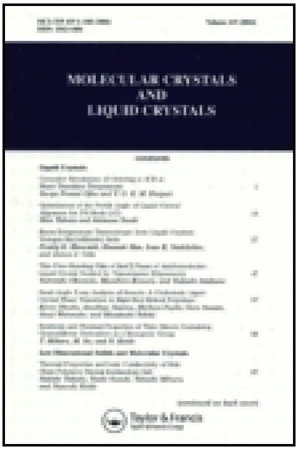


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Surface Phenomena of Liquid Crystalline Substances

Gong-Hao Chen [a], Jürgen Springer [a], Wolfgang Thyen [b] & Peter Zugenmaier [b]

[a] Institut für Technische Chemie der Technischen Universität Berlin, Fachgebiet Makromolekulare Chemie, Straße des 17. Juni 135, D-10623, Berlin, Germany

[b] Institut für Physikalische Chemie der Technischen Universität Clausthal, Arnold-Sommerfeld Straße 4, D-38678, Clausthal-Zellerfeld, Germany

To cite this article: Gong-Hao Chen, Jürgen Springer, Wolfgang Thyen & Peter Zugenmaier (1998): Surface Phenomena of Liquid Crystalline Substances, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 325:1, 99-116

To link to this article: http://dx.doi.org/10.1080/10587259808025387

Mol. Cryst. Liq. Cryst., Vol. 325, pp. 99-116
Reprints available directly from the publisher
Photocopying permitted by license only

Surface Phenomena of Liquid Crystalline Substances

Temperature-dependent Surface Tension of 4,4′-di-*n*-alkanoyloxybiphenyls

GONG-HAO CHEN[a], JÜRGEN SPRINGER[a,*], WOLFGANG THYEN[b]
and PETER ZUGENMAIER[b]

[a] *Institut für Technische Chemie der Technischen Universität Berlin, Fachgebiet Makromolekulare Chemie, Straße des 17. Juni 135, D-10623 Berlin, Germany;*
[b] *Institut für Physikalische Chemie der Technischen Universität Clausthal, Arnold-Sommerfeld Straße 4, D-38678 Clausthal-Zellerfeld, Germany*

(Received 9 February 1998; In final form 27 May 1998)

The surface tension-temperature characteristic of the homologous series 4,4′-di-*n*-alkanoyloxybiphenyls (BP-*n*: $C_nH_{2n+1}CO_2\text{-}C_6H_4\text{-}C_6H_4\text{-}CO_2C_nH_{2n+1}$) has been investigated by using the computer-aided pendant drop method. In case $n > 3$ BP-*n*'s are characterized by a highly ordered smectic G phase directly below the isotropic phase. Positive temperature coefficients of surface tension, which implies a surface-molecular excess order, are generally observed as the temperature is lowered to approach the phase transition. The remarkably wide temperature range of this anomaly is consistent with the suggestion that the existence of an underlying highly ordered phase favors the pretransitional surface ordering at the free surface of an isotropic phase.

Keywords: Surface tension; temperature dependence of surface tension; anomaly of temperature dependence in surface tension; temperature coefficient; pretransitional order; liquid crystals; 4,4′-di-*n*-alkanoyloxybiphenyls

INTRODUCTION

It is known that mesomorphic molecules or liquid crystals (LC's) often exhibit specific structures close to the free surface or the interface to solid

---

*Corresponding author. Phone: +49 30 314 22262, Fax: 79237.

substrates. They not only exist in the nematic (n) or smectic (s) mesophase but also in the isotropic (i) phase [1–7]. When the temperature of the material approaches a phase transition, such boundary layers show generally higher molecular order than in the bulk and surface smectic layers in the bulk n-phase and surface smectic or nematic layers in the bulk i-phase. This pretransitional surface ordering phenomenon can be observed with various experimental methods, *e.g.*, surface tension determination, reflection ellipsometry and X-ray reflectivity studies [1–7]. Also, theoretical discussions based on the Landau-de Gennes approach or mean-field treatment support this phenomenon [8–10]. However, the related investigations are far from being satisfactory.

In the present paper the pretransitional molecular order at the free surface of the homologous series 4,4′-di-*n*-alkanoyloxybiphenyls (BP-*n*) is investigated by surface tension determination. The results obtained are discussed with respect to the molecular order in the underlying mesophases.

The surface tension-temperature characteristic ($\gamma(T)$-curves) can be described by the Eötvös relation for almost all conventional liquids [11]: the surface tension monotonously increases, nearly linearly with the decrease of temperature. However, LC substances exhibit often anomalies in this behavior [1, 12–16]. In certain temperature ranges, in particular near the bulk phase transitions, their $\gamma(T)$-curves deviate distinctly from the normal behavior and show sections with positive or relatively small negative slopes or even discontinuities. Since for a one-component system, the surface excess entropy per unit area ($\Delta S^s = S^{\text{surface}} - S^{\text{bulk}}$) can be described as $\Delta S^s = (-d\gamma/dT)$ [17, 18], a positive temperature coefficient $d\gamma/dT$ signifies higher order at the surface than in the bulk. Consideration of the asymmetric (orienting) field conditions of mesogenic molecules which induce a strong anisotropic potential, leads to molecular ordering near the LC surface. The liquid character of the LC mesophases facilitates the experimental accessibility of the surface tension-temperature characteristic in the vicinity of the bulk phase transitions, and thus provides a novel possibility to explore the molecular behavior near LC surfaces.

Recently Song and Springer [19] have reported a strong and sharp decrease of the surface tension on some LC substances as the falling temperature approaches the crystallization point. This phenomenon was explained by proposing the occurrence of surface induced freezing at the liquid surface. It was suggested that such unusual behavior should be more likely to be observed by those LC's, which undergo either a transition from the isotropic phase directly into a highly ordered smectic phase or have a low temperature highly ordered phase, *e.g.*, highly ordered smectic or crystalline phase, which exists near the phase transition isotropic→mesophase.

Due to their highly ordered smectic ($n \geq 3$) and crystalline phases ($n < 3$) for BP-*n* directly below the i-phase, the BP-*n* homologous series is best suited for examining the stated hypothesis.

EXPERIMENTAL

(A) Materials

The phase behavior of 4,4′-di-*n*-alkanoyloxybiphenyls (BP-*n*'s) was investigated by DSC and X-ray studies after purification by recrystallization of the compounds with suitable solvents [20] (Fig. 1). Figure 2 shows the phase transition temperatures of BP-*n*'s as a function of the side group length *n*. The corresponding transition enthalpy and entropy values are listed in Table I.

Some remarkable regularities of the phase behavior can be observed on the substances with $n > 7$: (a) All the substances exhibit three phase transitions from the crystalline state at room temperature to the isotropic phase: crystalline 2(k_2)→crystalline 1(k_1)→smectic G(s_G)→isotropic. (b) The transition enthalpies of these substances behave in a similar way. For each substance the $s_G \rightarrow i$ transition enthalpy is generally slightly larger than the total enthalpy of the transitions k_2-k_1 and k_1-s_G. (c) The k_2-k_1 transition enthalpy is clearly smaller than the k_1-s_G. (d) An almost linearly increasing trend of the clearing enthalpy as function of *n* can be observed (Fig. 3). In case of the total melting enthalpy, the BP-*n*'s are well comparable to the corresponding odd members of *n*-paraffins [21], which indicates that the melting process for BP-*n*'s with $n > 7$ is dominated by the aliphatic parts of the molecules.

The two non-liquid crystalline substances BP-1 and BP-2 differ from the others with significant higher clearing temperatures as well as clearing enthalpies and entropies. They also differ in their packing arrangements (additionally BP-2 in space group symmetry) and density in their crystal structures. Some unidentified phases below the s_G-phase are observed for

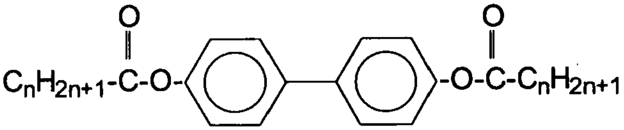


FIGURE 1 Chemical constitution of BP-*n*'s (4,4′-di-*n*-alkanoyloxybiphenyls).

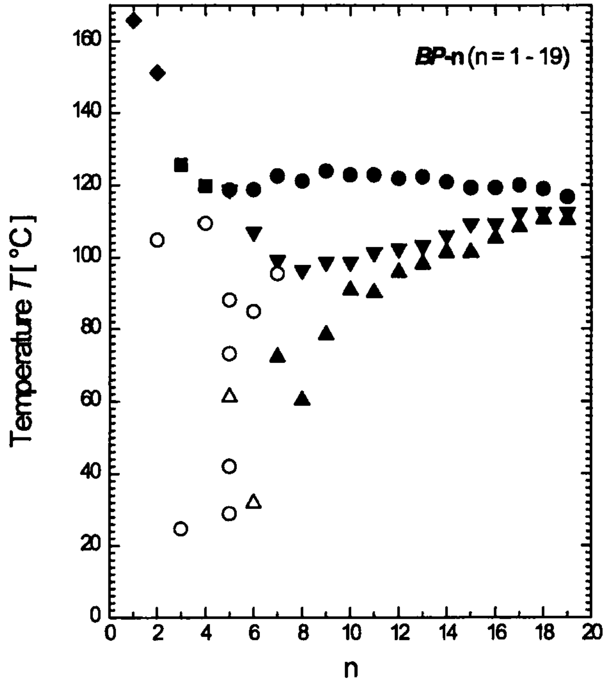


FIGURE 2 Transition temperatures of BP-*n*'s as a function of *n*. ◆ Crystalline→isotropic; ■ liquid crystalline (not characterized)→isotropic; ● s_G→isotropic; ▼ crystalline 1→s_G; ▲ crystalline 2→crystalline 1; △ extrapolated phase transition: crystalline 2→crystalline 1; ○ not characterized phase transition.

BP-5, 6 and 7. The liquid crystalline phase properties of BP-3 and BP-4 have not yet been studied [20].

Therefore, we chose BP-2, 5, 7, 8, 9, 10, 11 and 12 as representative samples for this study of the surface tension-temperature characteristic for the whole BP-*n* homologous series.

(B) Surface Tension Measurements

The surface/interfacial tension measurements of liquid/fluid-system were carried out by using a computer-aided pendant drop method [22] with a relative accuracy of ca. 0.05% on which we rely in this paper and an absolute accuracy of ca. 0.5%. The temperature scanning measurements of surface tension have been performed in N_2. A detailed description of the procedures has been provided elsewhere [15, 16, 22].

TABLE I Phase transition enthalpy and entropy of BP-*n*'s (DSC-results) [20]

n	*T*[°C]	ΔH[kJ/mol]	$\Delta S/R$1) [–]
1	165.8	31.35	8.59
2	104.8	1.23	0.39
	151.1	26.80	7.60
3	24.8	5.30	2.14
	125.6	17.50	5.28
4	–61.4	3.30	1.87
	109.4	0.10	0.03
	119.8	17.40	5.33
5	29.0	6.10	2.43
	42.1	12.90	4.92
	61.2	2.10	0.76
	73.3	0.40	0.14
	88.2	–	–
	118.7	16.50	5.06
7	72.3	2.75	0.96
	95.6	–	–
	99.2	(7.89)2)	(2.57)
	122.5	18.81	5.72
8	60.3	2.43	0.88
	96.5	10.89	3.54
	121.1	20.40	6.22
9	82.2	2.84	0.96
	98.7	12.81	4.14
	123.9	22.35	6.77
10	78.4	2.74	0.94
	98.7	14.76	4.77
	122.8	24.59	7.47
11	90.9	–	–
	101.3	(26.27)	(8.44)
	122.8	26.81	8.14
12	90.2	–	–
	102.3	(26.94)	(8.44)
	121.8	28.61	8.14
13	95.9	–	–
	103.2	(31.92)	(10.20)
	122.3	32.41	9.86
14	98.2	–	–
	106.0	(31.83)	(10.10)
	120.9	33.94	10.36
15	101.3	–	–
	109.2	(37.03)	(11.50)
	119.3	36.69	11.24
16	105.2	–	–
	109.2	(37.03)	(11.65)
	119.3	38.78	11.68
17	108.3	–	–
	112.2	(43.39)	(14.48)
	120.0	43.85	13.41
18	110.5	–	–
	112.3	(40.89)	(12.76)
	119.0	48.05	14.74
19	110.3	–	–
	112.4	–	–
	116.7	(100.79)	(31.09)

1) *R* is the universal gas constant.

2) The data in brackets indicate extrapolated values.

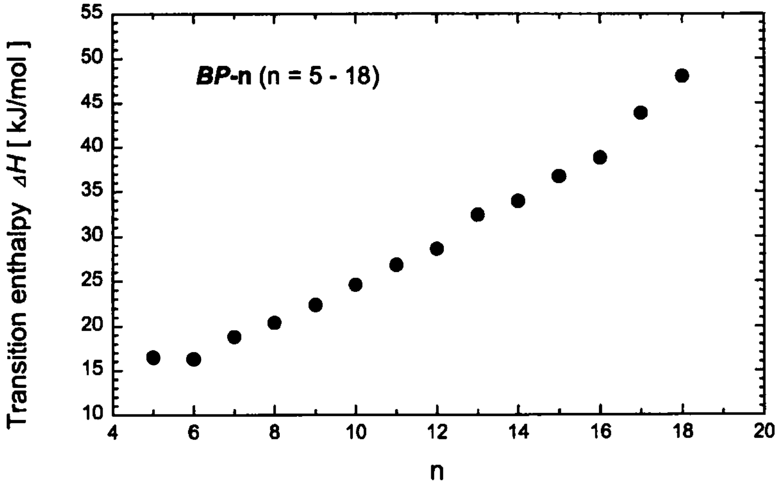


FIGURE 3 $s_G \rightarrow i$ transition enthalpy of BP-*n*'s as a function of *n* ($n \geq 5$).

(C) Density Determinations

The temperature dependence of the density ($\rho(T)$-curve) of the two fluid phases is necessary for a calculation of the surface/interfacial tension with the pendant drop method. The density of the gas phase (N_2, 1 bar) is neglected. The temperature dependent densities ($\rho(T)$-curves) of the BP-*n* samples were determined with a computer-aided precise capillary mercury dilatometer [23], on cooling and heating. The Figures 4a–h and Table II show the $\rho(T)$-curves and the resulting averaged expansion coefficients, respectively. Except for BP-8, the respective cooling and heating curves agree well over the whole temperature range. Although the temperature variations during the measurements has been controlled within a very low rate (0.2°C/min), a hysteresis from supercooling is visible and recognizable at the phase transitions. The s_G-phase of BP-8 shows a peculiar behavior in the density–temperature characteristic, indicated by the distinct difference between the $\rho(T)$-curves for cooling and heating. This deviation has to be attributed to an extraordinary structural change in the sample, since experimental errors can be ruled out.

As seen from the representations, all $\rho(T)$-curves in Figures 4a–h present distinct breaks at the phase transitions crystalline→isotropic (BP-2) and smectic→isotropic. For the smectic BP-*n*'s an trend of increasing discontinuities can be observed with molecular length at the transition crystalline→smectic and agrees with the transition enthalpy values presented in

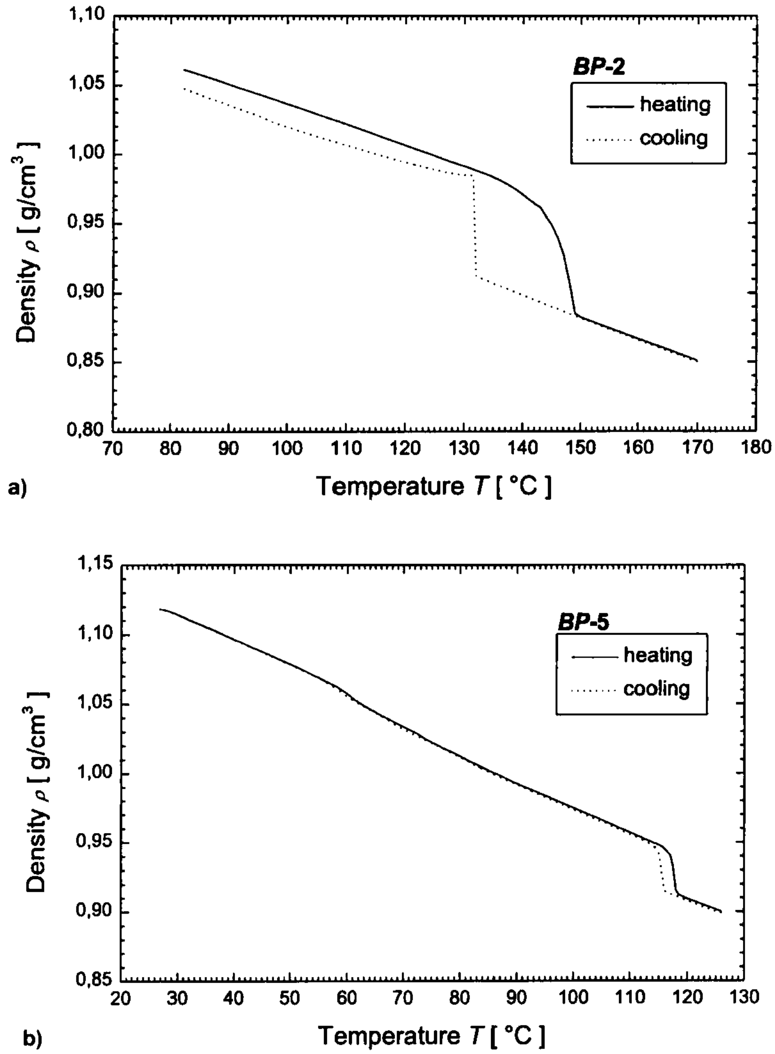


FIGURE 4 Temperature dependence of density of (a) BP-2, (b) BP-5, (c) BP-7, (d) BP-8, (e) BP-9, (f) BP-10, (g) BP-11, (h) BP-12.

Table I. It is found that the width of the discontinuity in density is proportional to the transition enthalpy.

If the $\rho(T)$-curves were not available for the calculation of the $\gamma(T)$-curves at high temperature ranges, the density of the samples has been deduced by extrapolation.

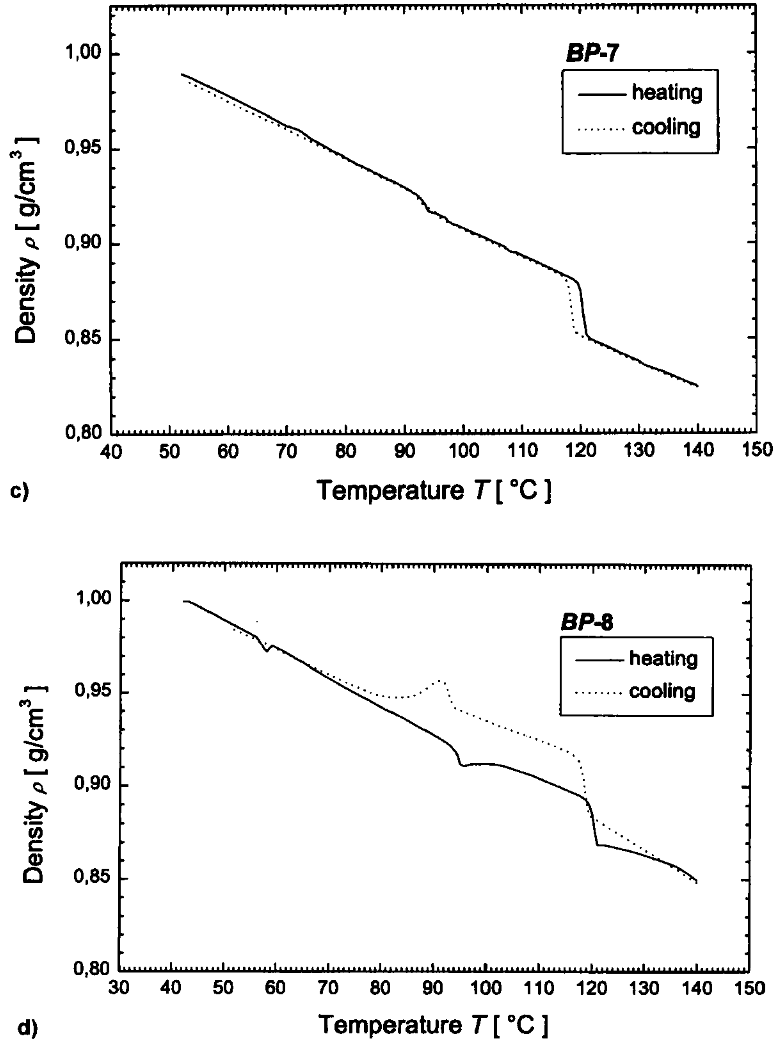
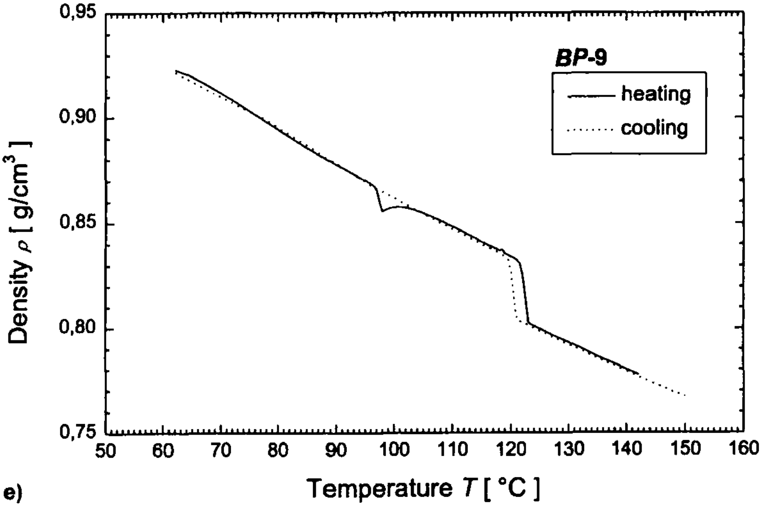


FIGURE 4 (Continued).

RESULTS AND DISCUSSIONS

The surface tensions as a function of temperature ($\gamma(T)$-curves) of BP-2, 5, 7, 8, 9, 10, 11 and 12 are shown in Figures 5a–h, respectively. For each sample measurements have been repeatedly performed both with increasing and decreasing temperature, each time with a newly formed drop. The samples allow an investigation in the isotropic phase till directly above the



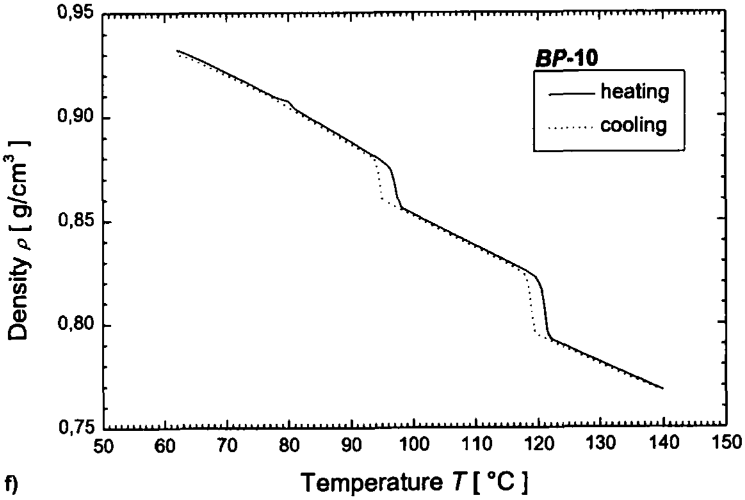


FIGURE 4 (Continued).

bulk phase transition $s_G \rightarrow i$ or $k \rightarrow i$ (BP-2). At lower temperatures all samples change to the solid state (BP-2) or a state resembling more a solid than a liquid. The profiles no longer fit the Laplace–Young's equation – the basis of the pendant drop method.

The compounds BP-5, 8, 10, 11 and 12 exhibit very similar behavior. Therefore, we will restrict ourselves to discuss primarily BP-11 which has

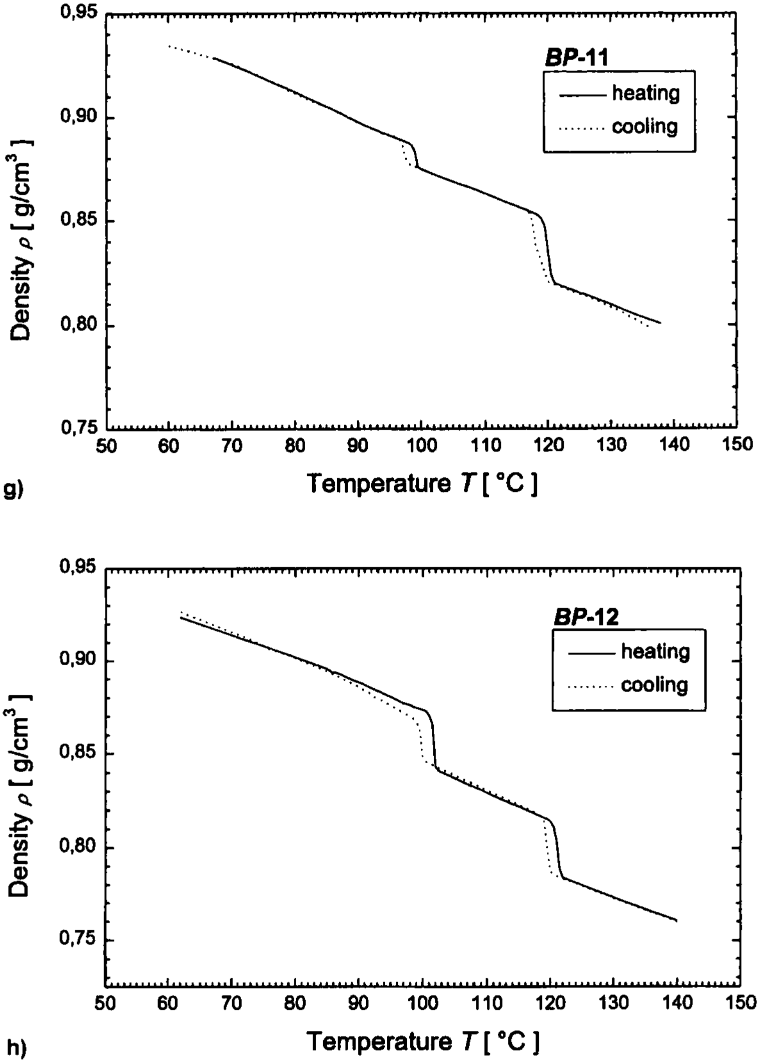


FIGURE 4 (Continued).

been thoroughly investigated with most experimental data. Figure 5g displays that the surface tension of BP-11 shows the expected behavior similar to conventional liquids well above the clearing temperature. The corresponding temperature coefficient of the surface tension $d\gamma/dT$ leads to a value about −0.06mN/m·K. "Inversion" temperatures (T_i's) are revealed by a change in slope on cooling, and the surface tension after T_i steadily falls

TABLE II Cubic expansion coefficient[3)] of BP-*n*'s

Compound	*Phase*	*Cubic expansion coefficient* [1/*K*] *Cooling*	 *Heating*
BP-2	i	$1.85*10^{-3}$	$1.82*10^{-3}$
	k	$1.11*10^{-3}$	$1.42*10^{-3}$
BP-5	i	$1.77*10^{-3}$	$2.16*10^{-3}$
	s_G	$1.85*10^{-3}$	$1.82*10^{-3}$
BP-7	i	$1.61*10^{-3}$	$1.61*10^{-3}$
	s_G	$1.60*10^{-3}$	$1.60*10^{-3}$
BP-8	i	$2.04*10^{-3}$	$1.19*10^{-3}$
	s_G	$1.17*10^{-3}$	$1.29*10^{-3}$
BP-9	i	$1.62*10^{-3}$	$1.70*10^{-3}$
	s_G	$1.70*10^{-3}$	$1.59*10^{-3}$
BP-10	i	$1.70*10^{-3}$	$1.73*10^{-3}$
	s_G	$1.85*10^{-3}$	$2.05*10^{-3}$
BP-11	i	$1.66*10^{-3}$	$1.42*10^{-3}$
	s_G	$1.41*10^{-3}$	$1.39*10^{-3}$
BP-12	i	$1.76*10^{-3}$	$1.69*10^{-3}$
	s_G	$1.92*10^{-3}$	$1.82*10^{-3}$

[3)] Cubic expansion coefficient: $\alpha = (V_{spez}(T_1) - V_{spez}(T_2)) / (0.5 \cdot (V_{spez}(T_1) + V_{spez}(T_2)) \cdot (T_1 - T_2))$, where V_{spez} refers to the specific volume of the sample.

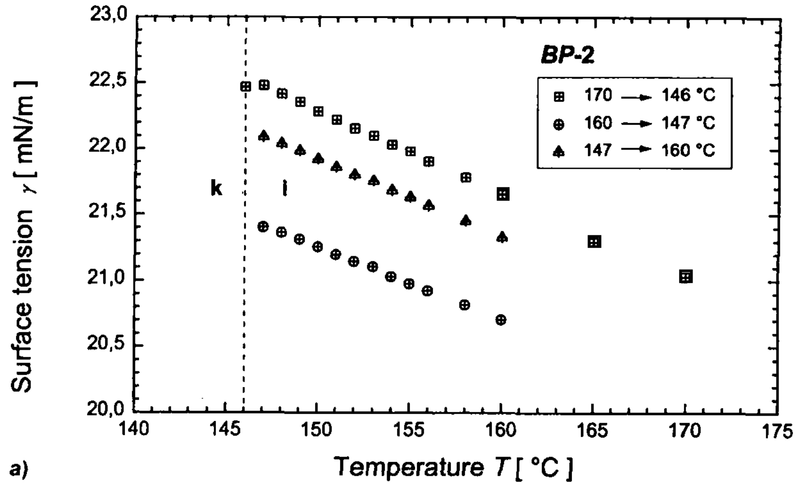


FIGURE 5 Temperature dependence of surface tension of (a) BP-2, (b) BP-5, (c) BP-7, (d) BP-8, (e) BP-9, (f) BP-10, (g) BP-11, (h) BP-12.

with decreasing temperature. The temperature coefficient exhibits a value of ca. + 0.3mN/m·K and increases to ca. + 1.3mN/m·K by approaching the underlying bulk phase transition. Limited by the high viscosity of the samples, the measurements were difficult to perform at temperatures very

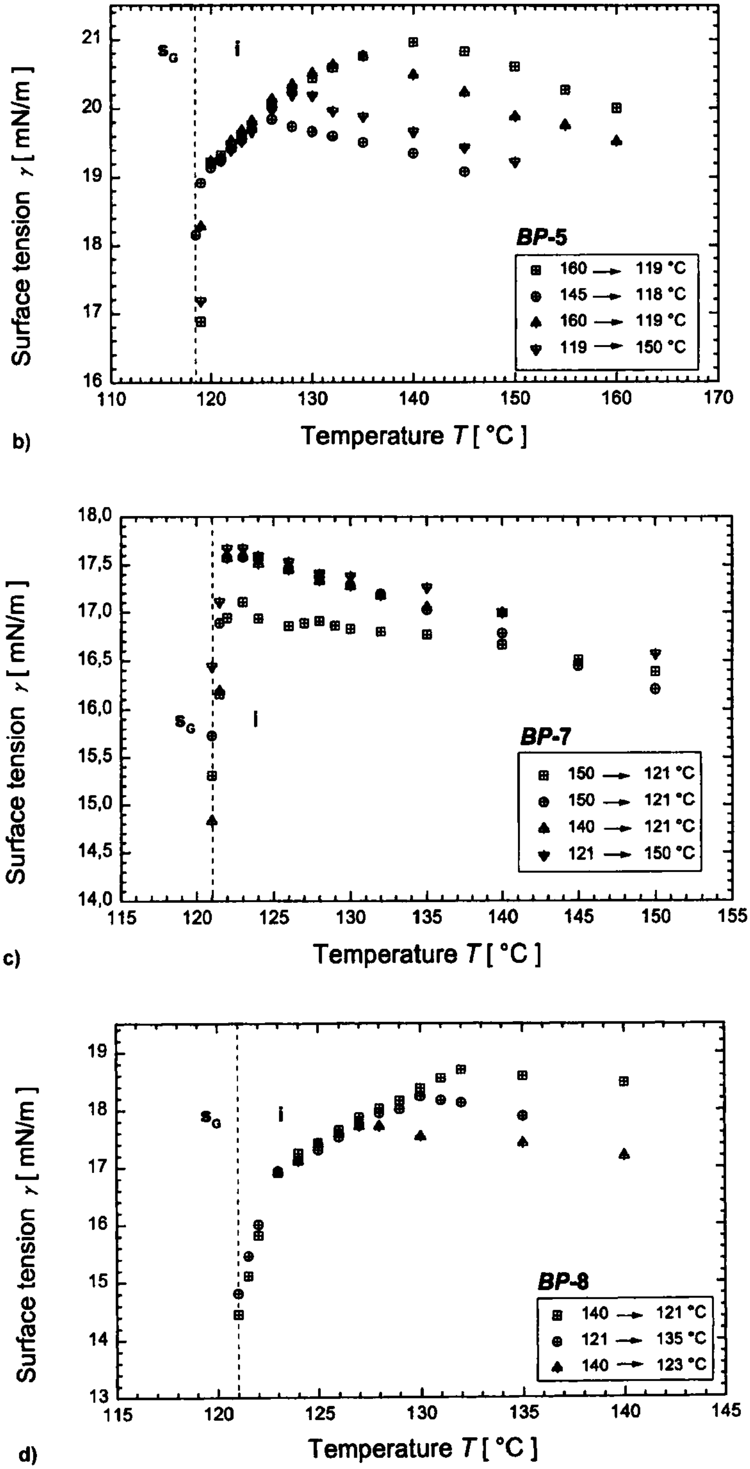


FIGURE 5 (Continued).

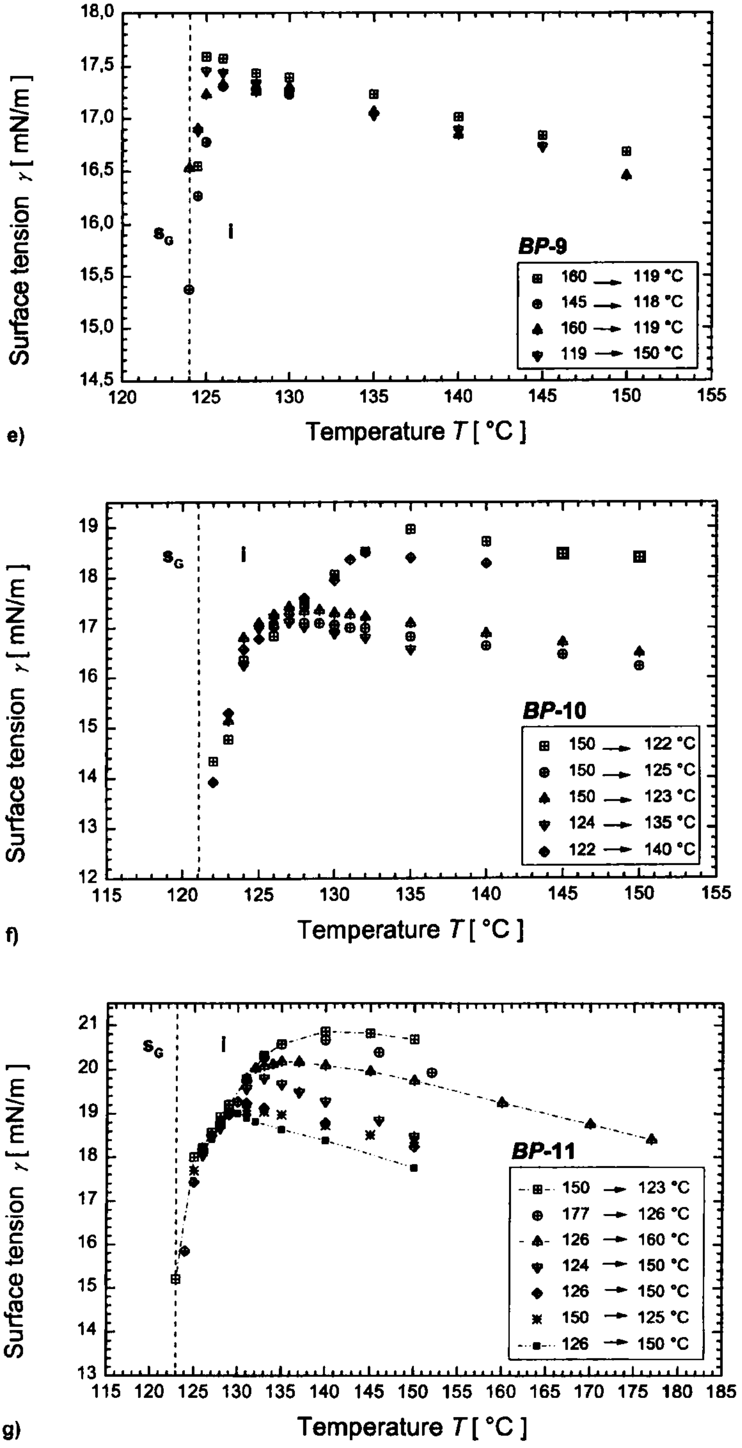


FIGURE 5 (Continued).

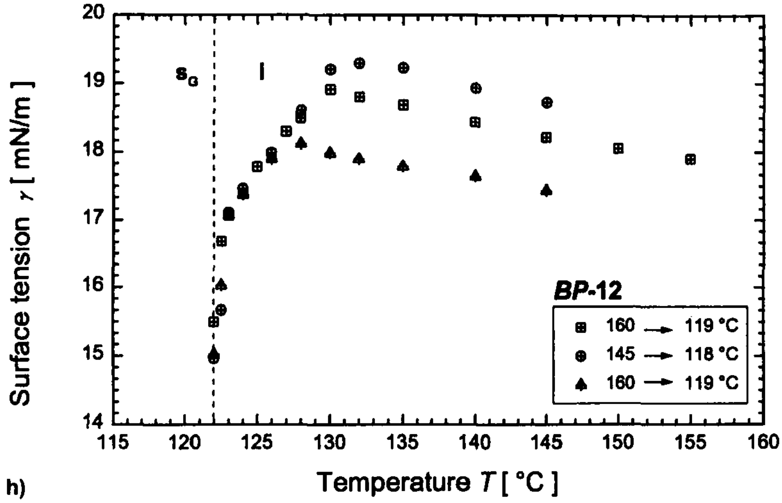


FIGURE 5 (Continued).

close to the clearing point, and a confidential value of the temperature coefficient cannot be given (this applies also to other samples). Due to this limitation, we were reluctant to propose the existence of a two-step anomaly from the measurements of BP-11 alone in our recently submitted communication [24]. Yet the combined results obtained for BP-5, 8, 10 and 12 seem to indicate a two-step anomaly. The following common characteristics are present: (a) All $\gamma(T)$-curves show an inversion temperature T_i, above which they behave similarly to conventional liquids. (b) In the range directly below T_i each substance gives a very good reproducibility in the slope of $\gamma(T)$ (anomaly step 1) so that the temperature coefficients can precisely be determined. (c) All the $\gamma(T)$-curves increase their slopes when the temperature is lowered to 1 – 2 K above the clearing point (anomaly step 2).

Table III summarizes the average $d\gamma/dT$-values of the BP-*n*'s studied in the three temperature sections, respectively. At higher temperatures all BP-*n*'s exhibit a value between −0.04 to −0.06 mN/m·K, comparable to normal liquids. Reliable $d\gamma/dT$-values obtained in anomaly step 1 show a surprising increasing trend with the molecular length *n*, which is consistent with the clearing enthalpy characteristic for increasing *n* as shown in Figure 3. In the vicinity of the clearing point, all BP-*n*'s exhibit distinctly higher $d\gamma/dT$-values in comparison with those in step 1, aside from a relatively high error in this temperature range, although the dependence on *n* may overinterpret

TABLE III Temperature coefficient of the surface tension of BP-*n*'s

Compound	*Temperature coefficient* $d\gamma/dT$ [*mN/m·K*] *High temperature i-phase*	*Anomaly step* 1	*Anomaly step* 2
BP-2	−0.06	–	–
BP-5	−0.05	+0.15	+1.53
BP-7	−0.04	–	+1.85
BP-8	−0.06	+0.18	+1.15
BP-9	−0.04	–	+1.32
BP-10	−0.04	+0.20	+1.34
BP-11	−0.06	+0.33	+1.30
BP-12	−0.04	+0.28	+1.92

these data. Yet the anomaly shows a very interesting similarity to that of normal alkanes [25] (see below).

In a one-component system like the present one, the temperature coefficient $d\gamma/dT$ represents the negative surface excess entropy per area (surface excess density), and the surface tension is related to the surface excess free energy [17–18]. Obviously, the change in the temperature coefficient indicates a phase transition affecting the surface layers: a negative coefficient above T_i indicates less ordered mesogenic molecules in the surface region than in the bulk, and a positive value below T_i indicates a reduction in the available degrees of freedom of motions in the surface layers and causes a surface excess order.

A defenitive interpretation of the enhancement of the anomaly near the clearing point cannot be provided by surface tension measurements only. This may be suggested as a further phase transition at the liquid surface.

Different $\gamma(T)$-curves have been obtained for a single compound and lead to changes of the inversion temperature and hence to a remarkable scattering in the absolute values of the surface tension in the high temperature range. This phenomenon may be caused by different factors. Among them the effects of the accumulation of impurities as well as the decomposition of LC samples during the measurements seem to play a certain role, since it was observed that the uppermost $\gamma(T)$-curves were more readily to be obtained at the beginning of the respective experimental series. The accumulation of surface active impurities at the liquid surface not only reduces the value of surface tension, but also affects the molecular ordering process and the resulting structures at the LC surface. The structure and ordering of surface molecules are known to be sensitive to the presence of other molecular species [19]. Yet it should be also pointed out, that the above effects seem not to be the only reason for the surface tension divergence in the high temperature range: since, as seen from the layouts in

Figures 5a–h, which downward the chronological experimental order indicate, in some cases the lowest surface tension values are not certainly related to the latest phases of the measurements. Also the very satisfying agreement of different $\gamma(T)$-curves (within the respective experimental series) in the relatively low temperature range seems to be opposed to the explanation in terms of the effects of impurities. Therefore, we suggest that the surface ordering process is additionally, strongly affected by other factors, *e.g.*, experimental conditions. For the above reasons, to gain a definitive explanation more experimental investigations directly aiming at the remarkable behavior described are required. This is planed in our laboratory.

The surface tension values at the transition anomaly step 1→step 2 for BP-8, 10, 11 and 12 are with those at the inversion temperature for BP-7 and 9 well comparable within 17–18 mN/m. Therefore, the peculiar shape of the $\gamma(T)$-curves of BP-7 and 9 may be interpreted that these two compounds tend to have a surface phase transition directly from the isotropic phase into anomaly step 2 without undergoing anomaly step 1, whereas the other BP-*n*'s more and less undergo the latter first. Figure 5f shows that BP-10 possesses both kinds of curves depending on the experimental conditions.

It is interesting to compare the above described surface tension-temperature characteristic with that of the normal alkanes. Earnshaw and Hughes [25] have investigated the temperature dependence of surface tension of normal alkanes with chain length between 15 and 18 carbon atoms by using the Wilhelmy method. In all cases the temperature coefficient $d\gamma/dT$ exhibits a well-defined change in behavior (from negative to positive on cooling and *vice versa*) at a temperature close to the melting point. This temperature lies 1 to 2 K above the melting for *n*-heptadecane and *n*-octadecane, respectively. They also found that the $d\gamma/dT$-values increase nearly linearly with the chain length of *n*-alkanes from ca. $+0.33$ mN/m·K for *n*-pentadecane to ca. $+0.91$ mN/m·K for *n*-octadecane. As stated above a similar regularity of the $d\gamma/dT$-values on temperatures directly above the clearing point couldn't be provided with the BP-*n*'s. With $+1.15$–$+1.92$ mN/m·K the BP-*n*'s exhibit larger, yet still comparable values in the temperature coefficients.

Concerning the molecular structures, some similarities exist between BP-*n*'s and *n*-alkanes, since the packing of BP-*n*'s is dominated by their aliphatic parts, particularly insofar as its surface properties are considered: both kinds of the compounds pack in a similar triclinic subcell for the C_2H_4 groups [20]. However, due to the underlying highly ordered liquid crystalline phase of BP-*n*'s ($n > 2$), the effect of surface ordering is much more distinct in comparison with *n*-alkanes. While the anomaly in the surface tension-temperature characteristic appears for the *n*-alkanes only by reducing the temperature very close to, or even below, their freezing points, it can be observed for BP-*n*'s at temperatures more than 10 K above the underlying phase transition.

In conclusion, the results of the present work reveal that the existence of a nearby low temperature highly ordered phase seems to favor the initiation of highly ordered molecular layers at the free surface. Based on this argument, it was expected that an even stronger anomaly of the temperature dependent surface tension should be observed for BP-2 which transforms into a crystalline phase directly below the clearing temperature. However, the freezing process was so sharp that the sample contracted spontaneously, no pendant drops suitable for measurements were formed, and no information about its anomaly can be provided (Fig. 4a).

Molecular excess order at the surface interface of LC's has also been reported by other authors [1 – 7, 26]. In some cases, especially for polymeric LC's, the highly ordered surface layers are maintained in a temperature range well above their clearing temperatures [7]. Such pretransitional surface excess order is generally considered to occur more readily for those LC's which possess low temperature highly ordered phases [4, 7, 26]. Our recent research on the influence of the gas sorption on the surface tension of LC's [16, 27 – 28] reveal that on all low molecular liquid crystals studied a surface molecular excess order can be induced by certain gases, both in the nematic and isotropic phase, and it can be enhanced by increasing gas pressure. With gas pressure high enough, this surface excess order may be stable not only throughout the whole n-phase but also over a wide temperature range after passing the n → i transition. Further investigations on LC side chain polymers confirm this effect [29].

SUMMARY

The temperature dependent surface tension of the homologous series 4,4′-di-*n*-alkanoyloxybiphenyls (BP-*n*) has been studied. For all liquid crystalline BP-*n*'s a distinct deviation was observed from the normal behavior below a certain inversion temperature. The formation of some highly ordered molecular structures at the liquid surface is revealed by two different positive slopes of the temperature coefficient $d\gamma/dT$ of the isotropic samples. These anomalies result in a two-step process: a large temperature coefficient at lower temperature can be observed for all the samples in the temperature range very close to the clearing point, while a lesser, high temperature one seems to occur selectively depending on the compound and the experimental conditions. The results obtained support the suggestion that the existence of an underlying highly ordered phase favors the pretransitional molecular ordering in the free surface of an isotropic phase.

Acknowledgements

Financial support by *the Fonds der Chemischen Industrie* is acknowledged. One of the authors (G.-H. Chen) thanks *the Graduiertenkolleg "Polymerwerkstoffe" of the Deutsche Forschungsgemeinschaft at the TU Berlin* for the scholarship.

References

[1] C. A. Gannon and T. E. Faber, *Phil. Mag. A*, **37**, 117 (1978).
[2] K. Miyano, *Phys. Rev. Lett.*, **43**, 51 (1979).
[3] W. Chen, L. J. Martinez-Miranda, H. Hsiung and Y. R. Shen, *Phys. Rev. Lett.*, **62**, 1860 (1989).
[4] P. S. Pershan, A. Braslau, A. H. Weiss and J. Als-Nielsen, *Phys. Rev.*, **A35**, 4800 (1987).
[5] D. Beaglehole, *Mol. Cryst. Liq. Cryst.*, **89**, 319 (1982).
[6] S. Immerschitt, T. Koch, W. Stille and G. Strobl, *J. Chem. Phys.*, **96**, 6249 (1992).
[7] H. Elben and G. Strobl, *Macromolecules*, **26**, 1013 (1993).
[8] P. Sheng, *Phys. Rev.*, **A26**, 1610 (1982).
[9] A. Mauger, G. Zribi, D. L. Mills and J. Toner, *Phys. Rev. Lett.*, **53**, 2485 (1984).
[10] M. M. Telo da Gama, *Mol. Phys.*, **52**, 585, 611 (1984).
[11] R. Eötvös, *Wied. Ann.*, **27**, 448 (1886).
[12] S. Krishnaswamy and R. Shashidhar, *Mol. Cryst. Liq. Cryst.*, **35**, 253 (1976).
[13] S. Krishnaswamy and R. Shashidhar, *Mol. Cryst. Liq. Cryst.*, **38**, 353 (1977).
[14] A. W. Neumann, R. W. Springer and R. T. Bruce, *Mol. Cryst. Liq. Cryst.*, **27**, 23 (1974).
[15] B. Song and J. Springer, *Mol. Cryst. Liq. Cryst.*, **293**, 39 (1997).
[16] G.-H. Chen and J. Springer, *Mol. Cryst. Liq. Cryst.*, in press (1998).
[17] L. Dufour and R. Defay, Thermodynamics of Clouds, Academic Press, New York and London (1963).
[18] J. S. Rowlinson and B. Widom, Molecular Theory of Capillary, Clarendon Press, Oxford (1982).
[19] B. Song and J. Springer, *Mol. Cryst. Liq. Cryst.*, **307**, 69 (1997).
[20] W. Thyen, *Doctoral Thesis*, Technical University Clausthal, Clausthal-Zellerfeld (1995).
[21] D. M. Small, In: Handbook of Lipid Research, Vol. 4, The Physical Chemistry of Lipids, Plenum Press, New York (1988).
[22] B. Song and J. Springer, *J. Colloid Interface. Sci.*, **184**, 64 (1996); **184**, 77 (1996).
[23] T. Runke, *Doctoral Thesis*, Technical University Berlin (1994).
[24] B. Song, G.-H. Chen, J. Springer, W. Thyen and P. Zugenmaier, *Mol. Cryst. Liq. Cryst.*, in press (1998).
[25] J. C. Earnshaw and C. J. Hughes, *Phys. Rev.*, **A35**, 4494 (1992).
[26] B. M. Ocko, A. Braslau, P. S. Pershan, J. Als-Nielsen and M. Deutsch, *Phys. Rev. Lett.*, **57**, 94 (1986).
[27] G.-H. Chen and J. Springer, *Mol. Cryst. Liq. Cryst.*, **307**, 89 (1997).
[28] G.-H. Chen and J. Springer, *Mol. Cryst. Liq. Cryst.*, **312**, 203 (1998).
[29] G.-H. Chen and J. Springer, in preparation.