Structure of polymer blends and copolymers based on liquid crystalline compounds from phenyl benzoates

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Structure analysis of liquid crystalline polymer blends and copolymers with side mesogenic groups from the phenyl benzoate series was carried out. Components of the polymer blends were shown to maintain their individual layer structure. However, upon mixing liquid crystalline ordering decreases. A new type of layer structure ensuring a denser packing of the side groups is realized in the copolymers. In isotropic melts, a weak inhomogeneity of density distribution due to the correlation hole effects is maintained.

(Keywords: liquid crystalline polymers; polymer blends; layer structure; one-dimensional order; small-angle X-ray scattering; one-dimensional correlation functions)

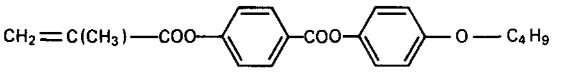
INTRODUCTION

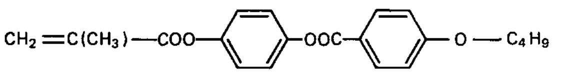
The use of liquid crystalline (LC) polymers has made it necessary to produce new LC polymer systems possessing a variety of properties. The expansion of the wide range of LC polymer materials via synthesis of novel compounds has become more and more irrational. Naturally, this has aroused great interest in producing new LC polymer materials by mixing several components being extensively used in polymer material science. Possible pathways for production are through 'physical' mixing of already known LC polymer components or through 'chemical' mixing, i.e. preparation of copolymers based on available mesogenic monomers of diverse nature[1,2]. Despite the obvious advantages of such an approach, these methods have not found wide practical application. A very limited number of investigations of such kinds of polymer blends has been carried out. In particular, it has been shown that LC polymer blends with corresponding LC monomers are totally or partly compatible in LC phase, depending on the chemical structure peculiarities of the monomers[3-6]. The investigated mixtures of LC polymers of diverse nature detected by Kostromin[7] are incompatible. The LC polymers based on the mesogenic groups of the cholesterol and phenyl benzoate series were investigated by Shibaev *et al.*[8] and Finkelmann *et al.*[9] The dependence of the phase transition parameters as well as that of the chromato–temperature characteristics (in the case of realizing the cholesteric mesophase) on the copolymer composition were studied.

However, no attempts have been made in the works cited above to compare the structural peculiarities of the LC polymer blends and copolymers with those of the corresponding homopolymers over a wide temperature range.

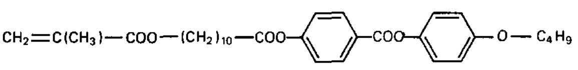
The purpose of the present work is to study the structure of two side-chain LC polymer systems, each of which involves an equimolar polymer blend and a copolymer of equimolar composition.

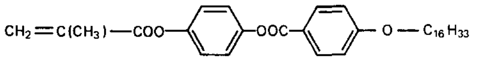
Polymer system I was obtained from the following monomers:


M–0.4


MB–0.4

by their polymerization, with subsequent mixing resulting in homopolymers PM-0.4 and PMB-0.4 (blend I), or by their copolymerization (copolymer I). Analogously, polymer system II was obtained from the following monomers:


M–10.4


MB–0.16

EXPERIMENTAL

Synthesis of the homopolymers and copolymers has been discussed earlier[10]. The polymer blends were prepared from a general solution in benzene. Before carrying out investigations, the samples were kept in vacuum to remove the residual solvent and were then heated to a temperature of 15–20°C above the glass transition temperature, T_g, after which they were annealed at a temperature of 5–10°C below T_g for 6–8 h and then slowly cooled (over 10 h) to room temperature. The samples for X-ray diffraction examination were placed between two 10 μm lavsan films. The phase transition parameters, T_{cl} and ΔH_{cl}, and T_g were determined by calorimetry and polarizing microscopy. A MIN-8 microscope equipped with a hot stage was used for optical observations.

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Calorimetric investigations were made in a DSM-2M calorimeter with heating rate 4°C min^{-1}.

Wide-angle X-ray scattering (WAXS) studies were made with a DRON-2.0 diffractometer. Small-angle X-ray scattering (SAXS) studies were carried out with a DRAM-2.0 diffractometer. Both diffractometers were operated in an automatic step scanning regime. A nickel filter was used for monochromatization of the copper anode radiation. Proportional detectors and amplitude discrimination were used to record the scattered radiation.

The X-ray scattering intensity curves were recorded in the range 0.04–7° with a step of 0.02°, and in the range 6–35° with a step of 0.5°. The background scattering involving absorption in the sample was subtracted from the resulting experimental curves. Temperature was maintained to an accuracy of ± 1°C.

A Kratky standard sample was used to reduce SAXS curves to absolute units[11]. SAXS data were processed according to the Vonk program[12]. The algorithm used involves the following procedure: summation of separate runs and combination of the total scattering curves; introduction of the collimation correction, taking into account the real intensity distribution along the primary beam (a case of end-slit height); subtraction of the WAXS background; normalization to the electron unit; estimation of the mean square of electron density fluctuation according to the following expression[11]:

$$\Delta\bar{\rho}^2 = 4\pi\int s^2 I(s)\,\mathrm{d}s \qquad (1)$$

where $s = 2\sin\theta/\lambda$; and estimation of the one-dimensional correlation function $\gamma_1(x)$ from the intensity curves multiplied by a Lorentz factor[11]:

$$\gamma_1(x) \sim \int s^2 I(s)\cos(sx)\,\mathrm{d}s \Big/ \int s^2 I(s)\,\mathrm{d}s \qquad (2)$$

RESULTS

As seen from the data in *Table 1*, the mixing of the homopolymers has little influence on T_{cl}. The phase transition enthalpies of the components in blend I are substantially decreased, while the ΔH_{cl} values for blend II are only slightly changed.

Copolymer I exhibits a phase transition, the parameters of which are far lower than those of both PM-0.4 and PMB-0.4. In the case of copolymer II two phase transitions with very low values of ΔH_{cl} are observed.

On the WAXS curve of all polymer systems a diffraction maximum at 19.5° is present. A halfwidth of the maximum for blend I and copolymer I is 6°, and for polymer system II is 4°. As seen in *Figure 1a* and *b* the profile and the position of the maximum for the polymer blend and copolymer coincide.

SAXS curves of the polymer systems at various temperatures are given in *Figure 2*. *Table 2* gives the layer spacings d and other structure parameters. In the small-angle region one observes substantial differences in the angular dependence of the scattering intensity for the polymer blends and the copolymers. The SAXS curve of blend I has a sharp maximum at 2.6° with halfwidth 0.4°, on the right-hand slope of which there is a shoulder at 3.2° and a small peak at 4.2°. A maximum at 2.6° with halfwidth 0.9° and a weak maximum at 3.6° is typical for

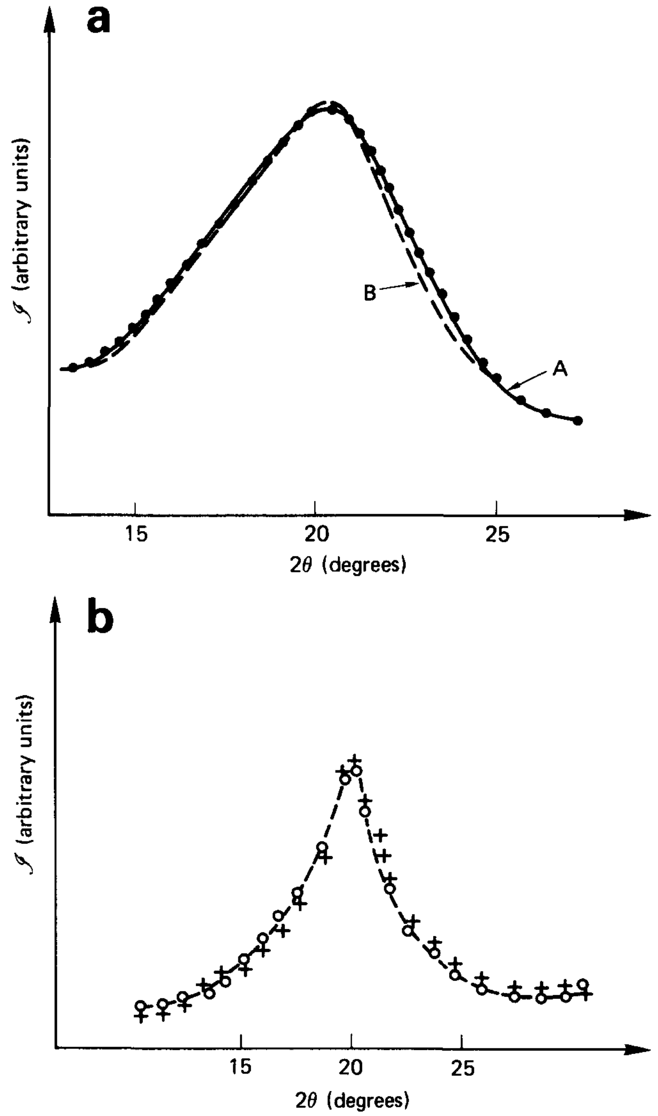


Figure 1 WAXS curves of: (a) blend I and copolymer I (●) and the additive curve (---); (b) blend II (+), copolymer II (○) and the additive curve (---)

Table 1 Phase transition parameters of the LC polymer systems

	Homopolymer			Polymer blends		Copolymer		
Component	T_g (°C)	T_{cl} (°C)	ΔH_{cl} (J g^{-1})	T_{cl} (°C)	ΔH_{cl} (J g^{-1})	T_g (°C)	T_{cl} (°C)	ΔH_{cl} (J g^{-1})
MB-0.4	180	254	27.8	253	5.3	135	245	5.3
M-0.4	140	264	22.9	263	7.9			
M-10.4	–	125	19.0	124.5	17.5	–	145	0.8
MB-0.16	160	213	9.2	215	6.4		167	2.4

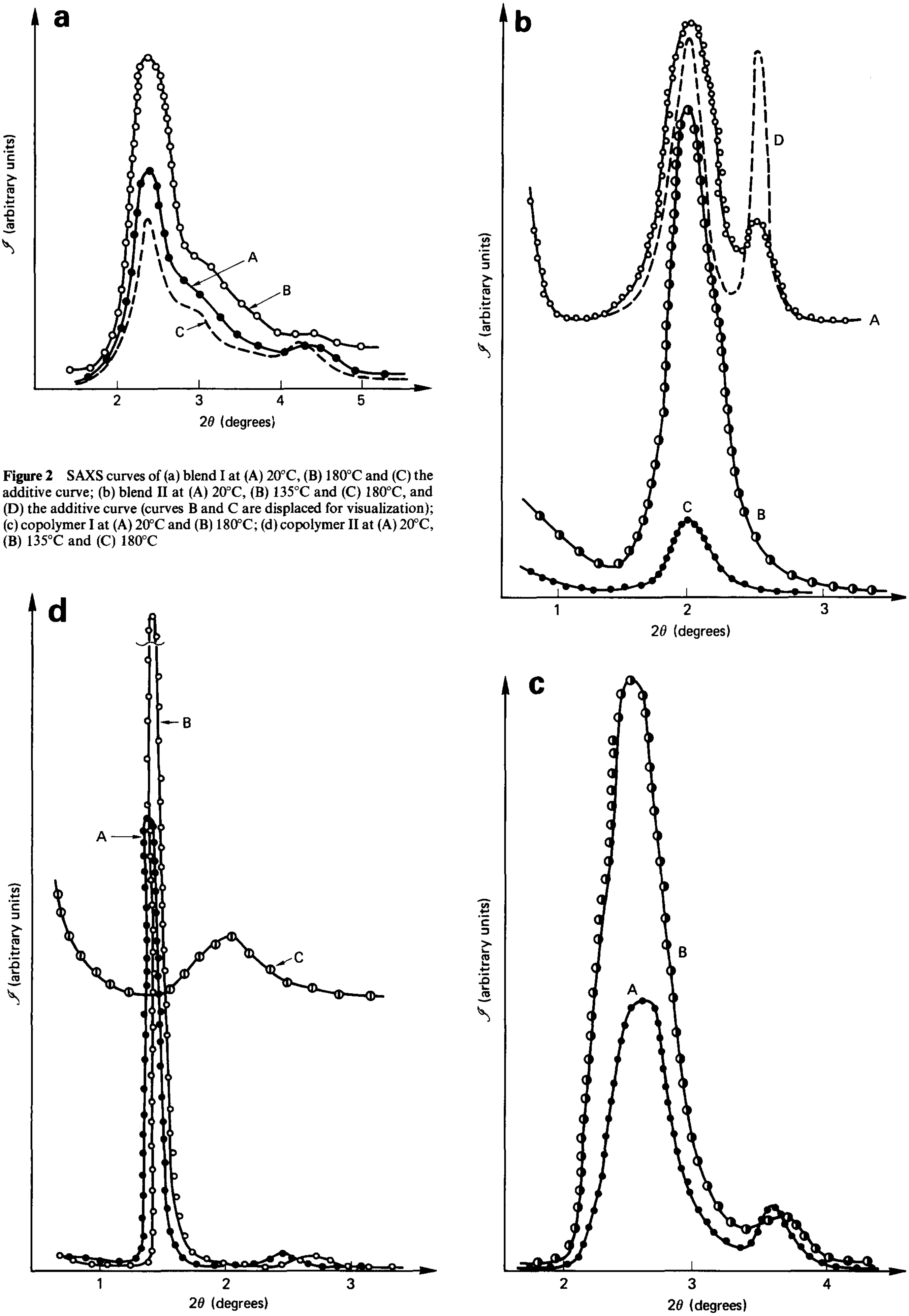


Figure 2 SAXS curves of (a) blend I at (A) 20°C, (B) 180°C and (C) the additive curve; (b) blend II at (A) 20°C, (B) 135°C and (C) 180°C, and (D) the additive curve (curves B and C are displaced for visualization); (c) copolymer I at (A) 20°C and (B) 180°C; (d) copolymer II at (A) 20°C, (B) 135°C and (C) 180°C

Table 2 Structure parameters of the LC polymer systems

		$\Delta\rho$ (e^2 Å^{-6})	d_1 (Å)	L (Å)	d_1^+ (Å)	d_2^+ (Å)	ξ (Å)
PM-0.4[a]		–	34.5	180	32.63	18	40
PMB-0.4[a]		–	26	340	26	22	90
Blend I	20°C	4.6×10^{-3}	31	280	34.45	21.18	64
	180°C	8.2×10^{-4}	33.6	390	35.54	–	105
Copolymer I	20°C	3.4×10^{-3}	26	160	29.6	20.16	50
	180°C	6.7×10^{-3}	28	150	29.85	19.74	50
PM-10.4[a]		–	32	680	31.79	17.65	180
PMB-0.16[a]		–	46	550	46	–	130
Blend II	20°C	1.39×10^{-3}	38	320	43.78	32.6	130
	135°C	1.8×10^{-3}	42	210	43.5	–	80
	180°C	2.2×10^{-4}	46	220	45.42	–	47
Copolymer II	20°C	2.0×10^{-3}	64	800	66.09	33.18	300
	135°C	2.4×10^{-3}	63	750	61.35	32	222
	180°C	5.1×10^{-4}	36	200	36.8	–	29

[a] From the position of the first maximum of the γ_1 curve
[b] From the Bragg equation
[c] Data from references 13 and 15–17

copolymer I. As temperature increases the main maxima of polymer system I are shifted in the direction of smaller angles and their intensity is slightly enhanced but their profiles hardly change.

An intensive maximum at 2° with a half-width 0.8° and a small sharp peak at 2.7° are present on the SAXS curve of blend II. The SAXS curve of copolymer II has a sharp intensive peak with halfwidth 0.2° at 1.4° and a second-order peak at 2.8°.

Figure 2b (curve B) shows the SAXS pattern for blend II at 135°C. The only maximum is at 2.0°. At 180°C the maximum is shifted in the direction of smaller scattering angles and its intensity is decreased (curve C).

Heating copolymer II is accompanied by an enhancement in the intensity of SAXS maxima and their shifting towards larger scattering angles (*Figure 2d*). The SAXS pattern of the sample in the isotropic melt (180°C), however, has one weak smeared peak.

To compare the structure parameters of the polymer blends and copolymers with those of the homopolymers, the additive scattering curves were calculated using the method described in reference 11. According to the method the X-ray scattering curve for a polymer blend $I_b(\theta)$ is the combination of the X-ray scattering curves for components $I_1(\theta)$, $I_2(\theta)$, ..., $I_n(\theta)$, taking into account their volume fractions $\phi_1, \phi_2, \ldots, \phi_n$:

$$I_b(\theta)=I_1(\theta)\phi_1+I_2(\theta)\phi_2+\ldots I_n(\theta)\phi_n$$

In this case, the components are assumed to be incompatible (total phase separation).

As seen in *Figure 1*, experimental WAXS curves are identical with calculated ones. Calculated SAXS profiles are essentially similar to experimental ones for the blends and are different from those for the copolymers.

One-dimensional correlation curves $\gamma_1(x)$ obtained by Fourier transformation of one-dimensional intensity curves according to equation (2) are given in *Figure 3*; their characteristics are listed in *Table 2*. Gradually damped oscillations with a period of 31 Å are seen on the correlation curves for blend I. Full damping of $\gamma_1(x)$ to zero occurs at 280 Å. The period of oscillations on the curve $\gamma_1(x)$ for copolymer I is 26 Å; the damping of $\gamma_1(x)$ to zero occurs considerably faster (at 160 Å). For blend I, above T_g a growth of the oscillation period is observed and a considerable increase in the distance x_m at which $\gamma_1 \to 0$.

The x_m value is known to determine the layer pack size, L, within the range of which the correlation in the arrangement of smectic layers is not changed. According to the data in *Figure 3* the pack size of blend I in a glassy LC state is 280 Å. Hence the layer pack includes 8–10 correlated spaced smectic layers. Accordingly, the correlation length in the layer packing as determined from the equation[11]

$$\gamma_1(x) \sim \exp(-x/\xi)$$

is 60 Å, which is typical of the PM-0.4 component, but significantly less than for the second component (*Table 2*).

For blend II, oscillations damp to zero at 320 Å, while for copolymer II they do so at significantly greater distances. The γ_1 function for copolymer II is characterized by narrower maxima than those for blend II.

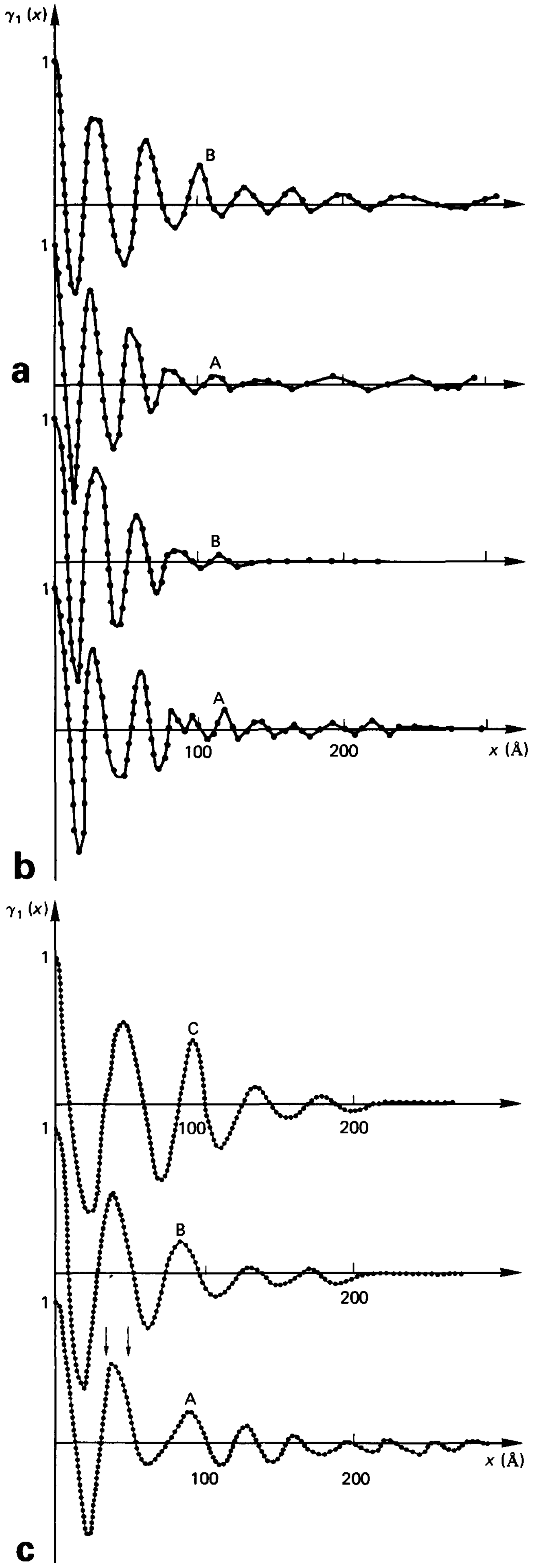
In contrast to polymer system I, heating of both blend II and copolymer II leads to a decrease in the L value with a change in the oscillation period. The mean square fluctuation of the electron density, $\Delta\bar{\rho}^2$, in both polymer systems decreases as the temperature rises.

DISCUSSION

The main problem concerning mixed compositions consists in examination of a degree of component compatibility. The change in the phase transition parameters in the polymer blends and the copolymers is mainly attributed to structure changes due to the compatibility of components such as macromolecules, in the case of the blends, or mesogenic repeated units, in the case of the copolymers, the latter involving detailed investigations on isolated macromolecules.

Valuable information on the effect of mixing homopolymers on structure changes can be obtained by comparing X-ray data for both the polymer blends and the copolymers with additive scattering curves.

It follows from comparison of the SAXS curve for blend I with the additive one in *Figure 2a* that the layer structure of the homopolymer does not change on mixing. Moreover, a degree of ordering of the layer packing for



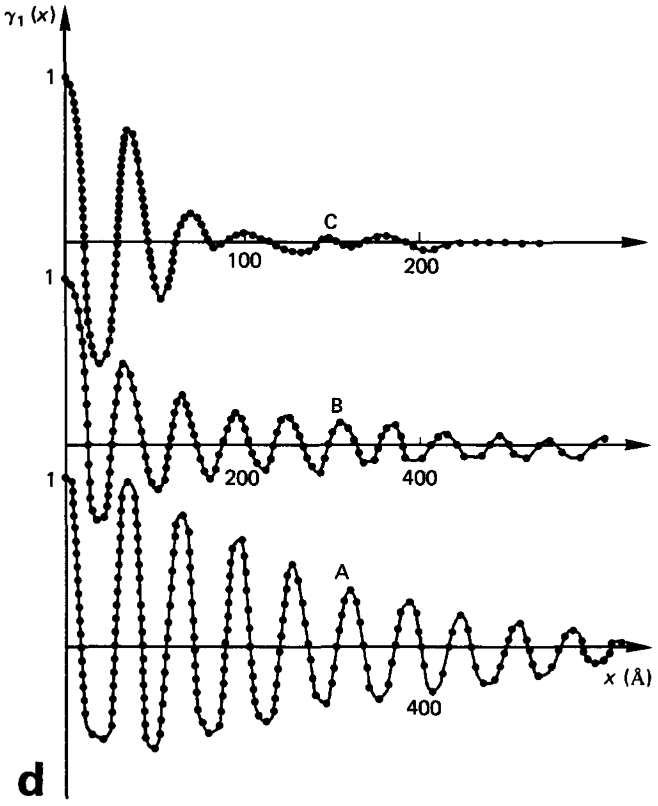


Figure 3 One-dimensional correlation curves of: (a) blend I at (A) 20°C and (B) 180°C; (b) copolymer I at (A) 20°C and (B) 180°C; (c) blend II at (A) 20°C, (B) 135°C and (C) 180°C; (d) copolymer II at (A) 20°C, (B) 135°C and (C) 180°C

the PM-0.4 component is also unchanged. As for the second component, a deterioration of the layer packing is observed, as evidenced by the weaker intensity and large halfwidth of the maxima at 3.2° ($d_2 = 26$ Å) and 3.6° ($d_3 = 22$ Å) (*Figure 4*). This is also confirmed by the data of the one-dimensional correlation analysis (*Figure 3a*). As is known, the $\gamma_1(x)$ curve for blend I represents a superposition of the distribution of the electron density waves along the normal to the smectic layer plane, typical of the separate component. The oscillation period on the $\gamma_1(x)$ curve for blend I is 31 Å, i.e. equal to the smectic layer thickness of the PM-0.4 component[15]. On the correlation curve, the periods of 22 and 26 Å, typical of the PMB-0.4 component, are absent. This is probably due to more defective layer packing of PMB-0.4 than of PM-0.4. As seen in *Table 2*, the layer pack sizes in blend I are between those in the homopolymers. Thus, against the above change in layer structure, concerning only the components in blend I, there is observed a considerable decrease in the ΔH_{cl} values of both components, while T_{cl} values are hardly changed.

The presence of the only endo-peak on the thermogram of copolymer I (*Table 1*) is indicative of the formation of a new LC structure. This is supported by comparison of the SAXS curve from the copolymer with the additive curve (*Figure 2a*). The spacing d calculated from the position of the first small-angle maximum does not agree with any of the layer packing specific to PMB-0.4 or PM-0.4. Layer packing with an overlapping of the mesogenic groups, as shown in *Figure 4d*, was proposed. According to calculation, the distance between the neighbouring main chains is equal to 30 Å, which is in agreement with experimental values (*Table 2*). The second weak

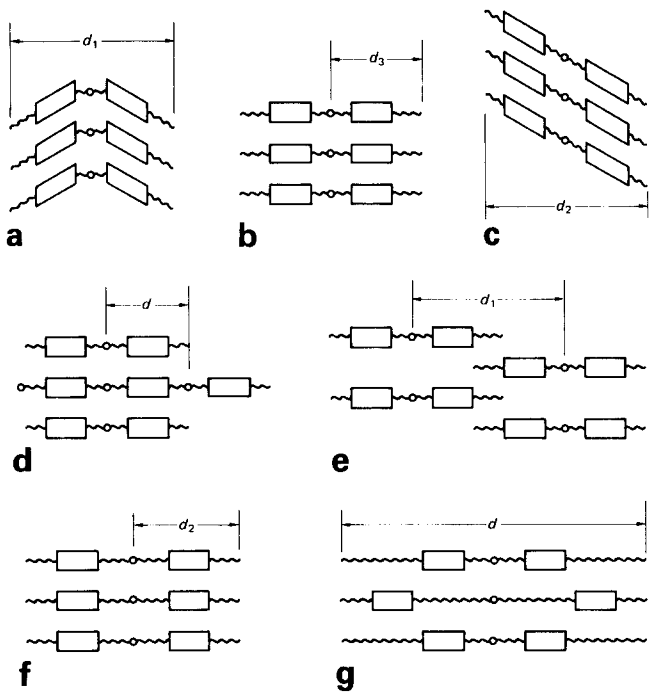


Figure 4 Layer packing models of: (a) PM-0.4; (b), (c) PMB-0.4; (d) copolymer I; (e) PMB-0.16; (f) PM-10.4; (g) copolymer II

maximum corresponds to the thickness of the smectic layer of 20 Å, indicating the one-layer packing of the mesogenic groups. The degree of ordering of the layer packing in the copolymer is lower than that in the homopolymers, as follows from the first maximum (*Figures 2a* and *2c*). Analysis of the correlation curve of the copolymer has revealed that the layer packing sizes are significantly smaller than those of the homopolymers (*Figure 3b*). They involve only four correlated smectic layers.

As comparison of the SAXS curve with the additive curve shows (*Figure 2b*), the layer packing of the components in blend II is unchanged. At the same time, an essential distinction in the intensity and halfwidth of the small-angle maxima of the experimental and calculated curves is evidence of a change in the degree of ordering of the layer packing of the components on mixing. The first maximum related to the layer structure of component PMB-0.16 ($d=46$ Å) has a large halfwidth value, whereas the maximum corresponding to the PM-10.4 layer packing displays a much lesser intensity than that on the additive curve. A decrease in the degree of ordering of the layer packing of the components is clearly reflected on the $\gamma_1(x)$ curves (*Figure 3*). The presence of oscillations on the $\gamma_1(x)$ curve is due to the periodicity in the alteration of the regions with elevated and reduced electron density, whereas the decrease in γ_1 to zero attests to damping of the correlations in the arrangement of the layers. The periodicity in the distribution of the electron density in blend II is 38 Å, which is between 46 and 32 Å, thus corresponding to the individual homopolymers. The positions of the maxima related to the components are shown in *Figure 3c* by arrows. It is obvious that the shape of the $\gamma_1(x)$ curve for blend II represents a superposition of electron density distributions for the individual components. It is the latter that obviously leads to a change in the total distribution of the electron density in the polymer blend and a broadening of the maxima on the $\gamma_1(x)$ curve.

The sizes of layer packs in blend II (320 Å) are also essentially smaller than those in the individual components (*Table 2*). The correlation length, ξ, in the arrangement of the smectic layers in blend II is only 50 Å, which is also significantly less than in the homopolymers. Thus it follows from the above data that the smectic ordering in blend II is substantially less than that in the homopolymers. This, however, does not practically influence the phase transition parameters of the components in blend II as distinct from blend I.

The SAXS curve for copolymer II has two orders of reflection, indicating a high degree of ordering in the layer structure[14,18]. The thickness of the smectic layers is 64 Å, which differs substantially from the values for the homopolymers (*Table 2*). Calculation of the length of the copolymer side chains has shown that this smectic layer thickness is attributable to the two-layer packing of the side groups. In this case the side groups are arranged in such a manner that the rigid fragments of MB-0.16 are located between the flexible spacers of M-10.4, whereas the rigid fragments of M-10.4 are located between the flexible terminal chains of MB-0.16. Such an arrangement of the mesogenic groups ensures the best dense packing (*Figure 4g*).

As follows from the $\gamma_1(x)$ curve, the layer pack sizes reached 800 Å and the correlation length is 300 Å, which substantially exceeds the corresponding values in the homopolymers (*Table 2*). Thus the LC copolymer structure is distinguished from that of the homopolymers both by the nature of the layer packing and by a higher degree of ordering of LC structure, which in no sense correlates with the low values of the phase transition parameters.

Let us consider the character of the change in the layer ordering of the polymer blends at elevated temperatures. The heating of blend I to 180°C leads to an increase in the smectic layer thickness by 1–2 Å and an increase in the layer pack sizes up to 390 Å. Accordingly, the correlation length is increased by a factor of 2. The increase in the smectic layer thickness is known to be due to the thermal expansion of the layer packing, with a coefficient of thermal expansion $K=3\times10^{-4}\,°\mathrm{C}^{-1}$, which is typical of smectic polymers[19,20].

An increase in the layer pack sizes is typical of LC polymers with mesogenic side groups connected directly to the main chain, including PM-0.4 and PMB-0.4[21]. Such an improvement of the layer ordering is related to an enhancement of the flexibility of the main chain[21,22], leading to greater freedom of movement of the mesogenic groups. Thus the thermal behaviour of polymer blend I corresponds to that of the individual components.

Heating copolymer I is attended by an increase in the smectic layer thickness, whereas the layer pack sizes do not change, practically.

The disappearance of the second small-angle maximum on the SAXS curve for blend II at 135°C is evidence of a complete destruction of the layer structure of the PM-10.4 component. As seen from the data of *Figure 2b* and *Table 2*, the type of layer structure of PMB-0.16 is unaffected, whereas the degree of ordering of the layer packing is reduced in the presence of isotropic melt of the PM-10.4 component.

Since PM-10.4 at 135°C is in isotropic melt, the $\gamma_1(x)$ curve is consistent with the electron density distribution of the PMB-0.16 component, leading to a certain narrowing of the maxima and to an increase in the period up to 42 Å. The considerable decrease in the intensity of the small-angle maxima and fluctuation of the electron density at 180°C is evidence of a deterioration of the layer packing, while the layer pack sizes are practically unaffected.

Heating copolymer II to 135°C is accompanied by a decrease of the smectic layer thickness, the layer pack sizes and the correlation length (*Figure 2d* and *Table 2*). Further heating the copolymer to 180°C causes destruction of the layer structure. At 180°C, only light tracks of inhomogeneity in the distribution of the electron density with a periodicity of 36 Å are present. The level of the electron density fluctuation drops by a factor of almost 10. The correlation length decreases to 30 Å, which is typical of the melts of common polymers[23], and only two weak maxima remain on the correlation curve. The preservation of the inhomogeneity in the electron density distribution in the isotropic melt of copolymer II can be associated with blocks of different electron densities within the macromolecule[16]. Such a correlation hole effect is well known for heterochain linear polymers and is considered in detail by de Gennes[23].

The above data on the structure of the LC polymer systems allow the following conclusions to be drawn. The components in the polymer blends keep their layer structures, but the degree of ordering of the layer packing decreases. The chemical bonding of the mesogenic units of different nature in the copolymer leads to the formation of a new type of layer packing, the degree of ordering of which may be higher than in the homopolymers.

In the polymer systems with direct connection of the mesogenic groups to the main chain, one can also observe the same temperature dependence of the structure parameters as for the homopolymers.

Heating the polymer systems containing the components with a flexibile spacer is attended by a decrease in the degree of ordering of submolecular structure.

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