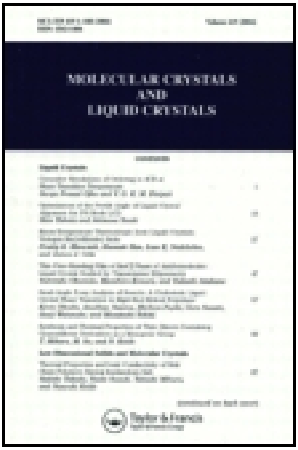

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Structure and Dilution of Mesogenic Side Chains in Liquid Crystalline Polysiloxanes

S. Diele [a], S. Oelsner [a], F. Kuschel [a], B. Hisgen [b] & H. Ringsdorf [b]

[a] Martin-Luther-Universität, Halle-Wittenberg Sektion Chemie, Mühlpforte 1, 4020, Halle, GDR

[b] B. Gutenberg Universität Mainz, Institut für Organische Chemie, J.-J.-Becher Weg 18-20, 6500, Mainz, FRG

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STRUCTURE AND DILUTION OF MESOGENIC SIDE CHAINS IN LIQUID CRYSTALLINE POLYSILOXANES

S. DIELE, S. OELSNER, F. KUSCHEL
Martin-Luther-Universität, Halle-Wittenberg
Sektion Chemie, Mühlpforte 1, 4020 Halle, GDR

B. HISGEN, H. RINGSDORF
J. Gutenberg Universität Mainz, Institut für
Organische Chemie, J.-J.-Becher Weg 18-20,
6500 Mainz, FRG

Abstract The structure of the smectic phases in four series of homo- and copolymers based on dimethylsiloxane chains with a definite variation of the concentration of the paired mesogenic side chains has been investigated by means of X-ray methods. The dilution of the mesogenic moiety was achieved by insertion of additional dimethylsiloxane segments. A nearly linear dependence of the layer spacings on the dilution has been found. A model of the structure is proposed which consists of two sublayers one of which contains the irregularly arranged main chain whereas the other one is formed by the side chains.

INTRODUCTION

In a preceding paper the influence of the dilution on the structure of the smectic phases in one series of dimesogenic side chain polymers has been reported /1/. Now results shall be reported obtained in four series of different chemical structure of the mesogenic groups /2/. The term "dilution" means that the concentration of the mesogenic side chains is reduced by insertion of additional dimethylsiloxane segments into the main chain.

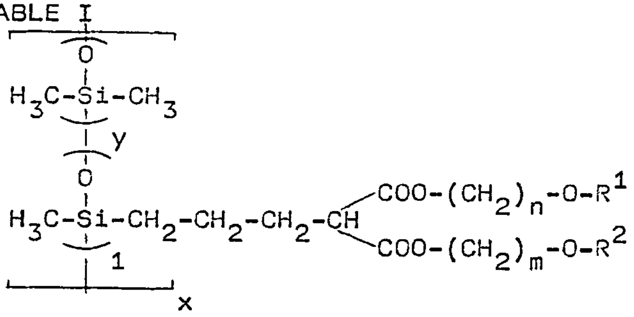
Usually due to the dilution by nonmesogenic groups a disordering of the liquid crystalline structure should be expected. On the other hand, a stabilization of the smectic phases has been achieved in the series under discussion by linkage of paired, dimesogenic moieties as side groups, leading to a high lateral interaction /2,3/. The role of the different building groups of liquid crystalline polymers - main chain, spacer, rigid moiety of the mesogenic group, flexible tail - has been often discussed. Sometimes the structure of the liquid crystalline polymers has been considered as a two- or polyphase system /4,5,6/. These conclusions have been drawn in more indirect way. The aim of this paper is to discuss the problem on the base of structure parameters obtained by X-ray methods.

RESULTS

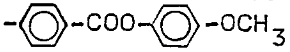
The observed phases are summarized in Table I together with the chemical formulas. The average number of dimethylsiloxane units between two neighbouring side groups is denoted by y /1/.The nematic phase appears only in nondiluted systems of two series. The X-ray pattern exhibits a crescent-like diffuse scattering at small angles ($\theta \approx 2^{o}$) and perpendicular to this a crescent-like "outer" diffuse scattering at angles between 9 and 12 degrees.

A smectic B phase could be identified in three diluted systems of one series. A sharp outer reflection besides the inner one is obtained at the

TABLE I



No. of substances

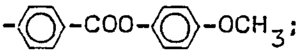
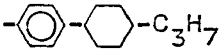
I/y n=m=2, $R^1=R^2=$ 

I/0 g 33 s_A 91 n 98 is

I/1 cr 30 s_A 90 is

I/5 cr 48 s_A 114 is

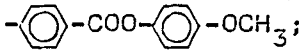
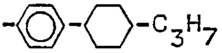
I/10 cr 30 s_A 107 is

II/y n=m=2, $R^1=$ ; $R^2=$ 

II/0 cr 73 s_A 104 is

II/5 cr 44 s_A 57 is

II/10 s_A 48 is

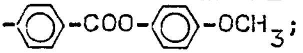
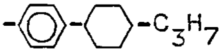
III/y n=2, m=6, $R^1=$ ; $R^2=$ 

III/0 cr 70 s_A 76 n 89 is

III/1 g 3,5 s_A 65 is

III/5 g -16 s_A 61,5 is

III/10 g -17 s_A 64 is

IV/y n=m=6, $R^1=$ ; $R^2=$ 

IV/0 g 9 s_A 115 is

IV/1 g 2 s_B 13 s_A 99 is

IV/5 g -16.5 s_B 23 s_A 88 is

IV/10 s_B 18 s_A 83 is

pattern of the smectic B phase pointing to a hexagonal structure (Fig. 1).

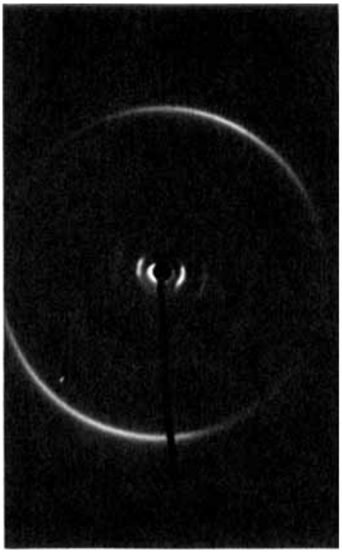


FIGURE 1. Pattern of an oriented sample of copolymer IV/1, smectic B phase.

FIGURE 2. Pattern of an oriented sample of copolymer I/5, smectic A phase. The magnetic field direction is indicated by arrow.

All investigated substances form smectic A phases. The patterns of oriented samples of the s_A phases exhibit the characteristic feature: the crescent-like diffuse outer scattering and - perpendicular to this - the spot-like inner reflections up to several orders (Fig. 2). The patterns prove that the building elements of the smectic layers (side chains) are arranged perpendicularly to the layers.

The lateral distances - measured by means of the outer ring in the case of the s_B phases and estimated by the Bragg-angle of the outer scattering maximum in the case of the s_A phase - do not show a dependence on the dilution. An averaged value of a = 0.51 nm has been obtained assuming a hexagonal cell. It agrees well with the values of the lateral distances found in low molecular weigth systems. It proves a close packing of the side chains independent on the inserted dimethylsiloxane segments.

From a structural point of view, the most exalting results are the dependence of the layer spacings on the dilution and the appearence of an additional closed diffuse scattering ring in all diluted systems with $y \geq 5$ (Fig. 2).

Fig. 3 displays the layer spacings of four investigated series as a function of the dilution. It can be seen that the dependence of the layer spacings on the number of the inserted dimethylsiloxane segments y is very similar in all series and can be approximated roughly by linear functions. The sequence of the intersections of these functions with the co-ordinate (y=0) corresponds to the side chain lengths. Than, the increase is the same in all series.

In addition to the well known patterns of the s_A and s_B phases a diffuse scattering is observed at all substances with $y \geq 5$. The averaged Bragg-angle of the scattering maximum is about 6 degrees. By investigation of well oriented samples irradiating the sample perpendicularly to the magnetic field a closed ring is observed which

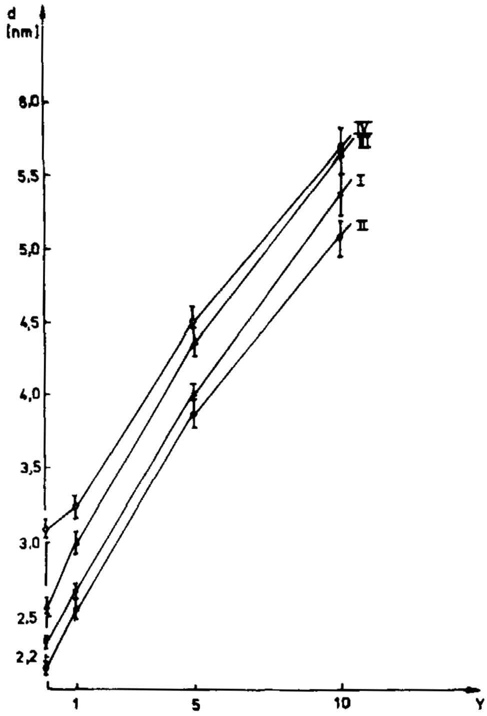


FIGURE **3.** Layer spacings (d) as a function of the number of inserted dimethylsiloxane units (y) for the four series

is split off on the meridian of the pattern (field direction).

The ring is observed, too, if the sample is irradiated parallel to the magnetic field. Heating the substance into the isotropic state, this diffuse scattering ring is maintained.

DISCUSSION OF THE LAYER SPACINGS

The surprising dependence of the layer spacings on the dilution y demands a special structural model in which the main chain itself partakes in the layer formation. The agreement between the layer spacings and the length of the side chains in the case of the nondiluted systems proves that the layers are formed by the side chains. The paired mesogenic groups must be arranged parallel to each other as sketched in Fig. 4. An irregular

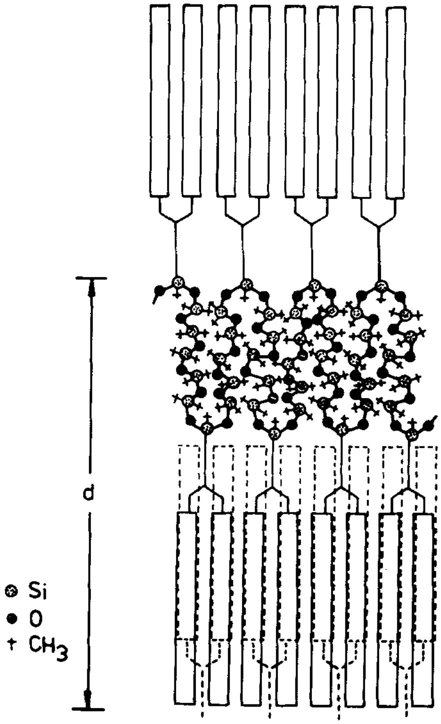


FIGURE 4. Schematic model of the layer of the copolymer with y = 5.
The dashed side groups are positioned above the drawing plane.

up and down alignment of the side chains must be assumed to explain the monolayer packing. The result that the lateral distances are not subjected to an alteration with increasing dilution demands the same lateral packing model as in the case of the nondiluted system. Therefore, the additionally inserted dimethylsiloxane segments of the main chain must be located outside of the layer consisting of the mesogenic groups. With respect to this the layer is divided into two sublayers, one of these consists of the dimethylsiloxane segments whereas the other one contains the mesogenic moieties.

By these experimental results a microphase separation is suggested. It can explain the observed nearly independence of the clearing temperatures on the dilution /3,7/.

DISCUSSION OF THE ADDITIONAL DIFFUSE SCATTERING RING

The molecular interpretation of the appearence of an additional closed scattering in all systems with $y \geq 5$ can be only a speculative one. However some experimental results have been observed suggesting that this scattering is caused by the main chain. Generally, the Si atoms should significantly contribute to the scattering of the sample. In the case of the nondiluted system they form flat layers perpendicular to the side chains exhibiting the same translation period.

Fig. 5 displays the micro-densitometer curves

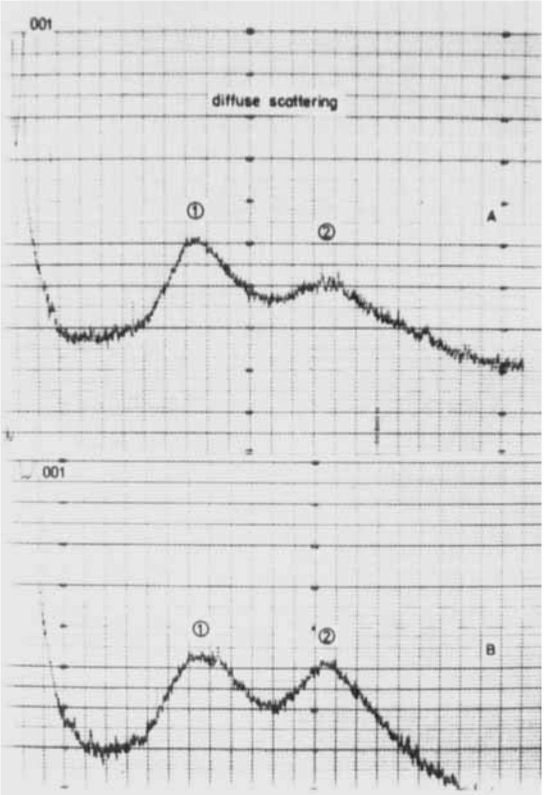


FIGURE 5. Micro-densitometer curves of copolymers II/10 (A) and II/5 (B).
① additional diffuse scattering
② diffuse scattering of the pattern of s_A phases

of the copolymers II/5 and II/10. The curves show an increase of the integral intensity of the additional diffuse scattering (indicated by ①) in relation to the usual outer scattering of the pattern of the s_A phase (indicated by ②) going from y=5 (part B) to y=10 (part A). The ratio is nearly doubled. The necessary increase of the corresponding scattering units can be explained only by the inserted dimethylsiloxane segments. Furthermore heating the sample into the isotropic state the diffuse ring is not altered. It should be emphasized that even the nonmodified isotropic poly(hydrogen-methylsiloxane) gives rise to a diffuse scattering at the same angle. Therefore it is assumed that in the case of the diluted systems the dimethylsiloxane segments are located in a sublayer in a more or less random manner.

The averaged d value of about 0.75 nm corresponds with the thickness of the dimethylsiloxane chains. The splitting off of the diffuse ring in field direction demands an additional periodicity in this direction which cannot be explained at the time.

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