*Macromolecules* **1993,** *26,* 2489–2495

# Bilayer Structures in Side Chain LC Copolymers

**H. J. Neumann, M. Jarek, and G. P. Hellmann***

*Deutsches Kunststoff-Institut, Schlossgartenstrasse 6, D-6100 Darmstadt, Germany*

*Received October 30, 1992; Revised Manuscript Received January 18, 1993*

ABSTRACT: Random copolymers $A_xB_{1-x}$ of two comonomers having sufficiently long and different side chains can form double comb conformations wherein the two types of side chains are demixed. These copolymers can build up bilayer structures, with alternating layers filled by the side chains of A and B. The structures and transition temperatures of such copolymers were studied, by DSC, light microscopy, and X-ray scattering. The main chain is always methacrylic; the side chains consist of spacer decoupled mesogens or of *n*-alkyl sequences. Three rings in the mesogenic side chains and ten methylene groups in the alkyl side chains are required for good bilayer structures. Calculations show that the bilayer structure is not hindered by the random comonomer sequence order in the $A_xB_{1-x}$ chains, unless $x$ is very large or small.

## 1. Introduction

Polymers with "side chains", i.e. with rodlike or chainlike substituents, often adopt the double comb conformation shown in Figure 1a. The main chain is extended, at least over several monomer units, and the side chains form the teeth of a double comb.

The double comb conformation enables the chains to pack in layer structures.[1-10] The main chains arrange often in a staggered fashion, so that the long period λ is equal to half the width of the double comb (Figure 1b). The side chain layers can have a crystalline or an amorphous order. The former is known from *n*-alkyl-substituted polymers[1-3] and the latter from smectic side chain LC polymers.[4-6] The flexible main chains can stabilize the order, since they connect the side chains, but can also hinder the order, since they tend toward irregular coil conformations. To optimize both effects, the main and the side chain motions are decoupled by inserting spacers.

This paper deals with random copolymers $A_xB_{1-x}$ where the comonomers A and B carry different side chains.

Whether copolymerization complicates the situation, depends on the miscibility of the side chains of A and B, as is illustrated by Figure 2. If A and B mix (*conformation I*), there is not much of a difference to a double comb of a homopolymer. If A and B do not mix, however, two chemically different combs result (*conformation II*). If only the side chains of A or B carry longitudinal dipoles, these are not compensated for along the main chain, in conformation II, as they are in conformation I or in the homopolymers.

The phase behavior and the structures of the copolymers shown in Figure 3 were investigated, by DSC, light microscopy, and X-ray scattering, to find out which comonomer pairs lead to conformation II. All polymers have methacrylic main chains. There are side chains (a) with *n*-alkyl sequences or (b) with mesogens of the *p*-alkoxybenzoic acid or the phenyl *p*-alkoxybenzoate type, carrying various end groups and being decoupled by a 6C spacer.

The first copolymers, $P(3CN_xOD_{1-x})$, have a mesogenic monomer with three phenyl rings and a CN end group (3CN) and a nonmesogenic monomer with a stearyl side chain (octadecyl, OD). Both homopolymers, P(3CN) and P(OD), exhibit ordered layer structures, the former being smectic and the latter being crystalline. Since 3CN is aromatic and OD is aliphatic, the interactions of 3CN and OD are bad enough to render the two monomers immiscible. These features favor conformation II, in the copolymers. The monomers of $P(3CN_xOD_{1-x})$ appear in the other copolymers, too. In two groups, one comonomer is always 3CN, in the other, one monomer is always OD.

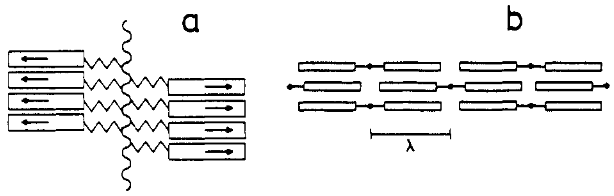


**Figure 1.** (a) Double comb homopolymer and (b) its crystalline or smectic structure (●: main chains, λ: long period). The arrows indicate dipoles.

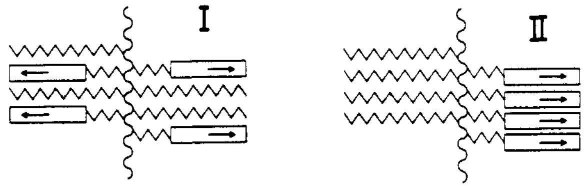


**Figure 2.** Double comb polymer with mixed (I) or demixed (II) side chains.

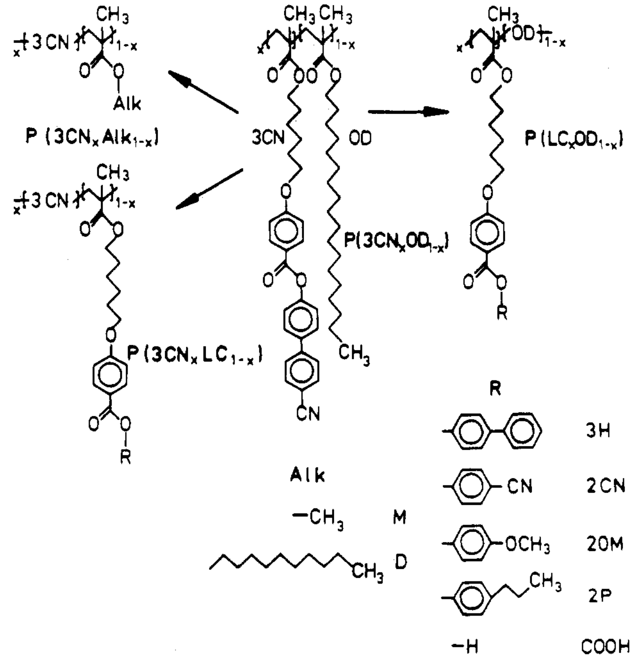


**Figure 3.** Copolymers; $x$: mole fraction.

---

* To whom all mail should be sent.

0024-9297/93/2226-2489$04.00/0

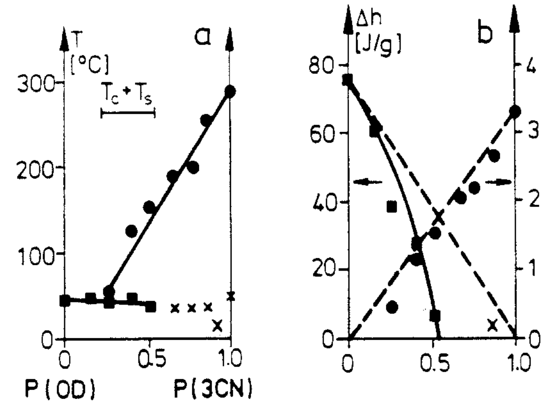


**Figure 4.** (a) Phase diagram and (b) specific heat of transition (- - -, ideal behavior) of copolymers P(3CN$_x$OD$_{1-x}$): (■) melting point $T_c$; (●) smectic transition point $T_s$; (×) glass transition temperature.

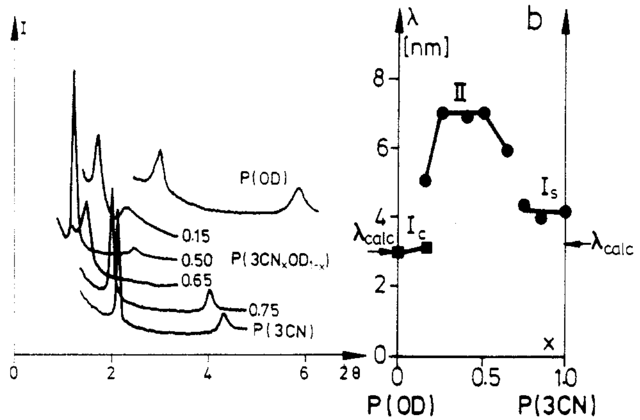


**Figure 5.** (a) X-ray curves (2θ: scattering angle) and (b) the long period of copolymers P(3CN$_x$OD$_{1-x}$).

## 2. Experimental Section

The LC monomers were synthesized as described in refs 11 and 12. Homopolymers and copolymers were prepared by radical polymerization in THF, with AIBN as the initiator (48 h, 65 °C), up to high conversion, since the copolymerizations are azeotropic.[13] The molecular weights $M_w$ are in the range 40 000–70 000, as measured by GPC with PMMA calibration. This is high enough for transition temperatures to be independent of molecular weight.[13] Polydispersities $M_w/M_n$ are in the range 1.5–2.5. The mole fraction $x$ in the copolymers is directly given by the composition of the comonomer feed, as was established by elemental analysis of products that were polymerized to low conversion.[13]

Prior to analysis, the polymers were always heated to a temperature where they are isotropic and left to cool down over hours, in the oven. Transitions were determined by DSC (at 20 K/min) and polarizing light microscopy (at 0.1–1 K/min). X-ray scattering was measured on films, in reflection (Siemens Kristalloflex 810, CuK$\alpha$ radiation).

## 3. Results

**Copolymers P(3CN$_x$OD$_{1-x}$).** The phase diagram and the heats of transition of the copolymers P(3CN$_x$OD$_{1-x}$) are shown in Figure 4, and X-ray scattering curves and the long periods of layer structures in Figure 5.

The homopolymer P(3CN) is smectic up to $T_s$ = 290 °C, the homopolymer P(OD) is crystalline up to $T_c$ = 44 °C (Figure 4a). P(OD) has the higher heat of transition (Figure 4b), but P(3CN) yields the sharper X-ray peak (Figure 5a). The layers of the smectic structure "$I_s$" of P(3CN) are thus better ordered than the layers of the crystalline structure "$I_c$" of P(OD) (Figure 5b). Comparison of the long periods λ and $\lambda_{calc}$ reveals that $I_c$ and $I_s$ are structures as shown in Figure 1b, with a staggered array of main chains. The structure of P(3CN) has λ = 4.2 nm > $\lambda_{calc}$, meaning that it is a bit extended. Due to dipole interactions, the mesogens are packed one directly on top of the other, not in a zigzag as indicated in Figure 1b. ($\lambda_{calc}$ is the length of an all-trans conformation of the side chain, from the axis of the main chain to the end group, with 0.25 nm added for half a van der Waals distance.) Extended layer structures are known from low molecular weight mesogens with CN end groups.[14,15]

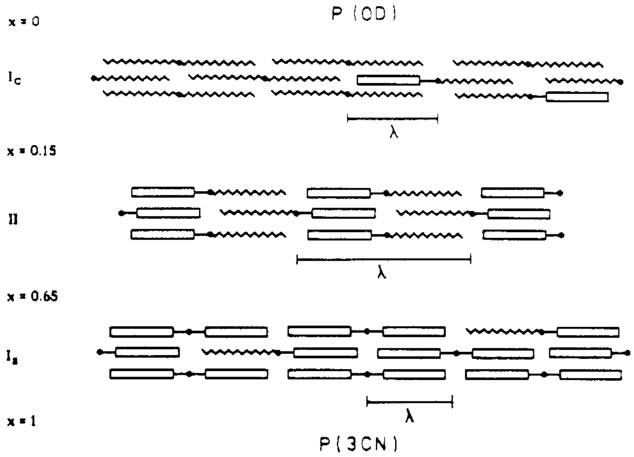


**Figure 6.** Structures of $I_c$, $I_s$, and II of copolymers P(3CN$_x$OD$_{1-x}$) between the indicated compositions $x$; λ: long period.

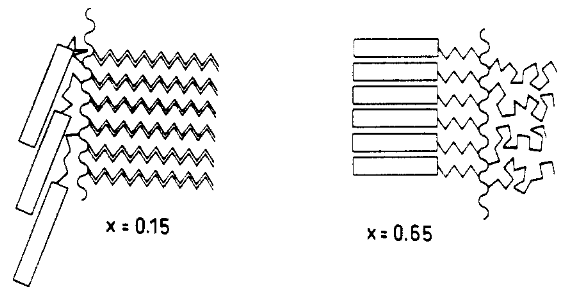


**Figure 7.** Double comb conformations of copolymers P(3CN$_x$OD$_{1-x}$) at the transition compositions $x$ = 0.15 and $x$ = 0.65.

The side chains of the copolymers P(3CN$_x$OD$_{1-x}$) seem to form a eutectic system, with the eutectic point at $x \cong 0.2$ (Figure 4a). However, there is the anomaly of an overlap region "$T_c + T_s$" where the copolymers have a melting point as well as a smectic transition.

The long periods in Figure 5b suggest the structure shown in Figure 6 and Figure 7. Copolymers not far from $x$ = 0 or $x$ = 1 still have the structures of the homopolymers, $I_c$ or $I_s$. The copolymer chains must be in conformation I (Figure 2), the side chains of the minor component being randomly dispersed between those of the major component (Figure 6).

Copolymers of intermediate $x$, in the range "II" of Figure 5b, have a long period equal to the sum of those of the homopolymers. These copolymers have their chains in conformation II (Figure 2). The structure II consists of stacks of alternating 3CN and OD layers (Figure 6). The latter are crystalline and melt at $T_c$, leaving a smectic structure, up to $T_s$.

The bilayer structure II is best ordered if both comonomers fill evenly one side chain layer. This happens around $x$ = 0.4, the midpoint of range II. The chains at $x$ = 0.4 have some OD in excess, which is apparently necessary, since the cross section of OD is smaller than that of the mesogen of 3CN.

Problems arise at the fringes of range II. The copolymer chains with $x$ = 0.15 and $x$ = 0.65 have too many side

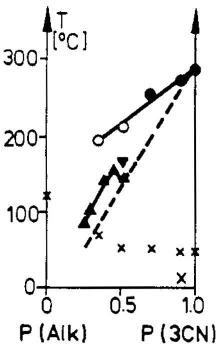


**Figure 8.** LC transitions of copolymers $P(3CN_xM_{1-x})$ (● $T_s$; ○, $T_n$), $P(3CN_xD_{1-x})$ (▼), and $P[3CN_{0.5y}\ (OD_{0.5}M_{0.5(1-y)})]$ (▲, $x = 0.5y$): (- - -) $T_s$ from Figure 4a; (×) glass transition temperature of the copolymers P $(3CN_xM_{1-x})$.

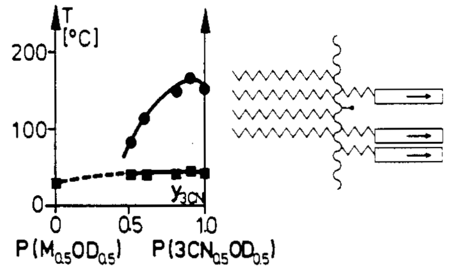


**Figure 9.** Phase diagram of the ternary copolymers $P[(3CN_yM_{(1-y)})_{0.5}OD_{0.5}]$: (■) $T_c$; (●) $T_s$.

chains of one comonomer and not enough of the other. Long periods between those of $I_c$ or $I_s$ and II are observed (Figure 5b). Possible structures are indicated in Figure 7. The major component fills one comb layer. The minor component fills the other layer, by coiling up its side chains, in case of the flexible OD ($x = 0.65$), or by tilting them, in case of the rigid 3CN ($x = 0.15$). At $x = 0.15$, where OD is the major component, its side chains probably double up. With the 3CN side chains tilted, the conformation at $x = 0.15$ should be of the $S_C$ type, instead of the $S_A$ type.

In summary, the copolymers $P(3CN_xOD_{1-x})$ can form the bilayer structure II shown in Figure 6, with demixed side chains in the separate layers. To investigate if these copolymers are exceptionally suited for structure II, others were analyzed, with less promising comonomer pairs.

**Copolymers $P(3CN_xAlk_{1-x})$.** The range $T_c + T_s$ in Figure 4a and the range II in Figure 5b are similar, seemingly indicating that crystallization of the OD side chains is necessary for good structures II. But crystallinity of the copolymers $P(3CN_xOD_{1-x})$ is very reduced in range II (Figure 4b) because crystallization takes place in the smectic state. Moreover, the copolymers yield unchanged X-ray curves, at temperatures $T_c < T < T_s$, where the OD layers are liquid. This rather shows that crystallinity is inessential, which was proved, more generally, with other copolymers $P(3CN_xAlk_{1-x})$, carrying mostly alkyl side chains unable to crystallize (Figure 3).

The phase diagrams are discussed first. Figure 8 shows that of copolymers with methyl or decyl side groups. The shorter alkyl sequences lead to higher transition temperatures.

Ternary copolymers $P[(3CN_yM_{1-y})_{0.5}OD_{0.5}]$ having both OD and methyl side groups fit into the picture (Figure 9). Like the binary copolymers $P(3CN_{0.5}OD_{0.5})$, these copolymers have enough OD side chains to fill one layer of structure II, but the 3CN side chain concentration is reduced, by insertion of the methyl side groups. The transition points are shown in Figure 9, as a function of $y$. As expected, the melting points are constant, indicating undisturbed OD layers. The smectic transition points, $T_s$, by contrast, drop considerably.

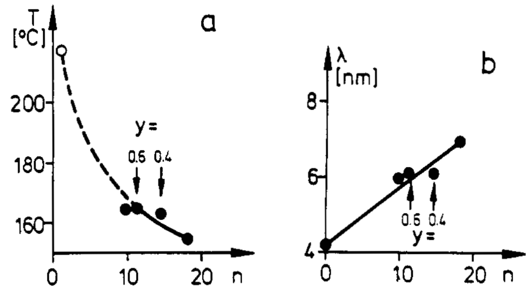


**Figure 10.** (a) LC transitions (●, $T_s$; ○ $T_n$) and (b) the long period of copolymers $P(3CN_xAlk_{1-x})$, as a function of the number $n$ of carbon atoms in the $n$-alkyl side chains. The composition $y$ of the ternary copolymes of Figure 11 is indicated.

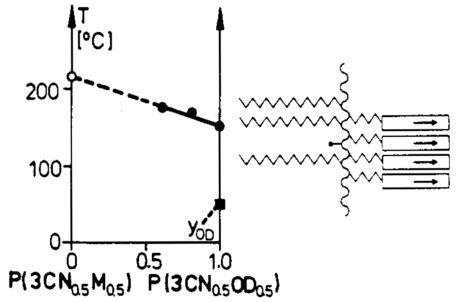


**Figure 11.** Phase diagram of ternary copolymers $P[3CN_{0.5}(OD_yM_{1-y})_{0.5}]$: (■ $T_c$; (●) $T_s$; (○) $T_n$.

This decay of $T_s$ is not in any way different from that of the binary copolymers $P(3CN_xAlk_{1-x})$. The ternary copolymers can be written in the form $P[3CN_{0.5y}(OD_{0.5}M_{0.5(1-y)})]$ and be conceived as binary copolymers, with $x = 0.5_y$ and an "alkyl comonomer" $OD_{0.5}M_{0.5(1-y)}$ having an average side chain length shorter than stearyl. In fact, the transition point curve of the ternary copolymers is in Figure 8 in line with the transition point of the binary decyl copolymer $P(3CN_{0.5}D_{0.5})$.

Figure 10a shows the transition temperatures of the binary copolymers $P(3CN_{0.5}Alk_{0.5})$, as a function of the number $n$ of carbon atoms in the alkyl side chains. To test again the effect of mixed alkyl comonomers, a second type of ternary copolymers, $P[3CN_{0.5}(OD_yM_{1-y})]$, was analyzed (Figure 11). This time, there are enough 3CN side chains to fill one layer of structure II, while the OD side chains and the methyl groups share the other. The transition temperatures are shown in Figure 11, as a function of $y$. As expected, the methyl groups have now an effect opposite to that in Figure 9. The OD crystallinity is lost, while the smectic phase is not destabilized, $T_s$ interpolating linearly. Again, there is no special effect due to mixed alkyl comonomers. The transition points of the ternary copolymers fit well into the curve in Figure 10a, if placed at an average $n$ depending on $y$.

All of the copolymers, binary or ternary, form good layer structures II, except the copolymers $P(3CN_xM_{1-x})$. The long periods of the copolymers $P(3CN_{0.5}Alk_{0.5})$ are shown in Figure 10b. They grow linearly with $n$. In the ternary copolymers, the OD side chains coil up, to fill the space left free by the methyl groups, as in Figure 7 ($x = 0.65$), where there were also not enough OD comonomers. The copolymers $P(3CN_xM_{1-x})$ are special. Structure $I_s$ was found at $x \geq 0.75$, but there was no smectic bilayer structure II at intermediate $x$. The structures at $x \leq 0.5$ are nematic, because the methyl group is not a side chain and cannot fill a separate layer.

In summary, the transition temperatures $T_s$ and the long periods λ of the copolymers $P(3CN_xAlk_{1-x})$ respond

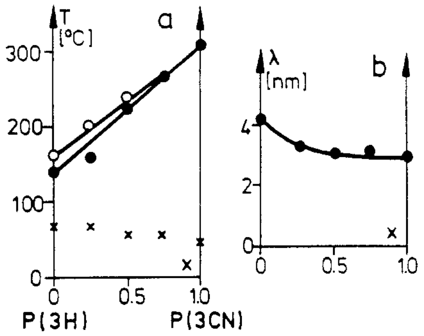


**Figure 12.** (a) Phase diagram and (b) the long period of copolymers P(3CN$_x$3H$_{1-x}$: (●) $T_s$; (○) $T_n$; (×) $T_g$.

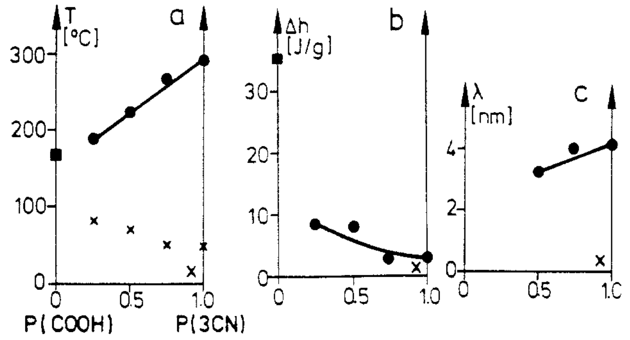


**Figure 13.** (a) Phase diagram, (b) specific heat of transition, and (c) the long period of copolymers P(3CN$_x$COOH$_{1-x}$): (■) $T_c$; (●) $T_s$; (×) $T_g$.

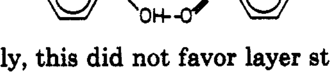
to the length of the alkyl side chains, but the quality of the bilayer structure II does not respond (with one exception) to the length or the order of the alkyl side chains.

**Copolymers P(3CN$_x$LC$_{1-x}$).** After 3CN had segregated readily from alkyl side chains, crystalline or amorphous, the suspicion arose that it might segregate from any comonomer. This was disproved with copolymers P(3CN$_x$LC$_{1-x}$) (Figure 3).

The phase diagram and the long periods of the copolymers P(3CN$_x$3H$_{1-x}$) are shown in Figure 12. The monomer 3H lacks the CN dipole of 3CN. This is a small difference, but the homopolymer P(3H) has a markedly lower $T_s$, and there is a nematic phase (Figure 12a).

Still, the side chains of 3CN and 3H mix, in the copolymers. The transition points $T_s$ interpolate linearly between those of the homopolymers. The X-ray curves showed not the slightest peak of the large long period of structure II (Figure 12b). Of course, the X-ray contrast is small, 3CN and 3H being so similar. But all combinations of the LC monomers in Figure 3 led to the same result that there is no LC–LC side chain segregation.

Therefore, 3CN was combined with the comonomer "COOH" carrying a *p*-alkoxybenzoic acid group (Figure 3). This monomer can have mesogenic properties, because the acid group can dimerize, forming a three-ring mesogen:[16]



Surprisingly, this did not favor layer structures. The phase diagram (Figure 13a) and the long periods (Figure 13c) of the copolymers P(3CN$_x$COOH$_{1-x}$) look similar to those in Figure 12. Even these two quite different monomers, 3CN and COOH, do not segregate but mix. In terms of layer structures II, the situation is even worse than with the other LC–LC copolymers. As is seen in Figure 13c, the homopolymer P(COOH) and copolymers with low $x$ do not form layers at all, although, judging from the heat of transition (Figure 13b), at least the homopolymer is crystalline. The role of the acid group is so far not understood.

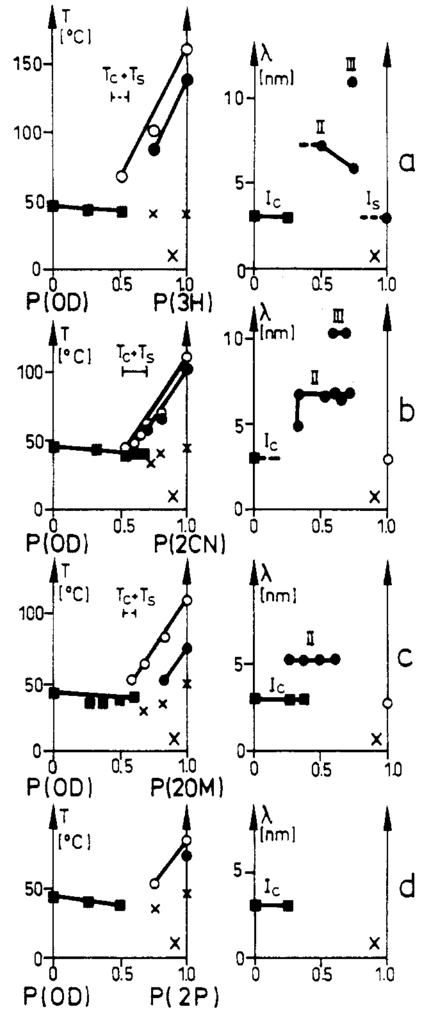


**Figure 14.** Phase diagrams (left) and the long periods (right) of copolymers (a) P(3H$_x$OD$_{1-x}$), (b) P(2CN$_x$OD$_{1-x}$), (c) P(2OM$_x$-OD$_{1-x}$), and (d) P(2P$_x$OD$_{1-x}$): (■) $T_c$; (●) $T_s$; (○) $T_n$; (×) $T_g$.

**Copolymers P(LC$_x$OD$_{1-x}$).** Since the copolymers P(3CN$_x$Alk$_{1-x}$) owed their good bilayer structures II to the 3CN side chains, the question arose if 3CN can be replaced by LC monomers of a weaker smectogenic power. This was studied with copolymers P(LC$_x$OD$_{1-x}$) (Figure 3).

Phase diagrams and long periods are shown in Figure 14. The LC monomers have mesogens with three (3H) or two phenyl rings, the latter carrying end groups of a decreasing dipole moment, CN (2CN), methoxy (2OM), or *n*-propyl (2P). All homopolymers are smectic, but the smectic state is destabilized and nematic phases appear. The transition temperature are lower the lower the number of rings present and the weaker a dipole the mesogen has.

Only the homopolymer P(3H) yields a sharp X-ray peak. Those of the homopolymers with two-ring mesogens are hardly discernable. The layer structure of the two-ring homopolymers shows up only in the oriented state, in drawn fibers.[13]

The copolymers have $T_s$ and $T_n$ decreasing at rates d$T$/d$x$ changing linearly with the transition temperatures of the homopolymers (Figure 15). On the other hand, the melting points are always similar. Consequently, the overlap region ($T_c + T_s$) gradually disappears in Figure 14a–d.

The copolymers with 3H and 2CN yield sharp peaks of structure II, those with 2OM yield broad peaks, and those

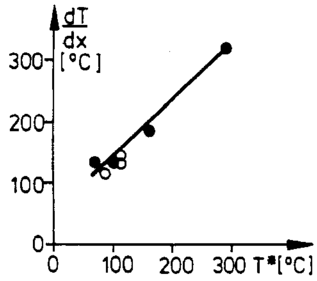


**Figure 15.** Change $dT/dx$ of the transition temperatures $T_s$ (●) and $T_n$ (○) from Figures 4a and 14, as a function of the transition temperatures $T_s$* and $T_n$* of the LC homopolymers.

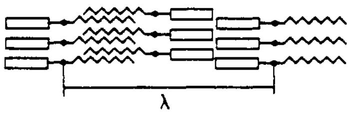


**Figure 16.** Structure III of copolymers $P(3H_xOD_{1-x})$ and $P(2CN_xOD_{1-x})$.

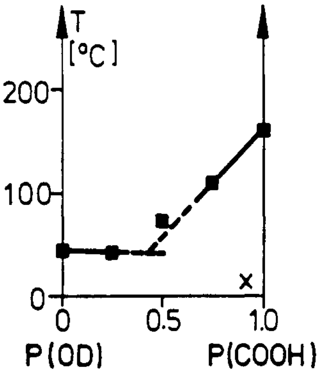


**Figure 17.** Phase diagram of copolymers $P(COOH_xOD_{1-x})$: (■) $T_c$.

with 2P do not form structure II anymore. In the copolymers with 3H and 2CN, the structure II must compete, at the transition $I_s \rightarrow$ II, with a new trilayer structure "III" having an extra large long period (Figure 14a,b). The major component, 3H or 2CN, forms in structure III a head-to-head double layer, while the minor component OD forms the third layer, as is shown in Figure 16. The balance of structures II and III is sensitive; their ratio varied sometimes irreproducibly.

Finally, copolymers $P(COOH_xOD_{1-x})$ were analyzed (Figure 3). The copolymers $P(3CN_xCOOH_{1-x})$ discussed above had not formed structure II, because 3CN and COOH mixed, in the side chain layers (Figure 13c). The comonomers COOH and OD were not expected to mix, because both homopolymers, P(COOH) and P(OD), are crystalline (Figures 4b and 13b). But the X-ray analysis yielded no peaks, except for P(OD). The phase diagram in Figure 17 can be interpreted in terms of the eutectic indicated, but the order in the phases remains obscure. The benzoic acid comonomer COOH is certainly unsuited for layer structure, in these copolymers.

In summary, the LC comonomer in copolymers $P(LC_xAlk_{1-x})$ must have three rings, or two rings with a strong dipole at the end, to yield good structures II.

## 4. Discussion

The conditions for the alternating bilayer structure II in double comb copolymers with a LC monomer are (a) that the LC monomer forms a homopolymer with a well-defined smectic structure and (b) that it has bad interactions with the other comonomer. In the frame of this study, this meant that a three-ring mesogen should be chosen for the LC comonomer and an *n*-alkyl side chain for the other comonomer.

Our hope had been that the simultaneous tendency toward order of the two comonomers might lead to copolymers $P(LC_xAlk_{1-x})$ with a structure II of a quality superior to that of the structures $I_c$ and $I_s$ of the homopolymers P(LC) and P(Alk). This hardly occurred. Structure II proved to consist of two quite independent layers. The transition points $T_s$ and the heats of transition $\Delta h_s$ were never overly high in range II, and the X-ray peaks for structure II were usually as broad or sharp as those of the structure of the better ordered homopolymer. A synergistic effect was only exhibited by the copolymers $P(2CN_xOD_{1-x})$. Their X-ray peaks are sharp for structure II, while P(OD) has a broad peak and P(2CN) has a peak only after orientation.

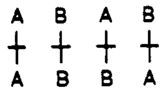
Most conclusion were drawn already in the previous sections. This section deals with two more questions, i.e. (a) why the main chains of random copolymers permit segregation of the side chains into two different layers, and (b) how the copolymers, in particular the copolymers $P(LC_xAlk_{1-x})$, compare with related systems.

### Segregation of Side Chains

The side chains of double comb polymers point away from the main chain, in an alternating fashion, thus forming an evenly filled double comb. Atactic homopolymers have a problem with this since the side chains are connected to the main chain not in alternating but in random directions. The main chain and the spacers must adjust in order to fit the side chains cleanly into the comb layers. This seems to work easily.

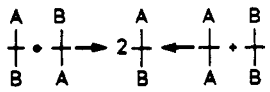
Atactic random copolymers have the same problem if forming double combs in conformation I, but they have even more problems if forming the double combs in the segregated bilayer conformation II (Figure 2). Segregation of the side chains into different combs is easy only in alternating copolymers. To clarify this point, the difficulties caused by a random comonomer sequence were studied by computer simulation.

Double comb copolymers $A_xB_{1-x}$ of two side chains A and B consist of the four diads

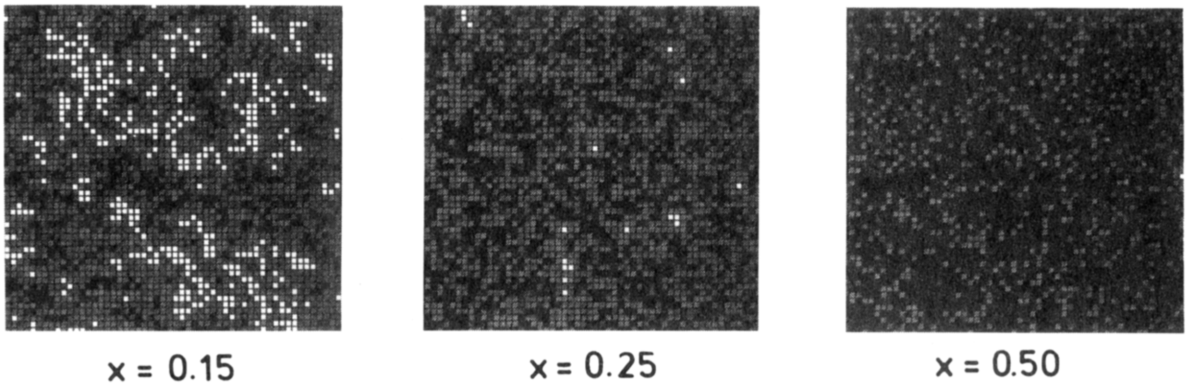


Their sequence in an array of chains was calculated on a square lattice, with infinitely long main chains in the horizontal direction (Figure 18). Considering diads instead of monomers ensures that the two comb layers are evenly filled.

A copolymer $A_{0.5}B_{0.5}$ in an ideal structure II has only diads AB (or only diads BA). If the diad sequence is random, in contrast, there is no order at all. To introduce order in an array of random copolymer chains, pairs of diads were changed by two mechanisms:



The left involves a rotation of one diad, and the right a rotation of one side chain each in both diads. There should usually be enough flexibility in the main chain segments and the spacers of A and B for these adjustments, to which all pairs of next-neighbor diads were subjected (also along the diagonals).



x = 0.15 x = 0.25 x = 0.50

**Figure 18.** Order of diads in an array of random double comb copolymers $A_xB_{1-x}$ (chains running horizontally in each line): (black) AB; (white) BA; (gray) AA or BB diad.

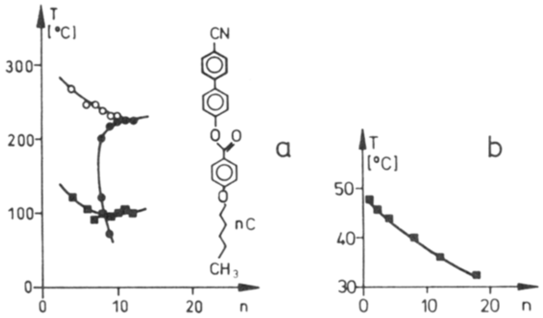


**Figure 19.** LC transition temperatures (●, $T_s$; ○, $T_n$) and melting points (■, $T_c$) of (a) the indicated monomeric LC compounds and (b) copolyacrylates P($ODA_xAlkA_{1-x}$) as a function of the number $n$ of carbon atoms in the $n$-alkyl tail or comonomer.

As is seen in Figure 18 for copolymers with $0 < x \leq 0.5$, considerable order can be achieved. Closer to $x = 0$, the matrix is made of BB diads, with dispersed clusters of AB and BA diads, and a structure I results. Since AB and BA appear in equal amounts, there is no contribution of structure II. Closer to $x = 0.5$, however, the matrix is made of AB diads (or alternatively of BA diads), meaning that the copolymers adopt structure II. The percolation threshold at the transition I → II, where the structure II takes over, is at $x = 0.2$.

This means that random double comb copolymers should indeed be able to adopt the pattern of structures $I_c$, $I_s$, and II shown in Figure 6, given sufficient flexibility in the main chain and the spacers. Figure 18 predicts that structure II is never perfect, in random copolymers, but that the transition I → II is sharp, as was indeed observed. (The model treats transitions as those shown in Figure 7 as regular structures II.) The sharp transition does not exclude metastable coexistence of domains of different structures, as was observed especially at the transitions $I_c$ → II of the copolymer P($2OM_xOD_{1-x}$) (Figure 14c).

## Comparison with Other Systems

The copolymers P($LC_xAlk_{1-x}$) with $n \geq 10$ adopted the smectic bilayer structure II while the methyl copolymers P($LC_xM_{1-x}$) were nematic.

The same has been observed in the series of the monomeric LC compounds shown in Figure 19a (from ref 17). These LC compounds are very similar to the heterodiads 3CN–Alk in the copolymers. It is only that the mesogen and the alkyl sequence are now directly connected, instead of being separated by a copolymer main chain segment and spacers. The variable $n$ in Figures 10a and 19a disregards this difference, but the two figures are quite similar.

The smectic state appears suddenly, in Figure 19a, at $n \geq 8$. The compound with $n = 9$ was found to exhibit a bilayer structure very similar to the structure II in Figure 6.[17] This compound forms, at lower temperatures, a reentrant nematic phase, indicating that the bilayer arrangement is not very stable yet.

Evidently, a bilayer structure needs side chains that are long enough to be conformationally decoupled. That this is not granted for short side chains is also reflected by the transition temperatures, which decay with increasing $n$. Parts a and b of Figure 19 show that this decay is observed also for melting points. In Figure 19b, copolyacrylates P($ODA_{0.5}AlkA_{0.5}$) are shown (from ref 18). These copolymers have stearyl (ODA) and alkyl (AlkA) side chains, of which only the ODA side chains crystallize.

The simple theory of melting point depression predicts for the latter copolymers

$$\mu_c = \Delta h_c^* \left( \frac{T_c - T_c^*}{T_c^*} \right) = \mu_{mix} \tag{1}$$

$$T_c = T_c^* \left( 1 + \frac{\mu_{mix}}{\Delta h_c^*} \right) \tag{2}$$

The specific chemical potential of the copolymers changes by $\mu_c$ upon crystallization and by $\mu_{mix}$ due to intermolecular mixing of the two comonomer units. $T_c$ and $\Delta h_c$ are the melting points and the heat of melting, a star indicating the crystallizing homopolymer.

With the assumptions of the "exclusion model", (i) total side chain segregation in the solid state and (ii) thorough side chain mixing in the liquid state, one obtains[20]

$$\frac{1}{T_c} \frac{dT_c}{dx} \cong \frac{1}{n} \frac{RT_c^*}{\Delta h_c^*} \tag{3}$$

where $n$ is the number of carbon atoms, i.e. the "degree of polymerization" of the alkyl side chains. Equation 3 was originally derived for mixtures, but it is instructive to use it also for crystalline or LC copolymers (for LC with an index exchange c → s, n). Equation 3 predicts correctly (a) that the transition temperatures decay faster the lower the heat of transition is, i.e. that $dT_i/dx \gg dT_c/dx$ (Figures 4, 9, and 14), because $\Delta h_i \ll \Delta h_c$ ($i$ = s, n), and (b) that they decay faster the higher the transition temperatures of the LC homopolymers are, i.e. that $dT_i/dx \propto T_i^*$ (i = s, n, Figure 15).

However, eq 3 predicts also that the transition points should increase with n, which is at odds with Figures 10a and 19. The transition points decrease with n. The model assumptions (i) and (ii) fail for short alkyl sequences, because short side groups are too strongly coupled to the mesogen (Figure 19a) or to the main chain segment (Figures

10 and 19b). Only the outer parts of longer alkyl side chains are conformationally independent enough to demix effectively, as is required for eq 3.

In summary, good bilayer structures II need, in LC monomers and copolymers alike, alkyl sequences of a minimum length of approximately $n = 10$. Currently, it is tested if this number can be reduced with fluorinated side chains.

**Acknowledgment.** We should like to thank the Röhm GmbH for some of the LC monomers. Financial support from the Bundesminister für Wirtschaft through the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen (AIF) is gratefully acknowledged.

## References and Notes

(1) Ailhaud, H.; Gallot, Y.; Skoulios, A. *C. R. Acad. Sci. Paris* **1968**, *C267*, 139.
(2) Plate, N. A.; Shibaev, V. P. *J. Polym. Sci., Macromol. Rev.* **1974**, *8*, 117.
(3) Magagnini, P. L. *Makromol. Chem. Suppl.* **1981**, *4*, 223.
(4) Wendorff, J. H.; Finkelmann, H.; Ringsdorf, H. In *Mesomorphic Order in Polymers*; Blumstein, A., Ed.; ACS Symposium Series 74; American Chemical Society: Washington, DC, 1978; p 22.
(5) Tsukruk, V. V.; Shilov, V. V.; Lipatov, Y. S. *Makromol. Chem.* **1982**, *183*, 2009.
(6) Diele, S.; Hisgen, B.; Reck, B.; Ringsdorf, H. *Makromol. Chem. Rapid Commun.* **1986**, *7*, 267.
(7) Alimoglu, A. K., Ledwith, A.; Gennell, P. A.; Lacy, F. R. S.; Lacy, D. *Polymer* **1984**, *25*, 1342.
(8) Lipatov, Y. S.; Tsukruk, V. V.; Lokhonya, O. A.; Shilov, V. V.; Amerik, Y. B., Konstantinov, I. I.; Grebneva, V. S. *Polymer* **1987**, *28*, 1370.
(9) Duran, R.; Guillon, D.; Gramain, P.; Skoulios, A. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 181.
(10) Frere, Y.; Yang, F.; Gramain, P.; Guillon, D.; Skoulios, A. *Makromol. Chem.* **1988**, *189*, 419.
(11) Finkelmann, H.; Ringsdorf, H.; Wendorff, H. J. *Makromol. Chem.* **1978**, *179*, 273.
(12) Portugall, M. Dissertation, Mainz, 1981.
(13) Braun, D.; Neumann, H. J.; Hellmann, G. P. *Makromol. Chem.* in press.
(14) Leadbetter, A. J.; Durrant, J. L. A.; Rugman, M. *Mol. Cryst. Liq. Cryst. Lett.* **1977**, *34*, 231.
(15) Bonsor, D. H.; Leadbetter, A. J.; Temme, F. P. *Mol. Phys.* **1978**, *36*, 1805.
(16) Gray, G. W.; Winsor, P. A., Eds. *Liquid Crystals and Plastic Crystals*; Ellis-Hardwood: New York, 1974; Vol. 1, Chapter 4.
(17) Sigaud, G.; Tihn, N. H.; Hardouin, F.; Gasparoux, H. *Mol. Cryst. Liq. Cryst.* **1981**, *69*, 81.
(18) Jorda, E. F.; Actymyshyn, B.; Speca, A.; Wrigley, A. N. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 3349.
(19) Sanchez, I. C.; DiMarzio, E. A. *Macromolecules* **1971**, *4*, 677.
(20) Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 279.