations as lamellar. The hydration behaviour of the polymers was investigated by ^{2}H-N.M.R. and isopiestic measurements.

1. Introduction

Detailed investigations in the past few years have proved that the linkage of amphiphilic low-molar-mass liquid crystals to suitable polymer backbones yields side-chain polymers. The observed mesophases of these side-chain polymers in aqueous solutions are similar to the well-known mesophases observed with conventional amphiphiles [1–5]. As a polymer-specific property, a stabilization of the mesomorphic state with respect to temperature and concentration range is observed [1–5].

Derivatives of diols may be considered as amphiphiles having a very simple molecular structure. The surfactant behaviour of *n*-alkane-1,2-diols [6, 7] and monoglycerides [8] is well documented. We have found that simple *n*-alkane-1,2-diols exhibit monotropic S_A^+ and S_B^+ phases even in the water-free state [9], while diols containing a cyclohexyl ring in the alkyl chain form stable thermotropic mesophases [10, 11]. All of these investigations have shown that the addition of water results in a depression of the melting points and an increase of the clearing points, i.e. water stabilizes the mesophases to a remarkable extent. In some cases liquid-crystalline phases could be observed only in the presence of water, for example, for *n*-alkane-1,3-diols [12].

As a continuation of our work on the phase and structural behaviour of the diol–water systems and their dependence on the chemical structure of the hydrophobic chain of the diols, the phase behaviour of a 1,3-diol with a linear alkyl chain in aqueous solution was investigated and the influence of the linkage of the amphiphilic molecule to different polymer backbones on the stability of the mesophase was shown.

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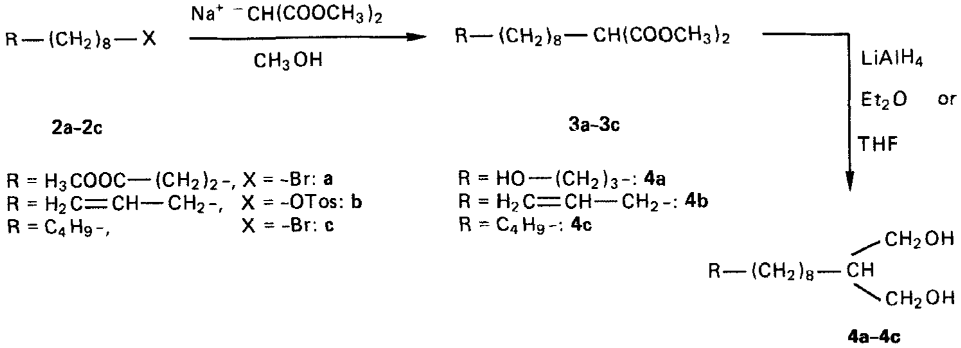
2. Experimental

2.1. *Synthesis*

Synthesis of the 2-substituted propane-1,3-diols

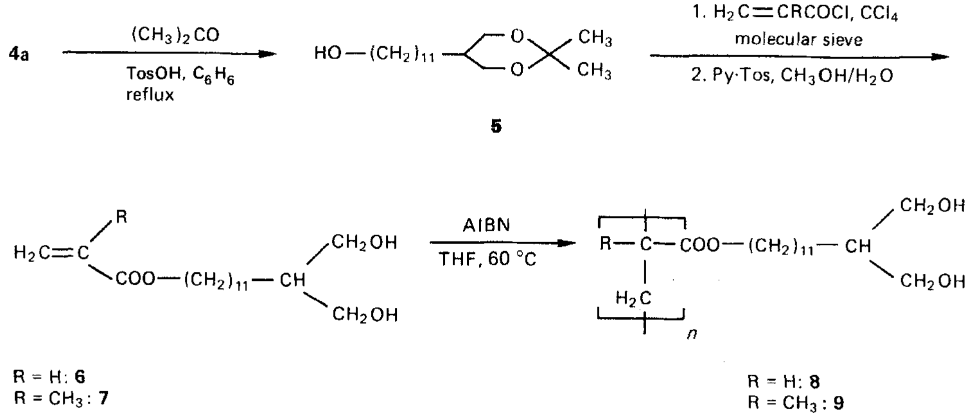
Commercially available 11-bromoundecanoic acid **1** and 1-bromododecane **2c** were used as starting materials in the synthesis. 11-Bromoundecanoic acid was esterified with methanol to yield the compound **2a**. 10-Undecenoic acid was transformed to the tosylate **2b** using literature procedures [13, 14]. The compounds **2a**–**2c** were treated with sodium dimethylmalonate [15, 16] to give the substituted dimethylmalonates **3a**–**3c**. Subsequent reduction with lithium aluminium hydride [15, 16] gave the 2-substituted propane-1,3-diols **4a**–**4c**. The final products **4b** and **4c** were recrystallized from *n*-hexane, while **4a** was recrystallized from ethyl acetate.



Synthesis of the polyacrylate **8** *and polymethacrylate* **9**

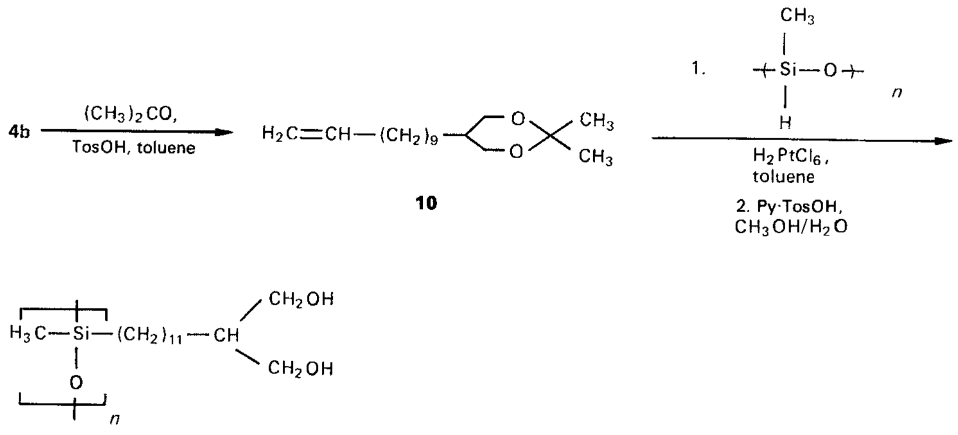
The synthesis of the acrylate **6** and the methacrylate **7** necessitates the protection of the 1,3-diol structural unit by transformation of the 2-hydroxymethyltridecane-1,13-diol **4a** into the 2,2-dimethyl-5-(11-hydroxyundecyl)-1,3-dioxane **5** and subsequent esterification. The esterifications with acryloyl chloride and methacryloyl chloride were carried out by heating the compound **5** with an excess of the acid chloride and powdered molecular sieve (3 Å) in CCl_4 [17]. The 1,3-diol structural unit was afterwards regenerated by deacetalization using pyridinium tosylate [18] in methanol/water.

The polyacrylate **8** and the polymethacrylate **9** were obtained by free-radical polymerization. The polymerizations were carried out with a monomer concentration of about 2 mol l^{-1} in tetrahydrofuran as solvent and 1 mol % AIBN as initiator. After polymerizing for 12 h at 60°C, the polymers were precipitated in excess *n*-hexane. They were purified by dissolving in THF and precipitation with *n*-hexane at least three times.



Synthesis of the polysiloxane **11**

The hydroxy groups of the 2-(10-undecenyl)propane-1,3-diol **4b** were protected by acetalization with acetone. The addition of the resulting 2,2-dimethyl-5-(10-undecenyl)-1,3-dioxane **10** to poly(methylhydrogensiloxane), in the presence of a Pt catalyst, gave the polysiloxane **11** after deacetalization.



11

The compounds were characterized by ^{1}H- and ^{13}C-N.M.R., I.R. measurements and quantitative analysis. For example, the ^{1}H-N.M.R. and I.R. results for the monomer **6** and the corresponding polymer **8** are as follows.

Compound **6**:

^{1}H-N.M.R. ($C^2H_3O^2H$, ppm): 6·41 (dd, J = 1·9 Hz, J = 17·2 Hz, 1 H, $=CH_2$); 6·14 (dd, J = 17·2 Hz, J = 10·2 Hz, 1 H, $=CH$); 5·86 (dd, J = 10·2 Hz, J = 1·9 Hz, 1 H, $=CH_2$); 4·14 (t, J = 6·5 Hz, 4 H, $-C\underline{H}_2OH$); 1·63 (broad, $-CH$, $-COOCH_2C\underline{H}_2-$); 1·31 (broad, 18 H, $-CH_2-$)

I.R. ($CHCl_3$, cm^{-1}): $\nu_{C=C}$ = 1630, $\nu_{C=O}$ = 1720, ν_{OH} = 3400.

Compound **8**:

^{1}H-N.M.R. ($C^2H_3O^2H$, ppm): 4·07 (broad, 2 H, $-COOCH_2-$); 3·56 (d, J = 5·5 Hz, 4 H, $-C\underline{H}_2OH$); 2·32 (broad, 1 H, $\underline{H}CCOO-$); 1·63 (broad, 3 H, $-CH$, $-COOCH_2C\underline{H}_2-$); 1·33 (broad, 20 H, $-CH_2-$)

I.R. (THF, cm^{-1}): $\nu_{C=O}$ = 1730; ν_{OH} = 3420.

The purity of the low-molar-mass surfactants was examined by T.L.C. The polymers were tested using polystyrene-calibrated GPC to give $\bar{M}_n$ values of 6900 (compound **8**) and 9800 (compound **9**). For the synthesis of compound **11** a polysiloxane with $n \approx 35$ was used.

2.2. *Methods*

Differential scanning microcalorimetry and optical polarizing microscopy were used to monitor the phase transitions. Differential scanning calorimetry (D.S.C.) was performed using a Perkin–Elmer DSC-2, which was standardized and operated as described in [19]. Optical studies of the various phases were carried out on a polarizing microscope equipped with a hot stage.

The X-ray diffraction measurements were carried out with a powder diffractometer HZG 4 (VEB Präzisionsmechanik Freiberg) using a transmission technique [20]. The ^{2}H-N.M.R. spectra were measured with a Bruker HX-90 spectrometer at 6·4 MHz and the specially constructed spectrometer UDRIS at 13·8 MHz. The pulse width was 4·8 μs and the pulse separation time was 2 s. The number of scans varied between 1000 and 2000.

The isopiestic measurements were carried out at 298 K. The dry samples together with defined aqueous solutions of H_2SO_4 were placed on metal blocks in desiccators and equilibrated for 25 days. The relative vapour pressure of water p/p_0 and the corresponding hydration numbers n_w (moles of water per mole of monomer units) were determined by weighing. The samples were dried in vacuum ($1{\cdot}33 \times 10^{-2}$ Pa) for 2 h over phosphorus pentoxide. Weighed amounts of the samples and water were sealed in aluminium D.S.C. pans or in glass tubes (X-ray and ^{2}H-N.M.R.).

3. Results

The D.S.C. data obtained for the low-molar-mass compounds are listed in table 1.

3.1. *Low-molar-mass surfactant* **4c**

The binary phase diagram of the two components H_2O and **4c** constructed from the calorimetric heating and cooling scans and contact preparations is presented in figure 1. The microscopic investigations show that a liquid-crystalline phase occurs only in the presence of water. A preliminary designation of the liquid-crystalline phases is given by comparing the observed textures with those described in the literature [21, 22]. A fan-like texture or an 'oily-streaks' texture with homeotropic regions could be observed. By tangentially shifting the cover slide of the microscopic preparation, a striated texture appears. The striated bands are arranged parallel to the direction of shear, which is characteristic of a lamellar mesophase [22].

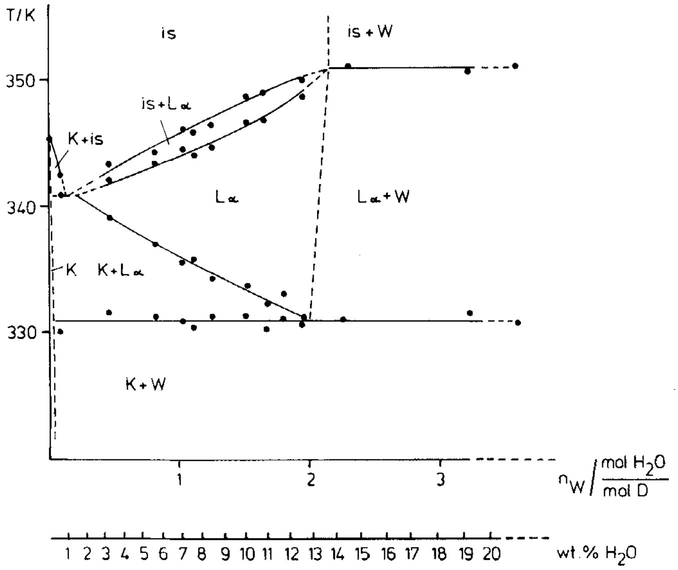


Figure 1. Phase diagram of the system H_2O–**4c**: is, isotropic; W, free water.

Table 1. D.S.C. results for low-molar-mass diols.

Compound	Water-free state			Water-saturated state			
	Transition	$T_{\max}$/K	ΔH/kJ mol^{-1}	Transition	$T_{\max}$/K	ΔH/kJ mol^{-1}	n_w/(mol H_2O/mol D)
4b	K → is	328	37·9	K(metastable) → K(stable)	*ca.* 305	−6·5	0
				K(stable) → L_α	318	41·9	
				K(metastable) → L_α	314	35·4	
				L_α → is	323	1·2	
4c	K → is	345	49·5	K → L_α	331	44·9	0
				L_α → is	351	1·2	
6	K → is	331	48·9	Melting-point depression, no mesophase formed			
7	K → is	316	36·0	Melting-point depression, no mesophase formed			

From the occurrence of a small ice peak even for the sample with the lowest water content a nearly complete dehydration in the crystalline state was deduced. It can be seen from figure 1 that the addition of water induces and stabilizes the mesophase L_α. Above a water content of approximately 2 mol H_2O/mol D the L_α phase exists between a constant melting temperature of 331 K and a constant clearing temperature of 351 K. The phase diagrams of monoglyceride/water systems [6–8] show higher hydration numbers and therefore more complicated lyotropic phase behaviour.

3.2. *Monomeric acrylate* **6** *and methacrylate* **7**

In the case of the two monomers **6** and **7** formation of liquid-crystalline phases has not been observed in either the presence or absence of water. The contact preparations showed a melting point depression with water for the two monomers.

3.3. *Polymers*

The D.S.C. results for the polymers are given in table 2. The enthalpies and hydration numbers are related to one mole monomer units (mol M).

*The system H_2O–***8**

For the polyacrylate **8** a liquid-crystalline phase was observed by polarizing microscopy in both the presence and absence of water. A broken fan-like texture found for the water-free substance is shown in figure 2. After shearing, a striated texture was found. The striated bands were arranged parallel to the direction of shear.

Structural information about the phase type was derived from the diffraction patterns at low and wide angles separately. In the investigated temperature region below the clearing point the long spacings of a sample with 66 per cent by weight of water were in the ratio 1/1 : 1/2 : 1/3, indicating the occurrence of lamellar phases. Averaged structure parameters d_L (repeat distance of lamellae) were calculated using least-square methods. The phase transition ice $\leftrightarrow$ water leads to changes in d_L (see figure 3). From the difference in d_L and the area per hydrocarbon chain A_k the amount of 'trapped water'—defined as removable water from the head group region—can be calculated [19, 23]. In our case we find approximately 1 mol H_2O/mol M. The transition between the L_β and L_α phases is characterized by a decrease in d_L. In the mesophase L_α, d_L decreases with increasing temperature.

The short spacings characterize the chain packing within a layer. In figure 4 the A_k values are plotted versus the temperature. In the low-temperature phase L_β, A_k is constant. In the transition region between L_β and L_α we find a jump in the A_k and d_L values. The lateral dilatation (increase in A_k values) together with the vertical contraction (decrease in d_L values) with increasing temperature are typical features of L_α mesophases. It should be mentioned that the A_k values of the low-temperature L_β phase are very high and the corresponding X-ray reflections are relatively broad. These X-ray results indicate that the order of the chains is lower than in the known L_β gel phases of phospholipids [19]. The A_k values of our L_α phase are somewhat lower than the A_k values of the neat phase of monoglycerides [8]. Thus the A_k jump at the transition $L_\beta \rightarrow L_\alpha$ is relatively small, which is in accordance with the small enthalpy value for this transition.

To get more information on the hydration behaviour of the polymer, ^{2}H-N.M.R. and isopiestic measurements were used. For two investigated samples with 5 mol ^2H_2O/mol M and 15 mol ^2H_2O/mol M the broad signal of the water molecules

Table 2. D.S.C. results for the polymers.

	Water-free state			Water-saturated state			
Compound	Transition	T_{max}/K	ΔH/kJ mol^{-1}	Transition	T_{max}/K	ΔH/kJ mol^{-1}	n_w/(mol H_2O/mol M)
8	K(stable) → L_α	311	3·7 ± 0·4				2
	L_β(metastable) → L_α	304	2·6 ± 0·4	L_β(stable) → L_α	299	3·1 ± 0·5	
	L_α → is	350	3·8 ± 1·2	L_α → is	382	4·8 ± 3·7	
9	K → is	361	4·7 ± 0·5	L_α → is	388	3·3 ± 0·2	2
11	K(stable → L_α	309	8·3 ± 1·8				2
	L_α → is	384	3·1 ± 2·9				
12	K(stable) → L_α	321	3·3 ± 0·7				2
	L_β(metastable) → L_α	318	2·1 ± 0·2	L_β(stable) → L_α	298	1·9 ± 0·3	
	L_α → is	353	4·2 ± 0·6	L_α → is	365	1·1 ± 0·1	

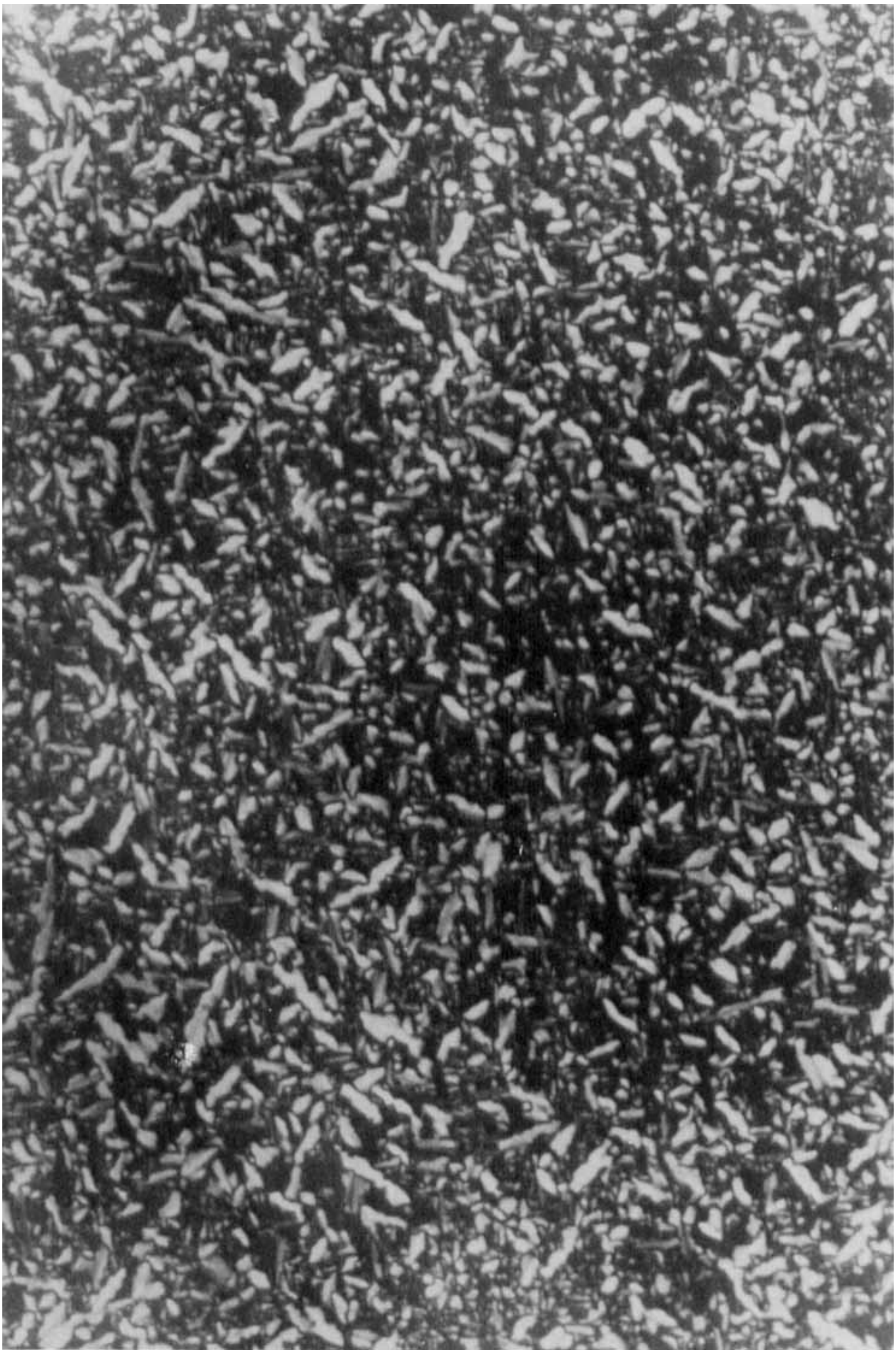


Figure 2. Broken fan-like texture of the water-free polyacrylate **8**.

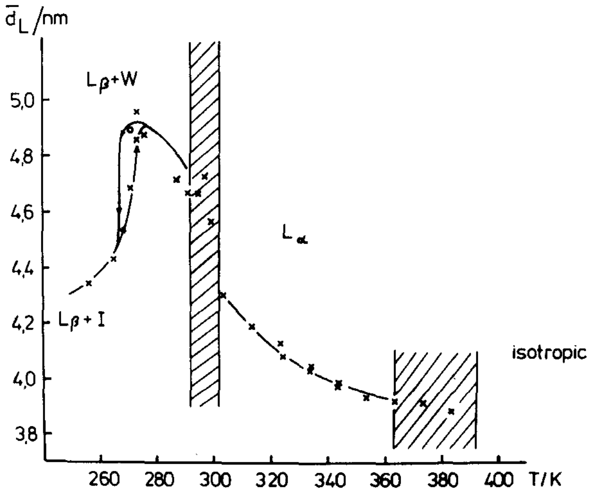


Figure 3. Dependence of the structural parameter d_L (lamellar spacing) of the system H_2O–polyacrylate **8** (66·6 per cent by weight water) on the temperature. W, free water; I, ice, ×, water in the stable phase, ○, supercooled water. The arrows show the direction of the temperature variation. The shaded regions are the transition intervals obtained by D.S.C.

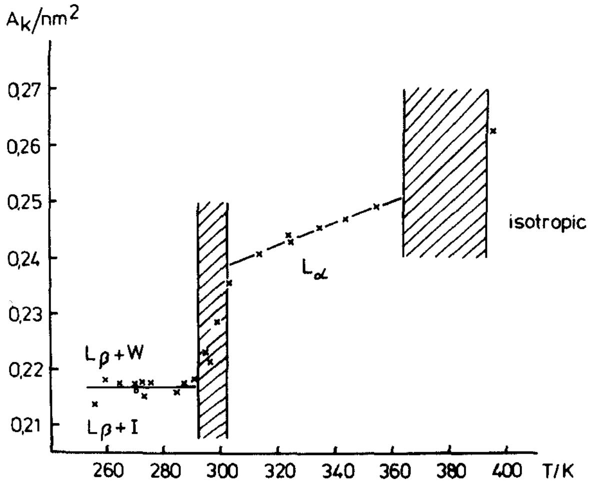


Figure 4. Dependence of the structural parameter A_k (area per hydrocarbon chain) of the system H_2O–polyacrylate **8** (66·6 per cent by weight water) on the temperature. From the position of the maximum of the wide-angle reflection a spacing d can be obtained. A_k was calculated on the assumption of a hexagonal chain packing according to $A_k = 2\sqrt{(\frac{1}{3})}\,d^2$. Since the wide-angle halo had been detected in the isotropic melt, an A_k value was obtained for this phase too. Symbols as in figure 3.

influenced by the head groups is overlapped by a sharp line due to the free water molecules. From the ratio of these two signals, the amount of influenced water can be calculated (figure 5). In the L_α phase n_w increases slightly with increasing temperature. In the temperature region of the clearing transition the n_w values decrease dramatically.

The adsorption isotherms of **8** and **9** in the region $p/p_0 \rightarrow 1$ show hydration values of approximately 3 mol H_2O/mol M. Despite the large deviations in the region

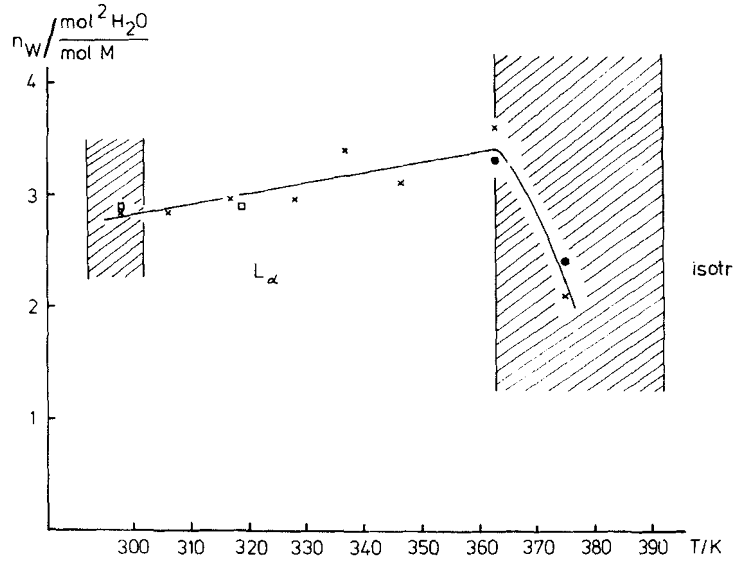


Figure 5. Temperature dependence of the hydration number n_w of the system H_2O–polyacrylate **8** from ^{2}H-N.M.R. measurements: □, sample with 15 mol ^2H_2O/mol M; x, sample with 5 mol ^2H_2O/mol M; ●, sample with 5 mol ^2H_2O/mol M after cooling from 395 K.

$p/p_0 \rightarrow 1$ due to condensation effects, the hydration value is of the same order as that found by ^{2}H-N.M.R. measurements.

The evaluation of the ice peak allows estimation of the amount of non-freezable 'bound' water. For the polymers, we found a value of approximately 2 mol H_2O/mol M. Together with the value of the 'trapped' water estimated by X-ray measurements, we find the same hydration number as by ^{2}H-N.M.R. and isopiestic measurements.

The phase diagram (figure 6) was constructed mainly from the D.S.C. data. It can be seen that at lower water concentrations both stable (figure 6 (*a*)) and metastable (figure 6 (*b*)) behaviour was found. At lower temperatures and lower water content there is a demixing region between the crystalline phase of the water-free polymer (K) and the hydrated L_β phase with a eutectic point at 290 K (see figure 6 (*a*)). Above the hydration value of 2 mol H_2O/mol M the hydrated L_β phase coexists with free water. On cooling the sample from the L_α phase, the L_β phase occurs as a metastable phase up to the water-free polymer (see figure 6 (*b*)). Because of the broad clearing transition, the construction of an exact phase diagram is difficult. The splitting of the clearing peak in the concentration region $n_w < 2$ mol H_2O/mol M can be explained by a demixing into a nearly water-free isotropic polymer melt and free water. This dehydration of the head group is in agreement with the N.M.R. results.

The system H_2O–9

The water-free polymethacrylate **9** melts directly to an isotropic phase. Only in the presence of water a lamellar mesophase is formed. The clearing transition of the system H_2O–**9** is sharper than that of the system H_2O–**8**. In the water-saturated region below the clearing point no other transitions except the ice melting could be detected.

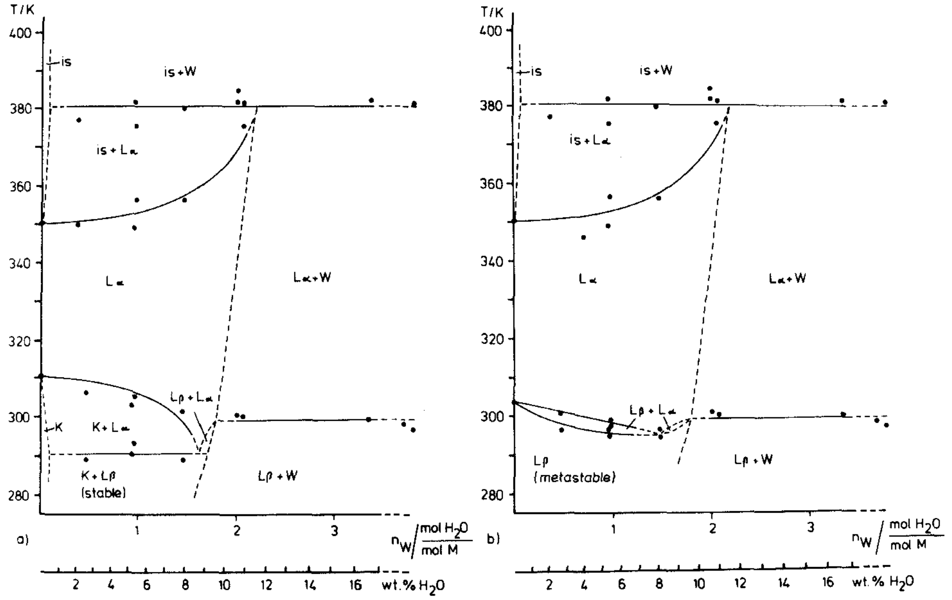


Figure 6. Phase diagram of the system H_2O–polyacrylate **8**: (*a*) stable form; (*b*) metastable form. W, free water; I, ice; is, isotropic.

*The system H_2O–***11**

For the polysiloxane **11** a liquid-crystalline phase could be observed in both the presence and absence of water. For the water-free polysiloxane **11** a low-temperature transition appears after prolonged storage at low temperatures. The width of the clearing peak is similar to that of the polyacrylate **8**. In the water-saturated state only the lamellar mesophase could be found. At low temperatures only the melting of ice appears, and the clearing temperature is considerably above 373 K and therefore not accessible to our microscopic and calorimetric measurements in the water-saturated region.

4. Discussion

For the diols **4c** and **4b** a stable lamellar mesophase could be observed in the presence of water. This agrees with the results on 2-[(*trans*-4-*n*-propylcyclohexyl) methyl]butane-1,4-diol [10]. The results clearly demonstrate that the addition of water

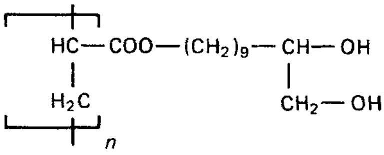
(i) induces liquid-crystalline phases if they do not exist in the water-free state;
(ii) stabilizes the liquid-crystalline phases resulting in a decrease in the melting point and an increase in the clearing point.

The investigated polymers **8**, **9** and **11** show the same behaviour. However, the linkage of the amphiphilic diols to the polymer backbone causes a stabilization of the lamellar mesophases in accordance with the results given in [1–5, 22].

The absence of the mesophases for the monomeric acrylate **6** and methacrylate **7** may be due to a disturbance of the hydrophilic/hydrophobic balance by the ester group.

The phase behaviour of the polyacrylate **8**, polymethacrylate **9**, and polysiloxane **11** indicates a strong influence of the polymer backbone. The polymethacrylate **9** with the least-flexible main chain exhibits the L_α mesophase only in the presence of water, whereas for the polyacrylate **8** and polysiloxane **11** the mesophase could be found in the water-free state too. The polysiloxane **11** with the most-flexible main-chain shows the highest clearing temperature, and the mesophase is stable over a broader temperature range than for the polymers **8** and **9**. Therefore we can assume the greater the flexibility of the polymer backbone, the more stable is the L_α mesophase. However, we cannot exclude any influence of the degrees of polymerization of the investigated polymers.

The influence of the type of main-chain on the phase behaviour is also indicated by the results for the polyacrylate



$$\left[\begin{array}{lll}\mathrm{HC{-}COO{-}(CH_2)_9{-}} & \mathrm{CH{-}OH} \\ \; | & \;| \\ \mathrm{H_2C} & \mathrm{CH_2{-}OH}\end{array}\right]_n$$

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Despite the shorter side-chain length and the different position of the hydroxyl groups, the microscopic and D.S.C. results show almost the same phase behaviour as found for the polyacrylate **8**, but the transition temperatures are shifted (see table 2).

The clearing enthalpies of the investigated polymers were found to be less than 5 kJ per mole monomer units. While these values are in the same range as the clearing enthalpies of the low-molar-mass diols **4b** and **4c**, the melting enthalpies of the low-molar-mass diols and of the corresponding polymers differ remarkably, which can be explained by the lower order parameters of the polymers in the low-temperature state.

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