One-dimensional correlations in ordered smectic phases of comb-like polymers

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The one-dimensional ordering of the ordered tilted (F) and normal (B) smectic phases of comb-like polymers is discussed. The one-dimensional correlation functions are calculated and the damping behaviour of one-dimensional correlations is characterized. The density distribution profiles along the normal to the plane of a smectic layer are determined. Finally, the variations of one-dimensional ordering during tilted–normal smectic phase transitions are examined.

(Keywords: smectic polymers; correlation functions; phase transition)

INTRODUCTION

During recent years our knowledge of possible polymorphism in macromolecular liquid-crystalline (LC) systems has become far more extensive. Ordinary smectics and nematics as well as polymers with ordered smectic phases having a two-dimensional lattice of B, F or H types were described earlier[1–5]. The structural data for such mesophases are confined, as a rule, only to the type of molecular packing.

In our previous studies[6,7], we examined the schemes of phase transitions for a number of acrylate and methacrylate polymers with ordered–disordered and tilted–normal smectic phase transitions (*Table 1*). For these systems, models of molecular packing were proposed and the variations of structural characteristics of intralayer packing during two-dimensional melting of a smectic phase were discussed. In this work, we present the results of further investigations of one-dimensional ordering in these systems, proceeding from the analysis of the correlation functions $\gamma_1(x)$ calculated from small-angle X-ray scattering (SAXS) intensity data.

EXPERIMENTAL

The SAXS data were obtained in an automatic DRAM-2.0 diffractometer with step-by-step scanning according to a conventional scheme[8]. The data were processed using FFSAXS program[9] and included the following procedures: subtraction of instrument background; subtraction of wide-angle X-ray scattering (WAXS) background; smoothing of scattering data; introduction of collimation corrections for the height of the primary beam; calculation of transition layer thicknesses; calculation of the one-dimensional correlation functions $\gamma_1(x)$ by the Fourier cosine transformation of the intensity data, taking account of the Lorentz factor (the use of the one-dimensional intensity function)[10]:

$$\gamma_1(x) = \int s^2 I(s) \cos(sx)\, \mathrm{d}s$$

where $s = 2 \sin \theta/\lambda$, θ is the scattering angle and λ is the wavelength.

The electron density distribution profiles along the normal to the plane of a smectic layer, $\rho(x)$, were obtained by graphic self-convolution of model profiles according to a procedure described in ref. 1.

RESULTS AND DISCUSSION

The one-dimensional correlation functions $\gamma_1(x)$ for all polymers under investigation are given in *Figure 1*. As can be seen, they are oscillating, gradually damping functions, showing a complex pattern of the electron density distribution $\rho(x)$. A special feature of correlation functions is the modulation of gradually damping maxima by a more complex function. Thus the final shape deviates considerably from the simple sinusoidal one characteristic of two-level lamellar systems[10]. The damping of $\gamma_1(x)$ for all the polymers occurs at distances $L = 600$–800 Å, which include 15–20 smectic layers (*Table 2*). There is no great difference in the values of L for tilted (F) and normal (B) smectic phases. To evaluate the damping of one-dimensional correlations and to calculate the corresponding longitudinal correlation lengths $\xi_{\parallel}$, the logarithms of the envelope curves of $\gamma_1(x)$ were plotted against distance x (*Figure 2*). As can be seen, over practically the whole range of distances x the ln γ_1 plots are well approximated by straight lines, which corresponds to the realization of the rapid exponential law of Debye correlation damping: $\gamma_1 \sim \exp(-x/\xi_{\parallel})^{10}$. The change in the slope of $\ln \gamma_1$ plots for polymers P4A and P7M can be associated with several types of layered packing having different scales of longitudinal correlations[6,7]. In refs. 6 and 7, the independent layer packing of the mesogenic groups, as in P4A and P7M, was shown. Thus, the ordered smectic phases are characterized by a high level of defects determining a rapid damping of one-dimensional correlations. In these systems, the exponential damping of correlations is observed, as opposed to the slower power one characteristic of low-molecular-weight smectic phases[11]. Small absolute values of the longitudinal correlation lengths $\xi_{\parallel}$ obtained from the Debye approximation are in the range 200–300 Å, which also provides evidence of a high level

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Table 1 Polymer characteristics

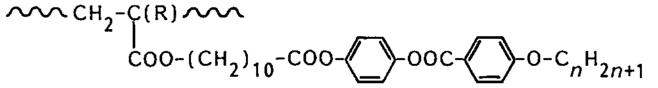
Polymer	Structure of monomer unit	Scheme of phase transitions (°C)	Refs.
			
P4A	R=H, n=4	$S_B \xrightarrow{66} S_A \xrightarrow{122} I$	6
P4M	R=CH$_3$, n=4	$S_F \xrightarrow{57} S_C \xrightarrow{66} S_A \xrightarrow{120} I$	6
P7A	R=H, n=7	$S_B \xrightarrow{79} S_A \xrightarrow{133} I$	7
P7M	R=CH$_3$, n=7	$S_F \xrightarrow{80} S_C \xrightarrow{139} I$	7

Table 2 Structural characteristics of smectic polymers

Polymer	Phase	T (°C)	d (Å)[a]	L (Å)[b]	$\xi_{\parallel}$	l_1 (Å)	l_2 (Å)	E (Å)
P7A	S_B	25	68	600	220	–	–	–
P7M	S_F	25	59	600	260, 80	–	–	–
P4A	S_B	25	41	650	240, 55	10	8	3
P4M	S_F	25	32	800	270	8	7	3
	S_C+S_A	60	33	520	180	–	–	–
	S_A	65	38	580	210	–	–	–
	S_A	71	38	350	130	–	–	–
	S_A	80	38	350	120	–	–	–

[a] Periodicity of the main order
[b] Determined from $\gamma_1(x)\to 0$

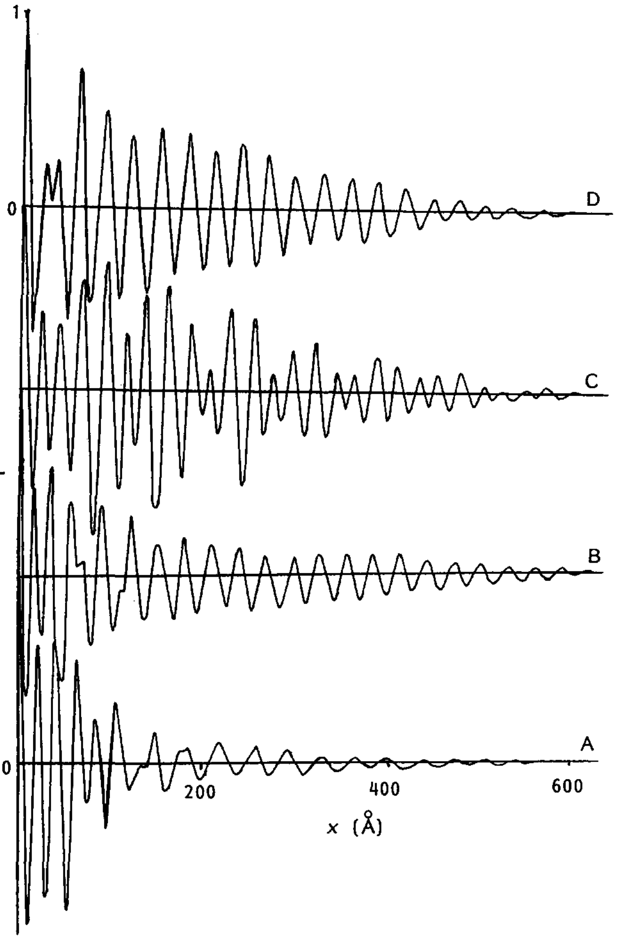


Figure 1 One-dimensional correlation functions: A, P4A; B, P4M; C, P7A; D, P7M

values are lower by 1–2 orders than in low-molecular-weight smectics[11].

The analysis of $\gamma_1(x)$ near zero and the first maximum makes it possible to come to certain conclusions on the of defects of one-dimensional order (*Table 2*). These density distribution $\rho(x)$ and to verify the models of molecular packing proposed earlier for those systems[6,7]. The first, most intensive peak on $\rho(x)$ represents the periodicity of the main structural order in the system, while the additional features present near the first minimum of $\gamma_1(x)$ are associated with a complex density modulation within this main order[1]. A simple sinusoidal shape of $\gamma_1(x)$ is indicative of two alternating interlayers with different electron densities. Additional interlayers within the layered structure results in an intermediate peak on $\gamma_1(x)$.

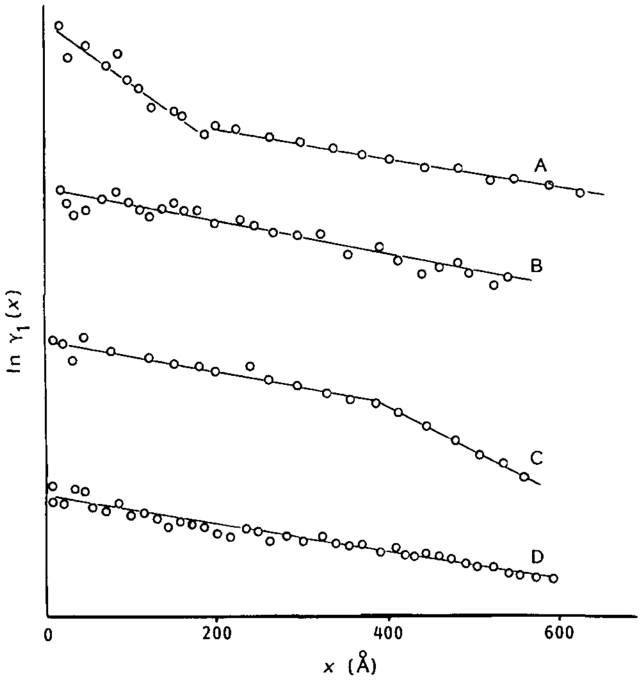


Figure 2 Logarithmic plots of envelope curves of one-dimensional correlation functions: A, P4A; B, P4M; C, P7A; D, P7M

The 41 Å period is the main order for the acrylate polymer P4A of smectic B type, which does not correspond to a simple one-layered packing proposed earlier based on the position of small-angle maxima[6]. In the methacrylate analogue P4M of smectic F type, the value of $d_1 = 32$ Å (*Figure 1*). An intermediate maximum on $\gamma_1(x)$ in the range 16–21 Å provides evidence of the realization of a more complex, three-level density distribution, with the formation of separate microregions containing rigid nuclei of mesogenic groups, flexible fragments and polymer main chains[1]. If we compare the profiles of $\rho(x)$ calculated from $\gamma_1(x)$ for the acrylate and methacrylate polymers, they appear to be quite similar (*Figure 3*). The differences refer to special features of $\rho(x)$ and consist of the following. For P4M the length of regions with higher electron density is much shorter and a lower density at the 'ends' of $\rho(x)$, absent for P4A, is quite evident (*Table 2*). The evaluation of different longitudinal arrangements of mesogenic fragments, taking account of the profiles $\rho(x)$ for the normal (P4A) and tilted (P4M) structures, demonstrates that for the acrylate polymer packing with overlap of rigid nuclei of mesogenic groups is realized (*Figure 3*). The length l of regions of higher density is 10 Å, which agrees with the longitudinal size of normally arranged phenylbenzoate groups. As can be seen in *Figure 3*, the 37 Å period corresponds to the distance between neighbouring regions of packing of rigid (l_1) fragments within the two-layered structures and not within the one-layered packing, as was hypothesized in ref. 6. The length of packing regions of main chains is 8 Å, i.e. they also include several nearest attachment groups. Such thicknesses of main-chain packing interlayers are characteristic of smectic comb-like polymers with rather long flexible (l_2) spacers[12]. Between the regions of different density, 3 Å long transition layers exist, which are somewhat shorter than those in disordered smectic polymers (5–8 Å)[13]. The thickness of gradient zones between regions with different densities ρ_1 and ρ_2 is given by E.

The profile for the methacrylate analogue with a tilted smectic F phase corresponds to an ordinary tilted two-layered packing, as was mentioned earlier[7]. In this case the repeat period is 64 Å, and the length of packing regions of rigid nuclei of mesogenic groups decrease to 6 Å, which agrees with the projection of a mesogenic group with account taken of the tilt angle ($\varphi = 36°$)[7]. A local density decrease in the region of contacts of chain ends of mesogenic fragments is distinctly represented on $\rho(x)$; transition layer thicknesses are also 3 Å (*Table 2*).

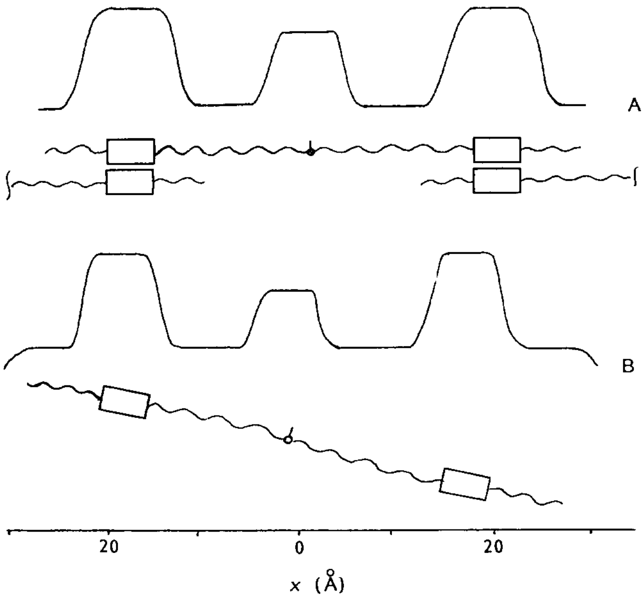


Figure 3 Profiles of the density distribution $\rho(x)$ and the corresponding schemes of molecular chain arrangements: A, P4A; B, P4M

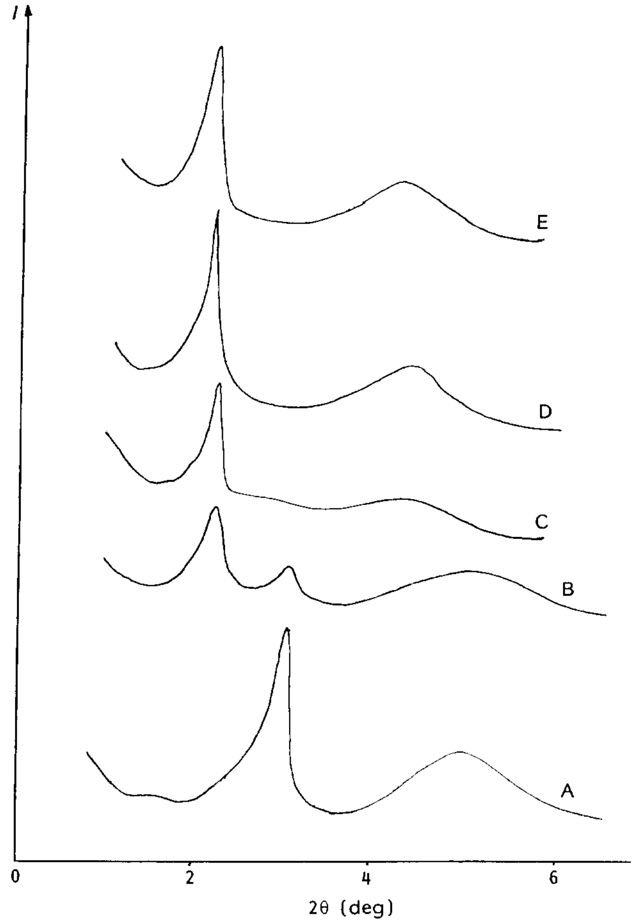


Figure 4 SAXS curves for P4M at different temperatures: A, 25°C; B, 60°C; C, 65°C; D, 71°C; E, 80°C

For the polymers P7A and P7M, a much more complex profile of $\gamma_1(x)$ is observed in this region. Here two additional maxima are present, and $\gamma_1(x)$ exhibits a complex modulated shape (*Figure 1*). The periodicity of the main order is 68 and 59 Å for P7A and P7M, respectively, which corresponds to the normal and tilted two-layered packings proposed earlier[7]. The complex shape of $\gamma_1(x)$ is probably associated with the realization of a density distribution profile that is more complex than three-level, or with the coexistence of two quite similar types of molecular packing.

In the methacrylate polymer P4M, according to ref. 6, a rather complex scheme of polymorphic transformations is realized, which includes ordered–disordered smectic phase (smectic F–smectic C) transitions and tilted–normal smectic phase (smectic C–smectic A) transitions (*Table 1*). To evaluate the changes in one-dimensional correlations as a result of phase transitions, we obtained a set of small-angle curves and correlation functions $\gamma_1(x)$ in the range of transition temperatures (*Figures 4* and *5*). As can be seen, up to 60°C the scattering curves still have a peak of lower intensity corresponding to the tilted packing ($2\theta = 2.98°$). Near this peak a new one appears corresponding to the normal packing ($2\theta = 2.18°$). In a certain temperature interval (from 57 to 64°C) both

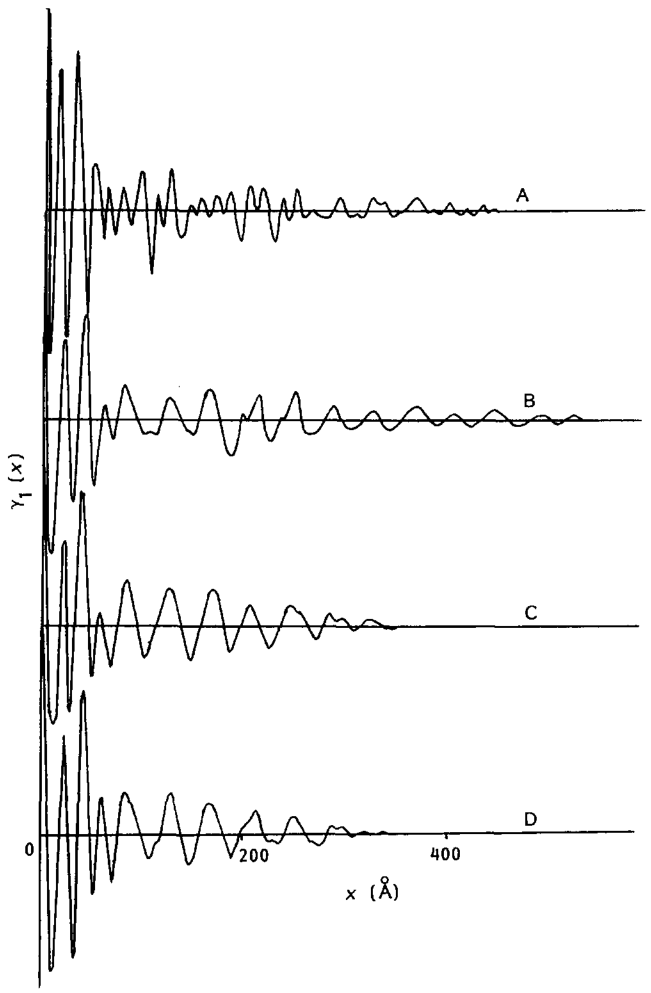


Figure 5 One-dimensional correlation functions for P4M at different temperatures: A, 60°C; B, 65°C; C, 71°C; D, 80°C

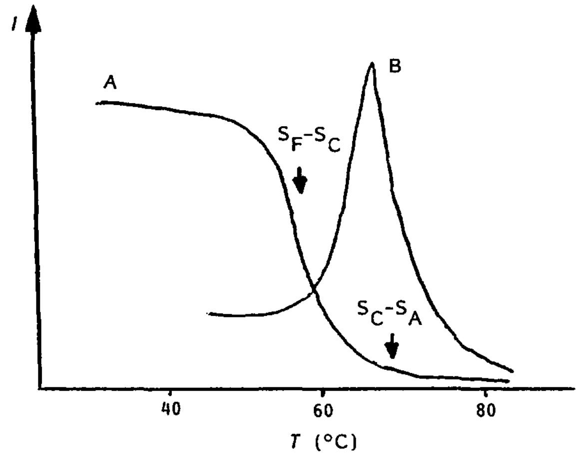


Figure 6 Small-angle maxima intensities as a function of temperature for P4M in the region of the smectic C–smectic A phase transition: A, corresponds to the S_C phase intensity; B, intensity of the S_A phase maximum (arrows show the S_F–S_C and S_C–S_A phase transitions)

maxima coexist (*Figure 6*), which provides evidence of a two-phase region in a polymer where the tilted and normal smectic phases coexist. On the corresponding correlation functions $\gamma_1(x)$, two density waves of different periodicity overlap one another distinctly in this temperature interval. The perfection of one-dimensional order also decreases greatly (decrease of $\xi_{\parallel}$ and L) (*Table 2*). A further temperature increase above 65°C and a complete transition to the normal smectic A phase result in a 'single-period' correlation function ($d_1 = 38$ Å), damping at much shorter distances ($\xi_{\parallel}$ decreases to 120–130 Å) (*Table 2*). As follows from the analysis of $\gamma_1(x)$, for small x, the three-level shape of the density distribution profile $\rho(x)$ is also preserved for the smectic A phase.

CONCLUSIONS

The above studies on a number of ordered smectic phases of comb-like polymers enable one to conclude that they are characterized by a high level of defects of one-dimensional order manifesting itself in a rapid exponential damping of one-dimensional correlations and in small absolute values of the longitudinal correlation lengths $\xi_{\parallel}$ (200–300 Å). As we demonstrated earlier, this is associated with additional disturbances introduced by an irregularly packed polymer main chain to the packing of mesogenic groups[14]. For a comb-like polymer the perfection of one-dimensional order is much higher in the ordered smectic phase than in the disordered one (longitudinal correlation lengths $\xi_{\parallel}$ are twice as high). In polymers with long flexible spacers between mesogenic groups and main chains, a complex three-level profile of the density distribution $\rho(x)$ is realized. Microregions of different electron densities are formed from separately packed rigid nuclei of mesogenic groups, flexible fragments and polymer main chains. The latter, as was shown in other work[12–14], is a result of microphase separation of different macromolecular fragments because of their thermodynamic incompatibility. In the region of the tilted–normal smectic phase transition, a two-phase region of coexistence of two smectic structures was revealed.

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REFERENCES

1 'Polymer Liquid Crystals' (Ed. N. A. Plate), Khimiya, Moscow, 1988
2 Tsukruk, V. V. and Shilov, V. V. 'The Structure of Polymer Liquid Crystals', Naukova Dumka, Kiev, 1989
3 Tsukruk, V. V., Shilov, V. V., Lipatov, Yu. S., Mogilevsky, L. Yu., Freidzon, Ya. S., Boiko, N. I. and Shibaev, V. P. *Crystallography* (*USSR*) 1988, **33**, 485
4 Shibaev, V. P. and Plate, N. A. *Adv. Polym. Sci.* 1984, **60/61**, 175
5 Freidzon, Ya. S., Boiko, N. I., Shibaev, V. P., *et al. Polym. Commun.* 1986, **26**, 647
6 Tsukruk, V. V., Kozlovsky, M. V., Shibaev, V. P., Shilov, V. V. and Lipatov, Yu. S. *Vysokomol. Soed.* (*A*) 1987, **29**, 2630
7 Tsukruk, V. V., Kozlovsky, M. V., Shibaev, V. P. and Shilov, V. V. *Crystallography* (*USSR*) 1988, **33**, 721
8 Lipatov, Yu. S., Shilov, V. V., Gomza, Yu. P. and Kruglyak, N. E. 'X-Ray Studies of Polymer Systems', Naukova Dumka, Kiev, 1982
9 Vonk, C. G. *J. Appl. Crystallogr.* 1973, **8**, 340
10 Feigin, L. A. and Svergun, D. I. 'Small-Angle X-Ray and Neutron Scattering', Nauka, Moscow, 1986
11 De Vries, A. *Mol. Cryst. Liq. Cryst.* 1985, **131**, 125
12 Tsukruk, V. V., Shilov, V. V. and Lipatov, Yu. S. *Macromolecules* 1986, **19**, 1308
13 Tsukruk, V. V., Shilov, V. V., Lokhonya, O. A. and Lipatov, Yu. S. *Crystallography* (*USSR*) 1987, **32**, 157
14 Tsukruk, V. V., Shilov, V. V. and Lipatov, Yu. S. *Acta Polym.* 1985, **36**, 403