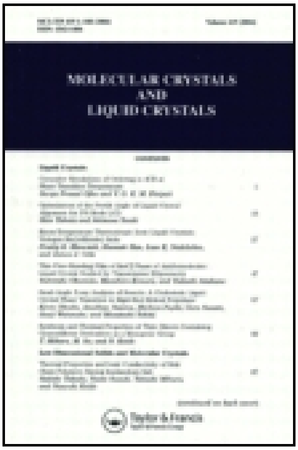

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Small Angle Neutron Scattering Study of Comb-Like Liquid Crystal Polysiloxane Macromolecule Conformation in Smectic Phase

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To cite this article: J. Kalus , S. G. Kostromin , V. P. Shibaev , A. B. Kunchenko , Yu. M. Ostanevich & D. A. Svetogorsky (1988): Small Angle Neutron Scattering Study of Comb-Like Liquid Crystal Polysiloxane Macromolecule Conformation in Smectic Phase, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 155:1, 347-356

To link to this article: http://dx.doi.org/10.1080/00268948808070377

Mol. Cryst. Liq. Cryst., 1988, Vol. 155, pp. 347-356
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Printed in the United States of America

SMALL ANGLE NEUTRON SCATTERING STUDY OF COMB-LIKE LIQUID CRYSTAL POLYSILOXANE MACROMOLECULE CONFORMATION IN SMECTIC PHASE^{x}

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Abstract The conformation of the main chain of the comb-like liquid crystalline polysiloxane with CN-containing biphenyl side groups (average polymerization degree 63) oriented in magnetic field was investigated in the smectic phase by small angle neutron scattering (SANS). The conformation is characterized by two projections of the radius of gyration $R_{\parallel}$ =10.9Å and $R_{\perp}$ = =17.2Å measured with the scattering vector along and perpendicular the smectic layers normal, respectively. The data are interpreted in the frame of the model assuming that the macromolecule backbone divides itself into quasi-two-dimensional subcoils, randomly placed in the neighboured, mainly alkyl, sublayers separated by the aromatic ones. The subcoils are connected with each other by the tie segments of the main chain accomplishing random walks through the mesogenic layers. The tie segments can be considered as defects in the smectic phase.

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^{x} Extended version submitted to "Liquid Crystals"

INTRODUCTION

In numerous publications[1-5] devoted to the study of liquid crystalline (LC) side-chain polymers the main attention is paid to a packing character of mesogenic side groups, determined, as a rule, the type of mesophase. At present, there are already known about a dozen polymorfic modifications of smectic polymers (smectics A, B, C, E, F, etc.) similar to the corresponding types of low molecular weight liquid crystals, which is in evidence of an essential role of mesogenic side groups[5]. However, the dual nature of the comb-like macromolecules being a combination of polymeric chains and strongly interacting mesogenic groups, evidently must reveal itself in their structure. In fact, some polymers having the same structure, but different chemical nature of the main chain or different lengths of spacers have different types of mesophase[1]. Naturally a question arises about the main chain effect on the structures of the LC polymer.

The small angle neutron scattering (SANS) method in combination with the method of isomorphic replacement of some parts in the studied macromolecule is, as a metter of fact, the only direct method to define the conformation of the labelled macromolecule in the medium of unlabelled ones[6,7].

The first LC polymer study by small angle neutron scattering method was performed on deuterated main chain comb-like polymethacrylates with phenylbenzoate side groups oriented in magnetic field[8,9]. The results showed that the main chain macromolecule had anisotropic conformation both in nematic and smectic mesophases; the anisotropy parameter for smectics being $a \approx 4$ (where a is a ratio of the largest $R_{\perp}$ to the smaller $R_{\|}$ projection of radius of gyration of the coil).

In refs.[10,11] from simplest theoretical considerations there follow the models of the LC polymer structure in nematic and smectic mesophases.These models satisfactorily describes not numerous experimental data received for LC polymers with a labelled main chain.

The present work deals with the study of the structure and conformation of the comb-like liquid crystalline polysiloxane in smectic phase with deuterated fractions of the spacers by means of X-ray and SANS methods.

The neutron diffraction pattern of the investigated hydrogenized LC polysiloxane is shown in Fig. 1. Diffraction maxima corresponding to the interlayer period D are directed along the X axis. Admixture, in the oriented sample, of some macromolecules with partially deuterated spacers results in small angle scattering (Fig. 2).

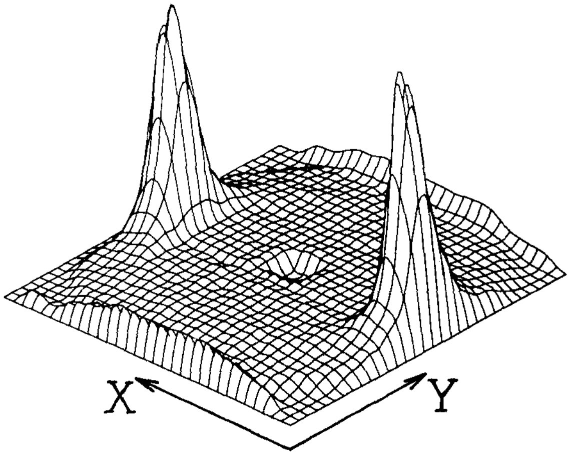


FIGURE 1. The neutron diffraction pattern of an oriented comb-like LC polysiloxane in a smectic phase, C(D)=0%. Smectic-layer normal is directed along the X axis.

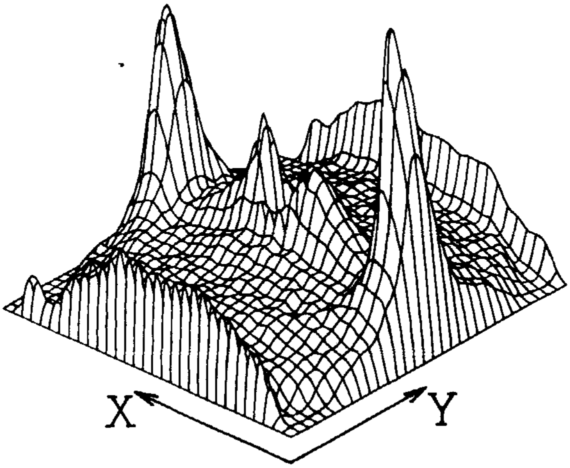
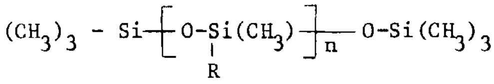


FIGURE 2. The neutron diffraction pattern of an oriented comb-like LC polysiloxane in a smectic phase, C(D)=30%. Presence in the sample of macromolecules with deuterated fractions of the spacers results in small angle scattering between diffraction maxima corresponding to the interlayer period D.

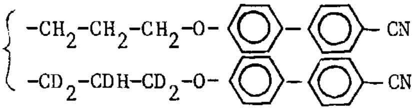
STUDIED OBJECTS

We have synthesized and investigated the following polymers.



$$(CH_3)_3-Si-\left[O-\underset{R}{\underset{|}{Si}}(CH_3)\right]_n-O-Si(CH_3)_3$$

where R =



(I)

(II)

with average degree of polymerization $\langle n \rangle = 63$. Principal characteristics of the above polymers are summerized in Table 1.

The clearing and glass transition temperatures, as well as the enthalpy of phase transitions of polymers I and II

TABLE I Properties of LC polysiloxane with phenylbenzoate mesogenic groups.

Polymer	Glass transition temperature	Phase and phase transition	Phase transition enthalpy ΔH_{cl}, J/g
I	35	S_A 144 I	4.2 ± 0.2
II	36	S_A 138 I	4.3 ± 0.2

were determined by the method of differential scanning microcalorimetry using the apparatus DSM-2 at a heating rate of 12.5° C/min. To perform neutron diffraction experiments there were prepared mixtures of these polymers with a weight concentration of I in II C(D) = 10% and C(D) = 30% by evaporation of solvent from solutions in dichlorethane.

All samples were macroscopically oriented in the magnetic field of about 2T under slow cooling from isotropic phase down to room temperature. The cooling rate near the clearing transition temperature (155-135°C) was 1°/hr. The data of X-ray investigations at large and small angles give evidence of the smectic S_A mesophase.

SMALL ANGLE NEUTRON SCATTERING

The oriented samples were investigated on the SANS apparatus/12/ at the pulsed reactor IBR-2/13/ of the Joint Institute for Nuclear Research in Dubna. Each sample with a specified C(D) was measured according to the standard procedure/12/, i.e. there were exposed in the beam the sample and then the sample with the standard scatterer from vanadium totally cancelling the beam transmitted through the sample.

The background sample (polyethylene) containing an equivalent amount of protons was subjected to the same procedure. Scattered neutrons were detected by an annular multiwire detector of thermal neutrons filled with He-3 /14/. The detector had no azimuthal sensitivity, so to measure the coil anisotropy there was used a cadmium screen in the form of a butterfly (wing angle 60°).

The differential scattering cross section of an anisotropic coil has the form /10/

$$\frac{d\Sigma}{d\Omega} \sim 1 - \varkappa^2 \left(R_{\parallel}^2\cos^2\varphi + R_{\perp}^2\sin^2\varphi\right) \tag{1}$$

where $\varkappa = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$ is the scattering wave vector module, θ is the scattering angle, φ is the azimuth angle counted from the liquid crystal ordering direction X (for a smectic sample X direction is a normal to the smectic layer plane). The mean square radius of gyration of the polymer coil is connected with the projections of the radius of gyration $R_{\parallel}$ and $R_{\perp}$ in the following way

$$R_g^2 = R_{\parallel}^2 + 2R_{\perp}^2 \tag{2}$$

With a proof sectorial screen in front of the detector the value measured in the small angle scattering experiment is /15/

$$R^2_{\langle\cos 2\varphi\rangle} = \frac{R_{\parallel}^2 + R_{\perp}^2}{2} + \frac{R_{\parallel}^2 - R_{\perp}^2}{2}\langle\cos 2\varphi\rangle \tag{3}$$

where

$$\langle\cos 2\varphi\rangle = \frac{\sum\limits_{i=1}^{2}\int\limits_{\varphi_1^i}^{\varphi_2^i}\cos 2\varphi \, d\varphi}{\sum\limits_{i=1}^{2}\left(\varphi_2^i - \varphi_1^i\right)} = \frac{\sum\limits_{i=1}^{2}\sin\left(\varphi_2^i - \varphi_1^i\right)\cos\left(\varphi_2^i + \varphi_1^i\right)}{\sum\limits_{i=1}^{2}\left(\varphi_2^i - \varphi_1^i\right)} \tag{4}$$

Here $\varphi^i_{1,2}$ are the azimuthal angles setting limits for the open areas of the detector. From (3) it is seen that $R^2_{\langle\cos 2\varphi\rangle}$ depends lineary on $\langle\cos 2\varphi\rangle$. Experimentally obtained values of $R^2_{\langle\cos 2\varphi\rangle}$ in dependence on $\langle\cos 2\varphi\rangle$ are given in Fig.3 and correspond to the cadmium screen rotation by an angles $\varphi' = 0^\circ$; 30°; 45°; 60° and 90°, where φ' is

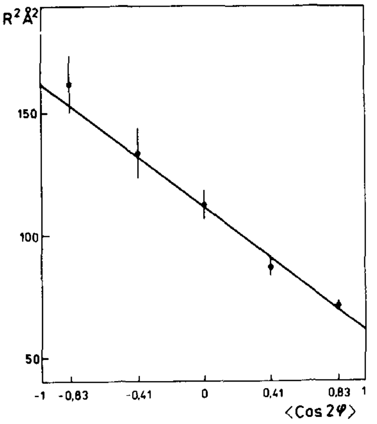


FIGURE 3. Dependence of $R^2_{\langle \cos 2\varphi \rangle}$ measured in the SANS experiment on $\langle \cos 2\varphi \rangle$ for the LC polysiloxane with deuterated polymer concentration C(D)=30%.

the angle between the bisectrix of the open part of the cadmium screen and the direction X. An extrapolation from $R^2_{\langle \cos 2\varphi \rangle}$ to $\langle \cos 2\varphi \rangle$ equal to -1 and +1, gives mean square projections of the radius of gyration of the coil $R^2_{\perp}$ and $R^2_{\parallel}$, respectively.

Experimental data obtained by diffuse SANS methods are summarized in Table 2.

The temperature dependence of the smectic interlayer period D is measured for the sample with C(D) = 10%, D = 25.12±0.01 Å for T = 20°C, D = 24.63±0.01 Å for T=75°C, and D=24.23±0.01 Å for T=115°C.

TABLE 2. SANS experimental data for mixtures of polymers I and II. The projections of radius of gyration are given in Å.

	T=20°C Smectic phase							T=115°C Smectic phase	T=175°C Isotropic melt
C(D)	$R_{\parallel}$	$R_{0.83}$	$R_{0.41}$	R_0	$R_{-0.41}$	$R_{-0.83}$	$R_{\perp}$	$R_{0.83}$	R^{iso}
30%	7.9 ±0.05	8.4 ±0.13	9.3 ±0.20	10.6 ±0.30	11.5 ±0.46	12.7 ±0.46	13.05 ±0.05		
10%	9.9 ±0.02	10.4 ±0.17				15.3 ±0.11	15.8 ±0.02	9.87 ±0.4	12.9 ±1.10

DISCUSSION

Though our measurements are of a preliminary character, let us note that, differently from available experimental data/9/, the projections of the radius of gyration of the main chain of LC polysiloxane (see Table 2) are different for two concentrations C(D). An absence of the radius of gyration dependence on concentration is characteristic for an ideal two-component mixture of H- and D-polymers/16/. It is supposed there that the macromolecular chain has three dimensions, the number of units is large and there is precise compensation of intra- and intermolecular interactions.

There is no reason to think that these conditions are fulfilled in the smectic LC polysiloxane. The only way then of measuring the formfactor of an individual molecule is to choose the mixture of H- and D-polymers with $\bar{a} = 0$ (where $\bar{a}$ is the average scattering amplitude per a monomeric unit of the sample), i.e. the interparticle interference is negligibly small. It should be taken into account/17/ that the interlayer interference will not bring any distortions into scattering from inhomogenities in the layers, if their size $R_g \gg D/2\pi$. This condition is practically always fulfilled in polymers (see Fig. 2).

In other words one should exclude a mesogenic addition from the calculation of scattering amplitudes of the monomeric unit of H- and D-polymers. For the polysiloxane the mean scattering amplitude of the rigid part of the monomeric unit turns into zero at $C(D) \approx 0$. Under extrapolation of the projections of radius of gyration to C(D) = 0 we have obtained $R_{\parallel} = 10,9$ Å and $R_{\perp} = 17,2$ Å.

An application of the developed in /11/ procedure to our experimental data leads to following results.

The average number of defects per a macromolecule $N_{\parallel}$

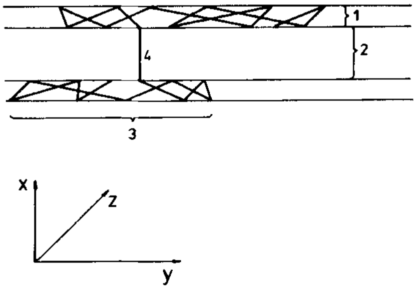


FIGURE 4. Conformation model for the main chain of the comb-like LC polysiloxane in smectic phase. The main chain of the macromolecule consists of quasi-two-dimensional subcoils 3 lying in intermediate layers 1. The subcoils are connected by the tie segment 4 forming a defect in the mesogenic layer 2.

is equal to 1.1, i.e. each macromolecule chain consists in average of two subcoils (Fig. 4).

The average projection of subcoil radius of gyration in the direction normal to the LC ordering axis $R_{\perp 1}$ is equal to 12 Å.

A comparison of the Kuhn segment of the LC polymer coil in the isotropic phase (b^{iso}=18,7 Å) and, estimated according to /11/, of the subcoil ($b_{\perp 1}$=31 Å) shows that a significant increase in rigidity of the main chain takes place at a transition from isotropic to smectic phase. Note, that a linear polymer similar to the main chain (polydimethylsiloxane in dilute solution, Θ-conditions) has b = 14 Å /18/.

CONCLUSION

Several samples of comb-like LC polysiloxane in smectic phase were studied by X-ray diffraction and small angle neutron scattering. The macromolecular coil was established to have anisotropy.

The $R_{\parallel}$ and $R_{\perp}$ projections of radius of gyration of anisotropic coil (Table 2) on the direction parallel and perpendicular to the LC ordering axis, respectively were estimated.

The transition from isotropic into smectic phase is followed by a slight increase in total radius of gyration of the macromolecular coil. The main chain of the macromolecule is divided in average in two quasi two-dimensional subcoils the rigidity of which exceeds significantly that of the macromolecule in isotropic phase. The subcoils are lying in neighbouring sublayers. The subcoils are connected with each other by the tie segment of the main chain which form a defect in the mesogenic layer.

REFERENCES

1. Shibaev V.P., Plate N.A., Comb-Like Polymers and Liquid Crystals (Khimiya, Moskow, 1980).
2. Liquid Crystalline Order in Polymers, edited by Blumstein A. (Academic Press, New York, London), 1978.
3. Polymers Liquid Crystals, edited by Ciferri A., Krigbaum W.R., Meyer R.D. (Academic Press, New York, London), 1982.
4. Ultra-High Modulus Polymers, edited by Ciferri A. and Ward I.M. (Applied Science Publishers, London), 1979.
5. Shibaev V.P., Plate N.A., Advances in Polymer Science, 1984, 60/61, 173.
6. Akcasu A.Z., Summerfield G.C., Jahshan S.N., Han C.C., Kim Y.C. and Yu H., J.Polym. Sci., Polym. Phys. Edn., 1980, 18, 863.
7. Benoit H., Picot C. and Benmouna M., J. Polym. Sci., Polym. Phys. Edn., 1984, 22, 1545.
8. Kirste R.G., Ohm H.G., Makromol. Chem., Rapid Commun., 1985, 6, 179.
9. Keller P., Carvalho B., Cotton J.P., Lambert M., Moussa F. and Pépy G., J. Physique Lett., 1985, 46, L 1065.
10. Kunchenko A.B., Svetogorsky D.A., JINR 14-86-89, Dubna, 1986 (submitted to "Liquid Crystals")
11. Kunchenko A.B., Svetogorsky D.A., J. Physique, 1986, 47, 2015.
12. Vagov V.A., Kunchenko A.B., Ostanevich Yu.M., Salamatin I.M., JINR P14-83-898, Dubna, 1983.
13. Ananjev V.D. et al., Atomnaya Energiya, 1984, 57, 227.
14. Ananjev B.N., Kunchenko A.B., Lazin V.I., Ostanevich Yu.M. Pikelner Y.Ia., JINR 3-11501, Dubna, 1978.
15. Kunchenko A.B., Svetogorsky D.A., JINR 14-86-855, Dubna, 1986.
16. De Gennes P.G., Scaling Concepts in Polymer Physics (Cornell Univ. Press. Ithaca and London, 1979).
17. Kunchenko A.B., JINR 14-87-360, Dubna, 1987.
18. Tsvetkov V.N., Eskin V.E., Frenkel S.Ia., Structure Macromolecules in Solutions (Nauka, Moskow, 1964).