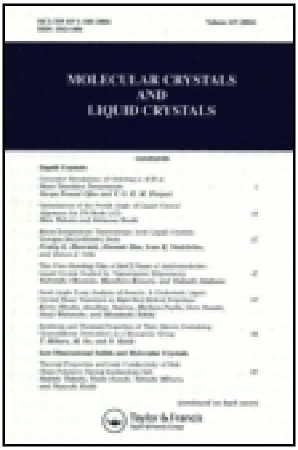


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Rigid Rod Polymers Having Flexible Side Chains. 3. Structural Investigations on a Novel Layered Mesophase Formed by Thermotropic Poly(1,4-phenylene-2,5-dialkoxy terephthalate)s

M. Ballauff [a] & G. F. Schmidt [b]
[a] Max-Planck-Institut für Polymerforschung, Postfach, 3148, 65 MAINZ, FRG
[b] Institut für Physikalische Chemie, Universität Mainz, Welderweg 15, 65, MAINZ, FRG

To cite this article: M. Ballauff & G. F. Schmidt (1987): Rigid Rod Polymers Having Flexible Side Chains. 3. Structural Investigations on a Novel Layered Mesophase Formed by Thermotropic Poly(1,4-phenylene-2,5-dialkoxy terephthalate)s, Molecular Crystals and Liquid Crystals, 147:1, 163-177

To link to this article: http://dx.doi.org/10.1080/00268948708084632

Mol. Cryst. Liq. Cryst., 1987, Vol. 147, pp. 163–177
Photocopying permitted by license only

Printed in the United States of America

Rigid Rod Polymers Having Flexible Side Chains. 3. Structural Investigations on a Novel Layered Mesophase Formed by Thermotropic Poly(1,4-phenylene-2,5-dialkoxy terephthalate)s

M. BALLAUFF†
Max-Planck-Institut für Polymerforschung, Postfach 3148, 65 MAINZ, FRG

and

G. F. SCHMIDT
Institut für Physikalische Chemie, Universität Mainz, Welderweg 15, 65 MAINZ, FRG

(*Received December 15, 1986*)

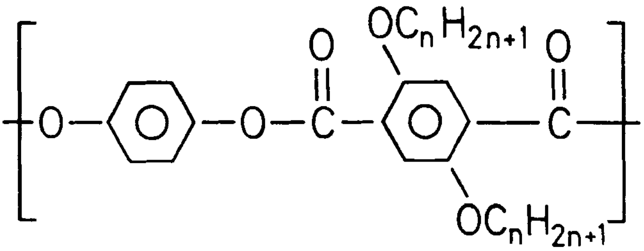
A series of thermotropic poly(1,4-phenylene-2,5-di-n-alkoxy terephthalate)s with the length of the n-alkoxy side chains being varied between $n = 2$ and $n = 18$ carbon atoms has been examined by optical microscopy, x-ray diffraction and DSC. All members of this series have a rigid backbone with attached flexible side chains and form mesomorphic melts. In polymers with side chains shorter than 7 C-atoms the mesophases are found to be nematic; longer side chains lead to the observation of a novel, layered mesophase (modification A). The layer spacing in this mesophase as revealed by x-ray analysis is shown to increase linearly with increasing length of the side chains. The observed increment of 1.25Å per CH_2 unit shows the side chains to protrude normal to the main chain axis. A comparison of the molecular size of the polyester molecule with the layer spacing suggests that the side chains interdigitate in the mesophase. A similar layered structure with a smaller increment (0.82Å/CH_2 unit) is found in the solid state. In contrast to modification A this structure (modification B) is highly crystalline. Packing considerations again suggest interdigitated side chains whereas the smaller spacing of the layers points to a staggered arrangement of the main chains.

---

†To whom all correspondence should be addressed

INTRODUCTION

Rigid chain polyesters usually exhibit melting points far above the temperature of decomposition which makes these materials difficult to process and to study. In addition, the strong steric repulsion of the rodlike molecules shifts the nematic–isotropic transition to temperatures above thermal decomposition even at comparatively small degrees of polymerization.[1,2] In a recent publication[3] it has been shown that these problems may be circumvented by appending flexible side chains to the rigid backbone of the stiff polymer. Based on the Flory lattice model of nematic liquids[1,4] these considerations demonstrated that the side chains act very similar to a solvent by diluting the steric and the attractive interactions between the rods. Hence, the melting point and the nematic–isotropic transition temperature should be adjustable by the volume fraction of flexible side chains affixed to the rigid cores. Investigations of Lenz and coworkers[5] as well as of Krigbaum *et al.*[6] on stiff chain polyesters based on terephthalic acid and 2-n-alkyl hydroquinones showed indeed that the alkyl side chains lower the melting point and the transition temperature drastically. Recently, a similar system derived from hydroquinone and 2,5-di-n-alkoxy terephthalic acid has been introduced[7]:



As is the case for the system described by Lenz[5] even short side chains (n = 2, n: number of carbon atoms in the alkoxy side chains) suffice to decrease the melting point to approximately 250°C leading to the observation of a nematic mesophase. If longer side chains are appended to the rigid backbone ($n > 6$), a new type of mesophase consisting of a layered structure[7] has been observed. A similar mesophase has been found in the course of a study of polyamides derived from poly(1,4-phenylene terephthalamide)s substituted with n-alkoxy chains.[8] For further elucidation of this mesophase we present in this communication a X-ray study conducted on the above series of polyesters with n varying between 2 and 18. The synthesis of the members of this series with $n = 2,4,6,12,16$ has been reported in Reference 7; the properties of the intermediates and the monomers belonging to the remainder of this series ($n = 3,8,10,11,14,18$) will be given in a forthcoming publication.

EXPERIMENTAL

The X-ray reflections ($1 < 2\theta < 32$) were observed in reflection mode using Ni-filtered Cu-K_α radiation. All diffractograms are reported as observed. Samples for measurements were either a powder obtained by precipitation of the polymers from solution or bulk material melted in a sample holder equipped with an electric heating. The temperature was controlled better than ±0.2°C. The mesophases were observed with a Zeiss photomicroscope III equipped with a Mettler hot stage. All differential scanning calorimetry (DSC) measurements reported herein were performed on a Perkin-Elmer DSC-7. Intrinsic viscosities were determined at 25°C in chloroform using an Ubbelohde-type capillary viscometer.

RESULTS AND DISCUSSION

As shown by DSC in Reference 7 the polyesters under consideration here exhibit a low temperature ($-5°C$ – $+60°C$) solid-solid transition of first order which may be ascribed to an increase of conformational and positional disorder of the side chains similar to the defect structure ("rotator phase") found in n-alkane crystals.[9,10] Depending on molecular weight the transition to the mesophase occurs at temperatures between 100 and 200°C.[7]

Figure (1a–d) shows the typical results from the X-ray analysis obtained from a polyester with $n = 16$ side chains. Here, Figure (1a) refers to a material precipitated from solution; Figure (1b) to the same sample after being annealed at 90°C for 6 hours; Figure (1c) shows the diffraction pattern obtained for the sample being in its mesophase. Finally, Figure (1d) displays the data measured on the sample after being cooled down to room temperature from the mesophase. In all cases studied so far, the x-ray diffractograms of the polyesters being precipitated from solution show distinct reflections denoted as A and B in the region $1 < 2\theta < 5$. As is obvious from a comparison of (1a) and (1b), the peak A at lower angle increases with increasing temperature whereas the peak B at a slightly higher

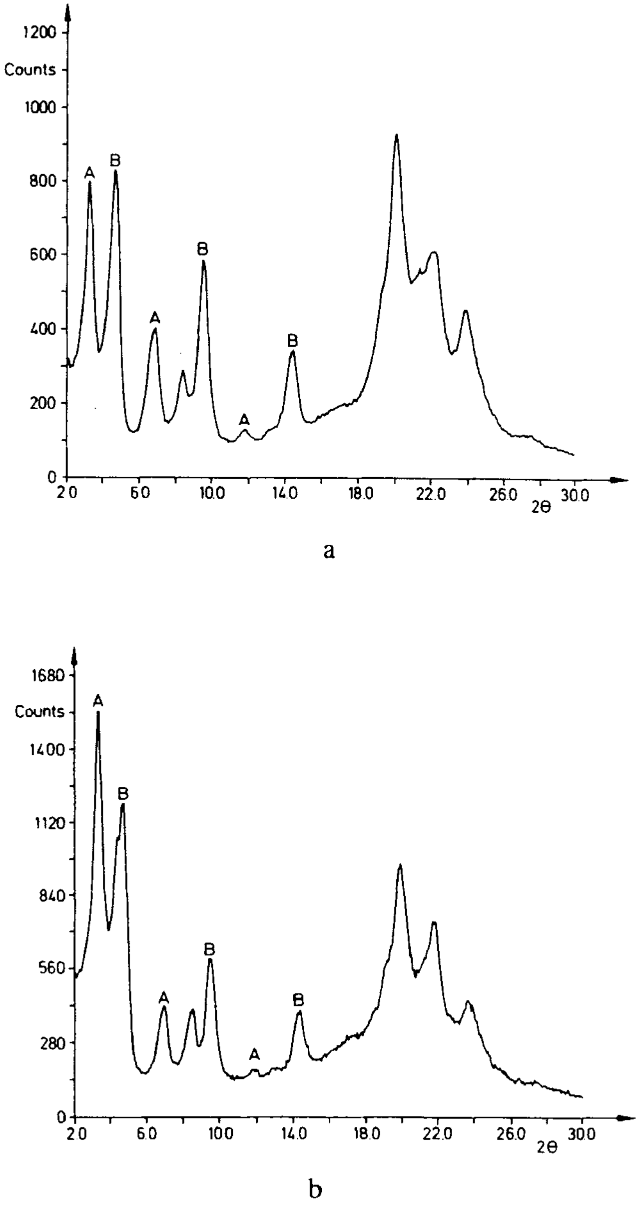
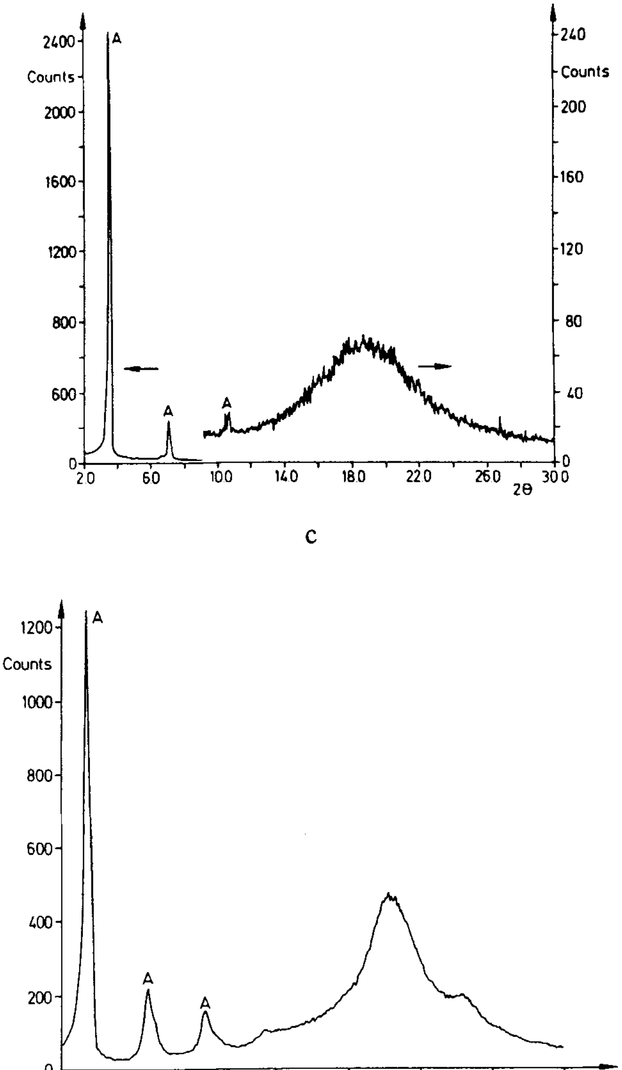


FIGURE 1(a–d) X-ray diffractograms for a polyester with hexadecyloxy (n = 16) side chains; (1a): precipitated material; (1b): after annealing at 90°C for 6 hours; (1c): of the meosphase at 120°C; (1d): after cooling down to room temperature.



c

d

FIGURE 1 (*continued*)

angle decreases. This finding suggests the existence of two separated phases having different structures to be present in the precipitated polyester. The sharp reflections at low scattering angles together with their higher orders (cf. Figure (1a) and (1b)) clearly indicate both phases A and B to exhibit a layered structure.[7] In Figure (2) the corresponding layer spacings *d* from reflections A and B as calculated by Bragg's law are plotted versus the number of carbon atoms in the alkoxy side chains.

In addition to the reflections attributed by structures A and B the polyesters with short side chains ($n = 2$–4) precipitated from solution exhibit a further reflection of low intensity in the low angle region (curve C, Figure (2)). If the side chains are long enough ($n > 6$) heating of the precipitated material leads to the disappearance of the set of reflection characteristic of structure B (Figure (2), curve B). Only the reflections caused by the layered structure of the mesophase together with an amorphous halo (cf. Figure (1c)) remain above the crystal to mesophase transition.

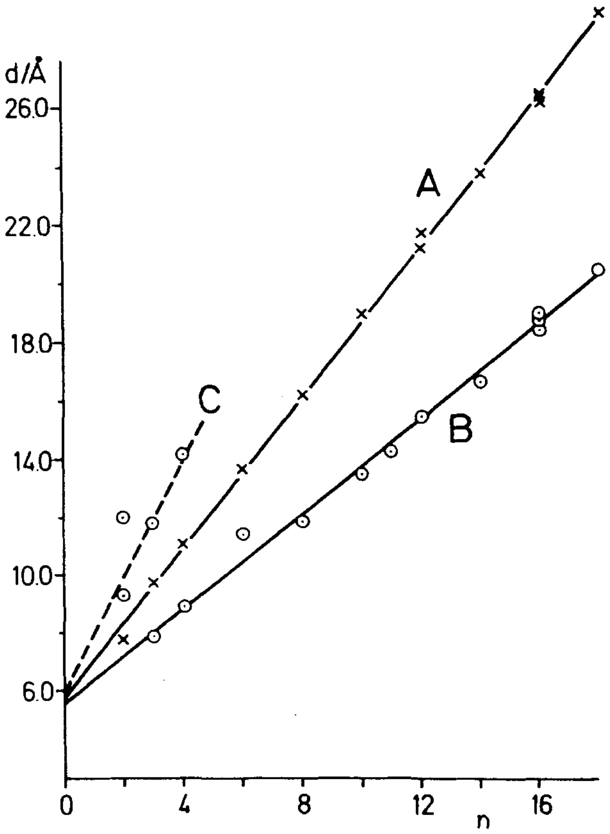


FIGURE 2 Layer spacing *d* calculated according to Bragg's law from the low angle x-ray reflections of the precipitated material as function of the n, number of carbon atoms in the side chains.

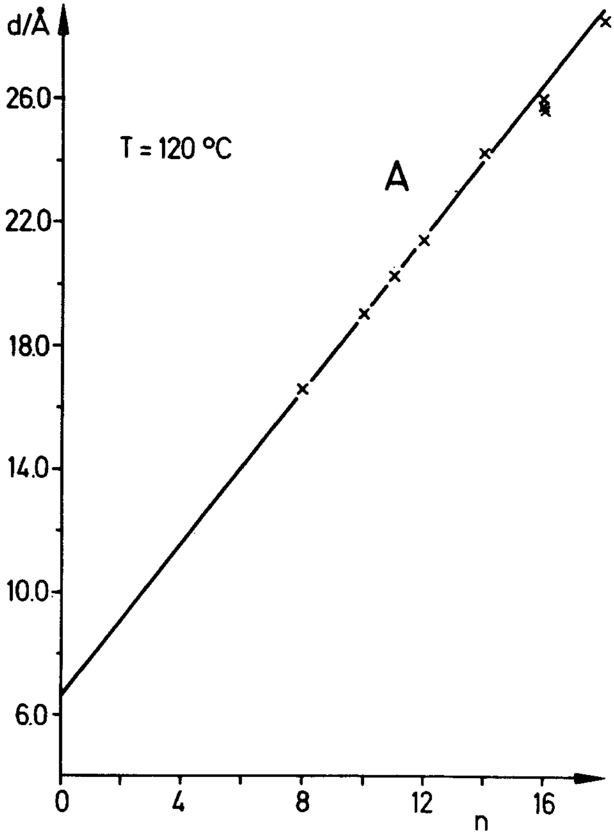


FIGURE 3 Layer spacing *d* calculated according to Bragg's law from the low angle x-ray reflection of the mesophase at 120°C as function of n, the number of carbon atoms in the side chains.

In Figure (3) the values of the layer spacings *d* observed at the samples being in the mesophase at 120°C are plotted versus *n*, the number of carbon atoms in the side chain. The slope of the curve is found to be 1.25Å per CH_2 unit. The texture of the mesophase observed under crossed polarization filters is displayed in Figure (4a) and shows in addition to the X-ray evidence that the mesophase is not of the nematic type.

For comparison, Figure (4b) displays the textures exhibited by a small droplet of the melt of the polyester bearing ethoxy side chains. The less well focussed areas in Figure (4b) originate from layers not thin enough to exhibit a meaningful texture. The Schlieren texture of the droplet demonstrates that the mesophase obtained in case of short side chains is nematic.

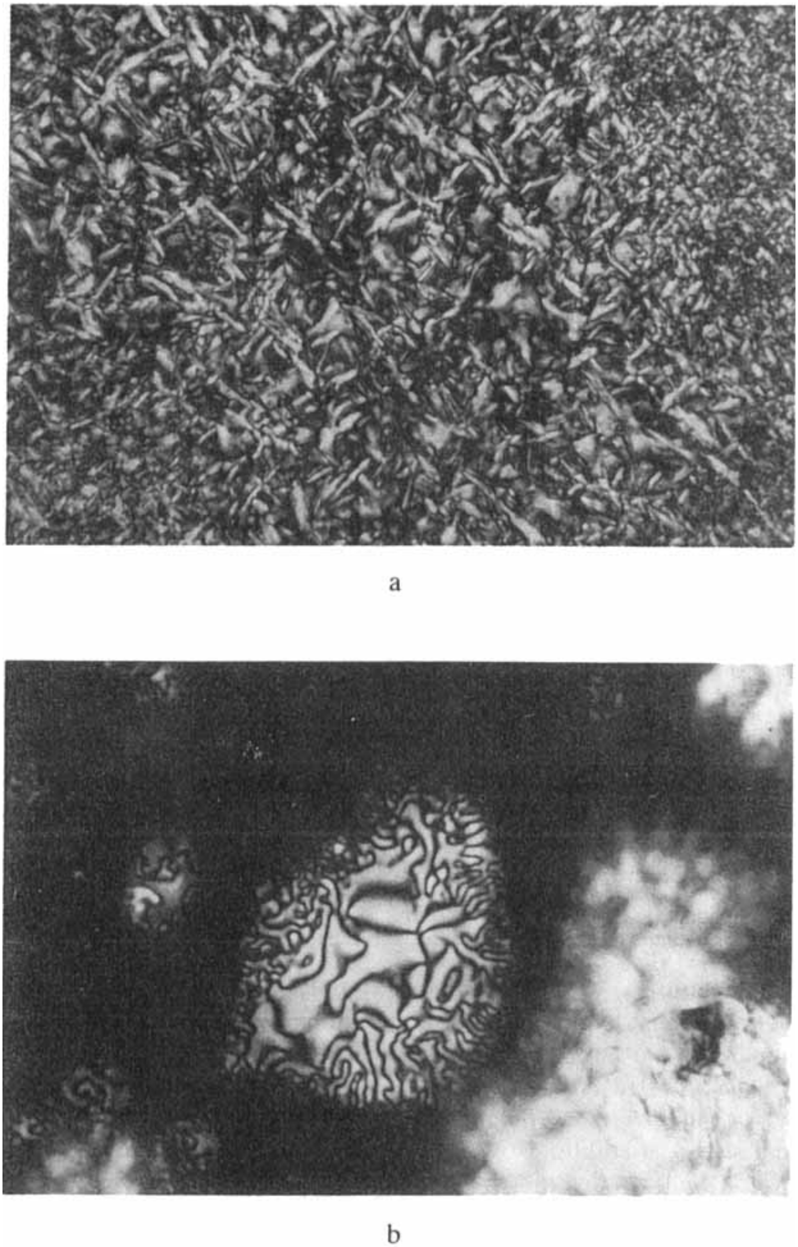
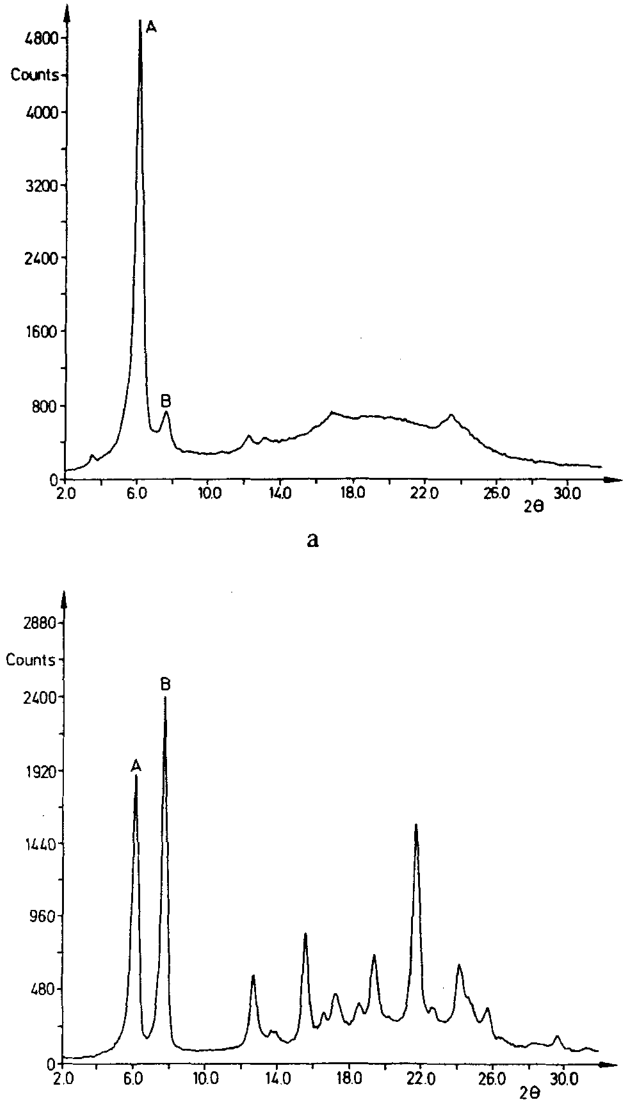


FIGURE 4a Textures of the layered mesophase (n = 16, T = 120°C) observed under crossed polarizers; (4b) Texture for the nematic melt of a polyester with short (n = 2) side chains. See Color Plate I.



a

b

FIGURE 5a, b X-ray diffractograms of the polyester bearing hexoxy side chains (*n* = 6); (5a): precipitated material; (5b): precipitated material after annealing for 0.5 hours at 170°C.

Contrary to the situation encountered in the case of long side chains, heating of polyesters with n = 4 and n = 6 is followed by the disappearance of the peak originating from the wider spacing (cf. Figure (5a, b)).

As is obvious from a comparison of Figure (5a) (precipitated material) with Figure (5b) displaying the X-ray pattern after 0.5 hours of annealing at 170°C, the reflection of structure A has become weaker whereas a strong reflection with the smaller spacing (curve B in Figure (2)) has appeared. Hence, structure B is the thermodynamically more stable modification under these circumstances for shorter side chains. The appearance of a number of well-defined peaks in the wide angle region (see Figure (5b)) associated with modification B furthermore demonstrates this structure to be highly crystallized. The corresponding X-ray pattern for A (Figure (5a) suggests a considerable lateral disorder in this modification. Still higher temperatures lead to a mesomorphic melt, most probably of the nematic type.

If the mesophase resulting from polyesters with long side chains ($n \geqslant 8$) is cooled again to room temperature, the modification B exhibiting the smaller spacing is not recovered but a certain ordering takes place under conservation of the layered structure (cf. Figure (1d)). The layer spacings obtained from the polymers in this phase at room temperature are displayed in Figure (6).

The slope of this curve coincides with the value found for structure A in the mesophase (see Figure (1c)) but the intercept is slightly higher. Table I summarizes the X-ray data together with the intrinsic viscosities of the various polymers measured in chloroform at 25°C and the transition temperatures. The transition from the mesophase to the isotropic state takes place within a rather broad temperature range (20°C), the data given in column 3 of Table I only give the temperature where the last anisotropic part of the melt vanishes as observed by polarizing microscopy. From the present results it is obvious that the dependence of the layer spacing d on molecular weight is very small in relation to the limits of error. Thus polymer samples can be compared with regard to the layer spacing d even if their molecular weights as characterized by the intrinsic viscosities differ markedly. But the temperature for the transition from the layered mesophase to the isotropic state clearly increases with increasing intrinsic viscosity, i.e., with higher molecular weight (see data for $n = 16$ in Table I). All layer spacings of the structure A for a given side chain length were recorded at the same temperature (120°C). Additional experiments revealed a decrease of ca. 1.2Å/100°C for the polyester with $n = 18$ with increasing temperature. Materials with shorter side chains showed a similar but less pronounced negative temperature coefficient of the layer spacing in the mesophase.

From these observations the following conclusion may be drawn:

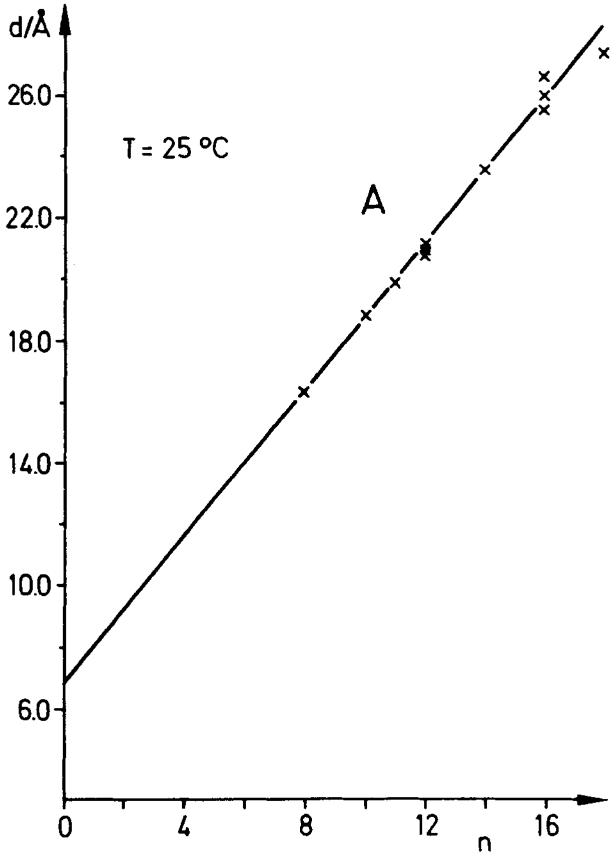


FIGURE 6 Layer spacing *d* calculated according to Bragg's law from the low angle x-ray reflection in the solid state after cooling down from the mesophase.

The polyesters under consideration here form layered, smectic-like mesophases if $n > 4$. If the side chain is long enough ($n > 8$), these mesophases are thermodynamically stable in the molten state. Only for $n = 4$ and $n = 6$, the material becomes crystallized upon annealing, further heating leads to the formation of a nematic melt. In the crystalline state (cf. Figure (2), lower curve), in the mesophase (Figure (3)), as well as in the crystalline form obtained by cooling of the mesophase (cf. Figure (1d) and (6)), a linear relationship between the layer spacing *d* and the number of carbon atoms in the side chains is observed. For the mesophase and for the material crystallized within the layers (Figure (6)) the increment $d/n = 1.25$Å indicates that the side chains protrude normal to the main chain direction. In addition,

TABLE I

Intrinsic viscosities, transition temperatures, and layer spacings of the poly(1,4-phenylene-2,5-dialkoxyterephthalate)s

n	$[\eta]/\frac{\text{dl}}{\text{g}}$	T_i/°C	d/Å at 300 K	d/Å at 393 K	d/Å at r.t.
2	—[a]	>350	12.0; 9.3(C); 7.8(A)	—	—
3	—	~300	11.8(C); 9.8(A); 7.9(B)	—	—
4	0.64	~298	14.2(C); 11.1(A); 8.9(B)	—	—
6	0.65	~250	13.7(A); 11.5(B)	—	—
8	0.19	~200	16.2(A); 11.9(B)	16.6(A)	16.3(A)
10	1.29	~230	19.0(A); 13.5(B)	19.1(A)	18.8(A)
11	0.32	~200	14.2(B)	20.3(A)	19.8(A)
12	0.83	~220	21.2(A);	21.5(A)	21.1(A)
12	0.38	~215	21.8(A); 15.5(B)	21.4(A)	20.7(A)
14	0.48	~210	23.8(A); 16.7(B)	24.2(A)	23.5(A)
16	0.12	~190	26.3(A); 18.8(B)	25.6(A)	26.5(A)
16	0.37	~200	26.4(A); 18.8(B)	26.0(A)	25.8(A)
16	0.5	~200	26.3(A); 19.0(B)	26.0(A)	25.4(A)
16	1.14	~215	26.2(A); 18.4(B)	25.7(A)	25.9(A)
18	0.39	~190	29.3(A); 20.6(B)	28.5(A)	28.5(A)

[a] not soluble in $CHCl_3$

Legend

Column 1: Number of carbon atoms in the alkyl side chains;
Column 2: Intrinsic viscosity measured at 25°C in chloroform.
Column 3: Transition temperature from the mesophase to the isotropic state;
Column 4: Layer spacings measured at room temperature on the precipitated polyester;
Column 5: Layer spacing in mesophase;
Column 6: Layer spacing after cooling down to room temperature.

the length of the side chains solely governs the width of the layers in both modifications A and B. Extrapolation to $n = 0$ of both phases for the precipitated material (see Figure (2)) consistently leads to a value of ca. 6Å resulting from the mean diameter of the polyester chain plus a certain increment for the oxygen atom. Similar extrapolations for higher temperatures (Figure (3)) as well as for the polyesters crystallized under preservation of the layers (see Figure (6)) have somewhat higher intercept indicating a lower density in these phases. Furthermore, the present results suggest that $n = 8$ is the minimum length of the side chains to render the layered structure A the thermodynamically stable modification above the melting point of the polyester.

Hence, the following preliminary model of the layered mesophase may be proposed (see Figure (7)). The liquid crystalline polester melt (modification A) consists of well-defined layers built up by the main chains. Packing requirements as well as a comparison of the lateral dimensions of the polyester molecule with the corresponding spacing *d* of the layers suggest that the side chains interdigitate as displayed in Figure (7). This model gains additional support from the fact that the side chains exhibit an extended conformation even at temperatures around 190°C. The negative temperature coefficient may be interpreted in terms of an increasing disorder of the side chains. The finite order parameter of the main chains together with residual dis-

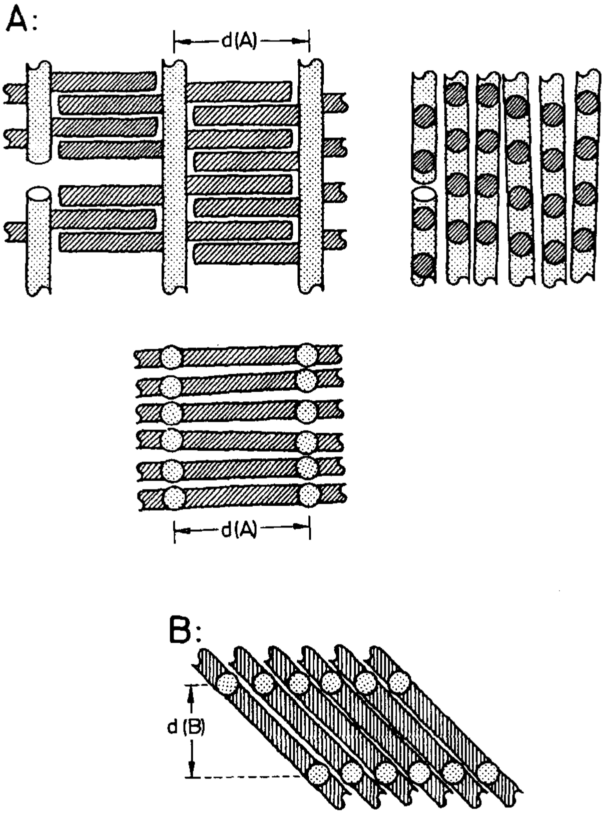


FIGURE 7 Model of molecular packing in the structures A (mesophase) and B (crystalline material); see text for explanation.

order of the side chains which will certainly have rotational degrees of freedom in the mesophase prevent the occurence of well-defined reflections in the wide angle region but give rise to a broad halo as is typical for liquids. An additional small disturbance of the layering will be effected by the ends of the main chains (see Figure (7)) but it is obvious that the present model of the mesophase (A) is compatible with the molecular nonuniformity of the main chains. However, the model requires the order parameter of the main chains to be quite high because a structure as suggested by Figure (7) can be realized only if the main chains are nearly planar. As may be argued from the absence of the reflection of the repeating unit there is no correlation of neighboring main chains (cf. Figure (7)). It has to be noted that Figure 7 only depicts an idealized model. In the vicinity of the isotropization temperature there will be an increasing disorder of the lateral packing of the side chains.

From the foregoing it is obvious that the present experimental data do not suffice for a complete proof of the proposed structure. However, among the different ways of accommodating the side chains in a layered structure the present suggestion displayed in Figure (7) seems to be the most probable one. It is interesting to note that a structure with interdigitating side chains similar to that shown in Figure (7) has been found recently by Watanabe, Ono, Uematsu and Abe when studying the different modifications of poly(L-glutamates) with long side chains.[11] Also, Hermann-Schönherr, Wendorff, Ringsdorf and Tschirner[12] recently found a similar layered mesophase in their study of poly(1,4-phenyleneterephthalamide)s substituted with 6 alkoxy side chains. Here both phenyl groups of the repeating unit along the main chain are substituted which obviously precludes the interdigitating of the side chains as displayed in Figure (7). Consequently the layer spacing found by Hermann-Schönherr *et al.* approximately corresponds to the full breadth of the polyamide molecule.

With regard to the crystalline state obtained by precipitation in case of long side chains and by melt recrystallization for $n < 6$ (modification B, see Figure (2)), the second distinct peak in the X-ray diffractograms together with the higher orders of reflection (see Figure (1a, b)) indicates a similarly layered structure. The smaller spacing as shown in Figure (2) (curve B) may be interpreted by the same model as displayed in Figure (7) but with a staggered arrangement of the main chains (cf. Figure (7)) leading to a tilt angle of 50 degrees. In addition, neighboring hydrocarbon side chains must be shifted by two CH_2 units to allow for an efficient packing. This requirement together with the tilt angle of approximately 50 degrees leads to a distance between neighboring side chains of ca. 3.8Å (cf. Figure (7)). The occurrence of a corresponding reflection in the diffractograms of polyesters exhibiting structure B (see (5c)) thus gives additional support for the present model of structure B. The structure C (cf. Figure (2)) exhibiting a higher increment (ca. 2Å/CH_2 unit) may be explained by a staggered but non-interdigitating crystalline modification, however, the present data do not allow any further conclusion.

CONCLUSION

The results presented herein demonstrate that small side chains act like a solvent in accord with the consideration given in Reference 3. In this case a nematic phase is observed above the melting temperature of the respective polyesters. If the side chains exceed a certain length ($n > 6$), a new type of mesophase exhibiting a layered structure is formed (modification A). A similar layering but with a smaller spacing (modification B) is found for the crystalline state obtained by melt recrystallization ($n < 8$) or precipitation from solution ($n > 6$).

Acknowledgment

The authors are indebted to G. Wegner and E. W. Fischer for helpful discussions and continuous support of this work. Financial support by the Bundesministerium für Forschung und Technologie, Projekt "Steife Makromoleküle" is gratefully acknowledged.

References

1. P. J. Flory, *Adv. Pol. Sci.*, **59**, 1 (1984).
2. M. Ballauff, Dacheng Wu, P. J. Flory, and E. M. Barrall II, *Ber. Bunsenges. Phys. Chem.*, **88**, 524 (1984).
3. M. Ballauff, *Macromolecules*, **19**, 1366 (1986).
4. P. J. Flory, *Proc. Royal Soc.*, London **A234**, 73 (1956).
5. J. Majnusz, J. M. Catala and R. W. Lenz, *Eur. Polym. J.*, **19**, 1043 (1983).
6. W. R. Krigbaum, H. Hakemi and R. Kotek, *Macromolecules*, **18**, 965 (1985).
7. M. Ballauff, *Makromol. Chem. Rapid Comm.*, **7**, 407 (1986).
8. M. Ballauff and G. F. Schmidt, *Makromol. Chem. Rapid Comm.*, submitted.
9. B. Ewen, G. R. Strobl and R. Richter, *Faraday Disc.*, **69**, 19 (1980).
10. R. S. Cantor and K. A. Dill, *Macromolecules*, **18**, 1875 (1985).
11. J. Watanabe, H. Ito, I. Uematsu and A. Abe, *Macromolecules*, **18**, 2141 (1985).
12. O. Hermann-Schönherr, J. H. Wendorff, H. Ringsdorf and P. Tschirner, *Makromol. Chem. Rapid Comm.*, submitted.