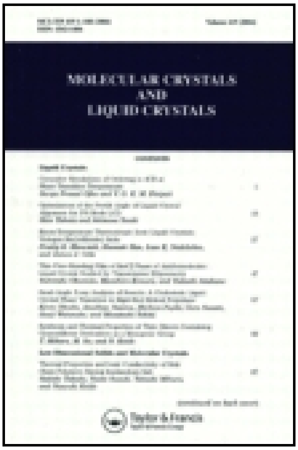

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Molecular Properties of Mesomorphic Poly (decamethyl-cyclohexasiloxane) in Solution

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Molecular Properties of Mesomorphic Poly (decamethyl-cyclohexasiloxane) in Solution

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The molecular properties of a non-classical mesogenic polymer – poly (decamethyl-cyclohexasiloxane), and low molecular analogs of its monomer unit have been studied by electrooptical Kerr effect in solution. It was shown that every polar hexasiloxane cycle in the polymer chain acts independently under influence of external electric field. Based on the results of the study of dipole moments and electrooptical properties of low- molecular-mass cyclohexasiloxanes with different polar side-groups (CH_3, $-C_6H_5$, -OH, $-OC_2H_5$) it was established that hexasiloxane cycle is able to preserve its conformation (i.e. its form and size) because of its polar properties depend weakly on the type of side-substituents. An observed stability of polar hexasiloxane cycle under the external action may be considered as responsible for the ability of poly(cyclohexasiloxanes) to form highly organized mesomorphic phases.

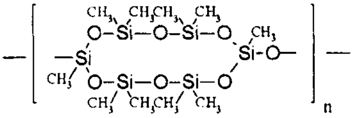
Keywords: Kerr effect; LC polymers; cyclo-linear polysiloxanes

INTRODUCTION

During the last decade new clases of mesomorphic polymers without typical mesogens in its structure have been synthesized. Among those polymers are cyclo-linear poly-organosiloxanes (PCSs) which form different types of thermotropic mesophase in a wide thermal regions [1-4]. The mesomorphic properties of PCS have a nature different from that of well-known comblike polymer LCs such as poly(methylsiloxanes) with a flexible backbone and mesogen containing side chain groups [5, 6]. The origin of PCS mesomorphism have been debated since its synthesis [1-4] Two possible reasons of PCS self-ordering in the mesomorphic state are discussed now: a crucial role of siloxane cycle conformation and a special type of intramolecular interaction.

The goal of the present work was to study the individual molecular properties of PCS containing hexasiloxane cycles - poly(decamethyl-cyclohexasiloxane) (PCHS) in dilute solutions under the influence of a sinusoidal electric field (electrooptical Kerr-effect). These experimental conditions have been chosen for an excluding of intramolecular interaction factor and for clearing the possible role of initial structural ordering in PCHS molecular chain.

Two samples of PCHS with the repeat unit chemical structure below and with of polymerization degree n = 56 (PCHS-1) and n= 80 (PCHS-2) have been investigated in carbon tetrachloride at 21°C:



PCHSs were synthesized as described in [2] and were characterized by a columnar type mesophase in a wide temperature ranging interval from the glass transition temperatures (near -90°C) up to the clearing point (~300 °C) [2-4].

In addition to the polymer samples five low molecular mass cyclohexasiloxanes with different side-chain substituents (as analogs of PCHS monomer unit) and PCHS oligomeres were studied for comparative purpose. The chemical structures are presented in Table 1. Low-molecular -mass cyclosiloxanes (CSs) were studied in toluene and carbon tetrachloride solutions. Dipole moments and specific Kerr-constants of the low molecular weight compounds and macromolecular samples were determined.

EXPERIMENTAL

The dipole moments μ of the samples were determined by Guggenheim-Smith method in solutions [7] using experimental dependencies of the electric permittivity increments ($\varepsilon_{12} - \varepsilon_1$) and refractive index increments ($n_{12}^2 - n_1^2$) *versus* concentration of the solute (here and below, the subscript 12, 1 and 2 refer to the solution, solvent and solute , respectively) (see Figs. 1a and 1b). The permittivity of solutions and solvents were measured at a frequency of 700 kHz using the zero-beat method [8] with an E-12-1 capacitance and a cylindrical titanium capacitor with an intrinsic capacity of 92.86 pF. The refractive indices of the solutions were determined using a refractometer IRF-23 at a wavelength of 578 nm.

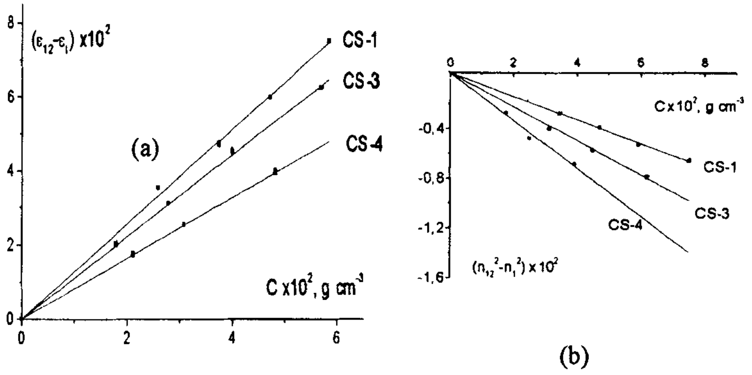


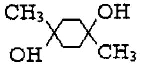
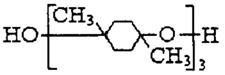
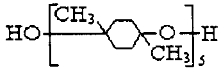
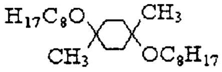
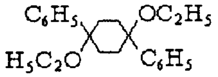
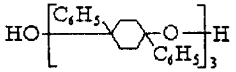
FIGURE 1 Concentration dependencies of the dielectric permittivity increment ($\varepsilon_{12} - \varepsilon_1$) (a) and the refractive index increment ($n_{12}^2 - n_1^2$) (b) for solutions of low-molecular-mass cyclosiloxanes CS-1, CS-3 and CS-4 in CCl_4.

The dipole moment values were calculated by formula

$$\mu^2 = 27\,kTM_2 \times [(\varepsilon_{12} - \varepsilon_1)/c - (n_{12}^2 - n_1^2)/c] / 4\pi N_A\,, \qquad (1)$$

Here k is the Boltzmann constant, N_A is the Avogadro number, T is the absolute temperature, M_2 is molecular mass of solute, and c is the solution concentration. The permanent dipole moments of the low molecular mass cyclosiloxanes in two solvents are presented in Table 1.

TABLE 1 Chemical structure, dipole moments μ and specific Kerr constants K for the low-molecular-mass cyclosiloxanes (CS) in toluene and carbon tetrachloride solutions and PCHS samples in carbon tetrachloride

Sample	Structure	μ D (toluene/CCl_4)	μ^2/M D^2/g	$K \cdot 10^{12}$ g^{-1} $cm^5(300V)^{-2}$ (toluene/CCl_4)
CS-1		2.23/ -	0.01	2.0/ -
CS-2		3.12/3.10	0.07	2.1/1.9
CS-3		4.10/4.20	0.08	2.0/1.9
CS-4		- /2.25	0.08	- /2.1
CS-5		- /2.12	0.07	- /2.0
CS-6		3.25/3.18	0.06	- /1.5
PCHS-1		- / 12.2	0.06	- /1.9
PCHS-2		- / 14.7	0.06	- /1.9

The Kerr effect in solutions of polymer and low-molecular-mass samples was measured in sinusoidal electric field at a frequency of 20 kHz. The electric field induced birefringence was detected by a technique described in [9]. Kerr effect measurements were performed in a glass cell with plane-parallel titanium electrodes. The cell length in the light beam direction was 2 cm; the gap between electrodes was 0.05

cm. All experimental measurements were carried out at 21°C; the temperature was controlled within 0.1°C.

The electrooptical properties of the samples were characterized by their specific Kerr constant K determined by the relation

$$K = \lim_{E,\, c \to 0} (\Delta n/E^2 c) \qquad (2)$$

where E is the electric field strength, and $(\Delta n/E^2c) = (\Delta n/E^2c)_{12} - (\Delta n/E^2c)_1$ is the solute part of the solution's birefringence which was determined as the difference of the slopes of the experimental dependencies of birefringence Δn versus electric field strength squared E^2 for the solution and solvent, respectively.

The Kerr effect observed in the solvents was close to published data. A linear growth of the electric birefringence value Δn with the squared electric field strength E^2 was observed in all investigated solutions in accord with the Kerr law (Fig. 2a). The electrooptical effect was positive in sign for PCHSs and low-molecular-mass samples in both the solvents used. Concentration dependence of the specific Kerr constant K for solutions of all the samples was absent (Fig. 2b). K values represented in the Table 1 were calculated as the average values over the concentration range.

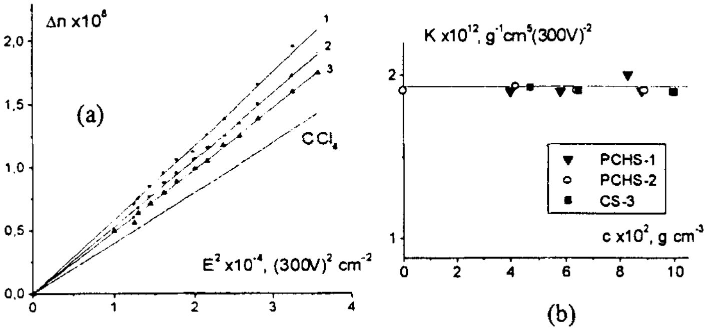


FIGURE 2 The dependence of birefringence value Δn *versus* the squared electric field strength E^2 for PCHS-2 in CCl_4 at concentrations: 1- 0.92; 2- 0.65; 3- 0.42×10^{-2} g cm^{-3} (a) and concentration depedencies of the specific Kerr constant for PCHS-1, PCHS-2 and CS-3 in the same solvent (b).

The necessity to work in two solvents is explained by the fact that one sample CS-1 in the homologous series (see Table 1, samples CS-1-3) did not dissolve in carbon tetrachloride in which the majority of measurement have been done. Therefore, a comparative study of polar properties of several CSs in two solvents have been carried out to be sure in a correct estimation of CS-1 dipole moment.

RESULTS AND DISCUSSION

The data obtained on the polarity of the samples show that dipole moments of all the low-molecular-mass CSs do not differ if compared the similar CSs (see CS-1, 4, 5 and CS-3, 6 in the Table 1). Thus, the polarity of cyclohexasiloxanes with various structures of side-chain substituents dos not change (within the accuracy of its determination) with the changes in chemical structure. This experimental fact is apparently related to the primary anti-parallel orientation of side substituents in the cycle and a comparatively rigid conformation of the cycle itself. As one can see (for instance, samples CS-1, CS-4 and CS-5 in the table 1) the dipole moments of CSs are not sensitive to the substitution of hydroxyalkyl and phenyl groups for on methyl sites.

PCHS and low-molecular-mass samples CS-1, CS-2 and CS-3 form a polymer-homologous series and possess virtually equal values of the specific dielectric polarization (see the column μ^2/M in the Table 1) and the specific Kerr constant *K*. This is evidence of the presence of common polar groups in its structure which are independently oriented under the influence of an applied electric field. It is naturally assumed that the cyclohexasiloxane chain element is capable of independent orientation in the field. On the basis of this assumption, we may use theoretical relationships for the specific Kerr constant to estimate some molecular parameters of the PCHS chain. In particular, using the following equation valid for the flexible-chain polymers modeled by a freely-joined chain of independently oriented fragments, we may evaluate the tilt angle β between the dipole moment of the PCHS monomer unit and the axis of its maximal optical polarizability [9]:

$$K = \frac{\pi N_A (n_1+2)^2 (\varepsilon+2)^2 \rho_1}{1215 kT n_1 M_0} \Delta b + \left[2\Delta b + \frac{\mu_0^2}{kT}\left(3\cos^2\beta - 1\right) \right] \quad (3)$$

Here Δb is the anisotropy of optical polarizability of the monomer unit, M_0 and μ_0 are the molecular mass and dipole moment of the mononer unit, and the other parameters are the same as in equation (1).

The value of Δb for decamethyl-cyclohexasiloxane fragment was estimated using the data on flow birefringence measurement performed for poly(dimethylsiloxane) from [10], where the value of optical anisotropy per unit length of polymer chain have been estimated as 0.4×10^{-17} cm^2. So far as the projection length λ of the PCHS monomer unit onto the backbone growth direction is known ($\lambda=8.8\times10^{-8}$ cm [11]), we have estimated the anisotropy of optical polarizability of decamethyl cyclohexasiloxane by the value $\Delta b\approx 3.5\times10^{-25}$ cm^3. It should be noted that this is a comparatively small value (for comparison, the corresponding characteristic of benzene cycle is 60×10^{-25} cm^3 [12]).

Assuming that a monomer unit of PCHS may be described by the following characteristics: $\mu_0=2.2$ D (this is an average value for CS-1, CS-4 and CS-5 samples), $\Delta b\approx 3.5\times10^{-25}$ cm^3, and using equation (3) with a specific Kerr constant of $K=1.9\times10^{-12}$ g^{-1} cm^5 (300V)$^{-2}$, we obtain an estimate of $\beta\approx0$ for the tilt angle of the dipole moment to the direction of maximal optical anisotropy of polarizability of the repeating PCHS unit. This result may explain, at least to a certain extent, the weak variation of the specific Kerr constant values (in general, this is highly sensitive to the details of intramolecular structure) for CSs with various side-chain substituents attached to the cycle with antiparallel orientation.

Equation (3) also shows that the specific Kerr constant is determined by the sum of two contributions: the first term is related only to the anisotropy of polarizability of the monomer unit (deformation factor), and the second term (orientation factor) is connected with the permanent dipole of this unit. For PCHS the second term in expression (3) exceeds the first by more than two orders of magnitude. Therefore, the electrooptical Kerr effect in PCHS solutions, as well as for low molecular mass cyclosiloxanes, mainly has an orientation character which is predominantly caused by the existence of a permanent dipole moment in the molecules of compounds under investigation.

The experimental data obtained in this work show that the behavior of PCHS molecules under the influence of an external electric field is typical of the flexible-chain polymers, for which the specific Kerr constants in polymer solutions were reported more than once to coincide with the same characteristic for low-molecular mass analogs modeling the monomer unit [9].

The study of polymer-homologous PCHS series by hydrodynamic methods [13] showed that this polymer possesses an equilibrium rigidity expressed in term of Kuhn segment length of 38 Å, whereby the neighboring chain units correlated within 4-5 cyclosiloxane fragments linked by oxygen bond. Upon exposure to the external field, PCHS behaves as a typical flexible-chain polymer, in which every repeating unit is oriented independently of neighboring chain units. However, it should be emphasized that a kinetic chain unit in PCHS is represented by a non-planar polar cycle [12], which retains its conformation in the external sinusoidal electric field. The longitudinal dimensions of cyclohexasiloxane component of PCHS chain (the length of projection onto the main chain direction is 8.8 Å) and the permanent dipole moment (2.2 D) are comparable to the molecular length and dipole moments of some typical low-molecular mass liquid crystals (e.g., LC benzoates [14]). These structural features of PCHS molecules, together with a high flexibility manifested under the influence of an external electric field, may well account for the existence of thermotropic mesomorphic state both in PCHS itself and in its cyclolinear polymer analogs.

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