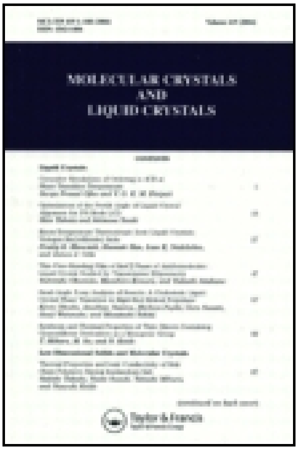

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Hydrodynamic and Conformational Properties of Aromatic Polyesters Containing Flexible Polyoxyethylene Fragments

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Hydrodynamic and Conformational Properties of Aromatic Polyesters Containing Flexible Polyoxyethylene Fragments

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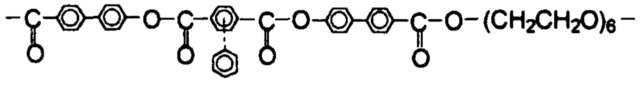
Conformational properties of molecules of the thermotropic aromatic polyesters containing mesogenic and flexible very long oxyethylene fragments are discussed on the basis of molecular hydrodynamic investigations. Changes in conformational properties and equilibrium flexibility of molecules, caused by changes in the way of biphenylene fragments insertion into the chain are analyzed. Intramolecular orientational mobility of mesogenic fragments is characterized by a dimentionless parameter λ/A.

Keywords: mesogenic polymer; conformation of the molecule; Kuhn segment; intramolecular orientational mobility

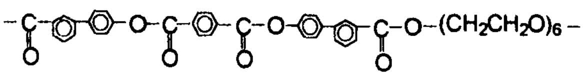
INTRODUCTION

Molecular characteristics of mesogenic aromatic polyesters in which the structure and length of rigid ester-aromatic portions and flexible portions separating them are varied have been investigated by the authors in several papers[1-6].

In the present work the conformational properties of two thermotropic aromatic polyesters



(Polymer I) and



$-C(=O)-C_6H_4-C_6H_4-O-C(=O)-C_6H_4-C(=O)-O-C_6H_4-C_6H_4-C(=O)-O-(CH_2CH_2O)_6-$

(Polymer II)

were investigated by the methods of molecular hydrodynamics.

Mesogenic fragments in these polymers are separated by flexible very long oxyethylene parts. Bis-4,4′-biphenylene groups contained in mesogenic fragments of polymer I, are replaced by bis-4,3′ and bis-3,4′ biphenylene groups in polymer II.

HYDRODYNAMIC PROPERTIES

Hydrodynamic properties (intrinsic viscosity [η], translation diffusion coefficient D , and velocity sedimentation coefficient s) were investigated in dilute

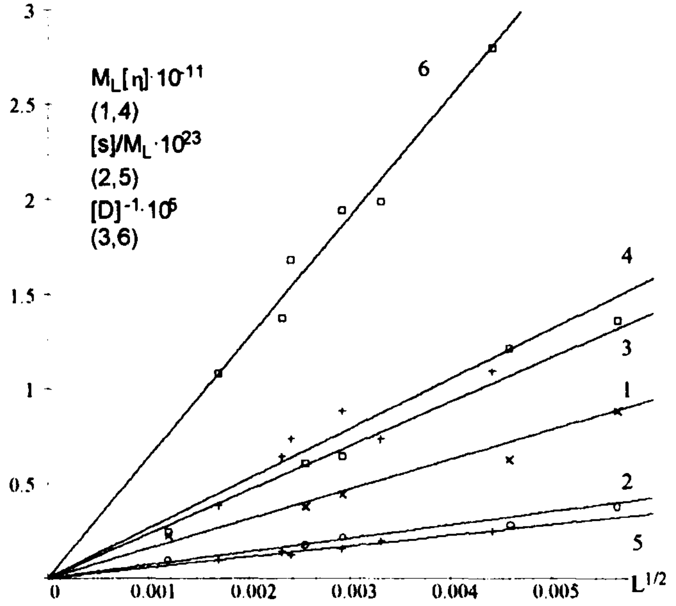


FIGURE 1 Dependences of hydrodynamic characteristics of polymer I and II on $L^{1/2}$.

dilute solutions of polymers I and II in two solvents (chloroform and dioxane). Molecular weight ranges of polymer fractions investigated are given in the table.

In order to compare hydrodynamic characteristics of polymers I and II, the dependencies of values of $[\eta]M_L$, $[s]/M_L$, and $[D]^{-1}$ on $L^{1/2}$ are shown in Fig.1. In this figure $[s]=\eta_0 s/(1-v\rho_0)$; $[D]=\eta_0 D/kT$; ρ_0 is the solvent density and η_0 is its viscosity, v is the partial specific volume of the polymer (0.76 and 0.80 cm^3/g for polymers I and II, respectively); $L=M/M_L$; $M_L=M_0/\lambda$ (M_0 is the molecular weight of the monomer unit , λ is its length along the direction of the extended chain); and k is the Boltzmann constant.

The above values of λ for polymer I and II were found from the structure of their repeat units when the macromolecules are completely extended (Fig.2). The value of λ_{II} is higher than that of λ_I (see the table). This is due to different angles α of the slope of rigid fragments of polymers I and II with respect to the direction of the extended chain (35° and 25° for polymers I and II, respectively).

The experimental dependences in Fig.1 were approximated by straight lines passing through the origin. The values of $[\eta]M_L$ (straight line 1) and $[D]^{-1}$ (straight line 3) for polymer II are smaller and the values of $[s]/M_L$ (straight line 2) are greater than those for polymer I (straight lines 4, 6, and 5, respectively). This ratio of these values may be associated with higher coiling of the molecules of polymer II than that of the molecules of polymer I. The lengths of Kuhn segments A were calculated from the slopes of dependences in Fig.1 according to the equation

$$M_L[\eta]/L^{1/2}=\Phi A^{3/2};\quad [D]^{-1}/L^{1/2}=PA^{1/2};\quad ([s]/M_L)/L^{1/2}=(PN_A A^{1/2})^{-1} \quad (1)$$

were Φ is the Flory constant ($\Phi=2.87\cdot10^{23}$ mole^{-1}), P is the constant in the theory of translational friction of a wormlike chain (P=5.11), and N_A is the Avogadro number. The resulting values of A (from $[\eta]$ measurements we obtain A_η and from those of D and s we have A_f , the average value of A is $(A_\eta+A_f)/2$) are given in the table.

TABLE Molecular characteristics of polymers I and II.

Polymer	MW Range $M\cdot10^{-3}$	$\lambda\cdot10^8$ cm	$M_L\cdot10^{-8}$ cm^{-1}	$A_\eta\cdot10^8$ cm	$A_f\cdot10^8$ cm	$(A_\eta+A_f)/2\cdot10^8$ cm	λ/A
I	5.3÷36	47.6	18.5	21	31	26	1.8
II	2.3÷50	50.7	15.9	14.5	21	18	2.9

CONFORMATIONAL PROPERTIES

The conformational properties and the flexibility of the molecules of polymers being investigated are determined by the alternation of flexible and rigid parts contained in the chain. The contribution of different chain parts to the flexibility of molecules can be evaluated on the basis of the additivity principle[7] which was repeatedly applied in the conformational analysis of polymers[1].

The main structural features of molecules of these polymers are illustrated in structures shown in Fig.2.

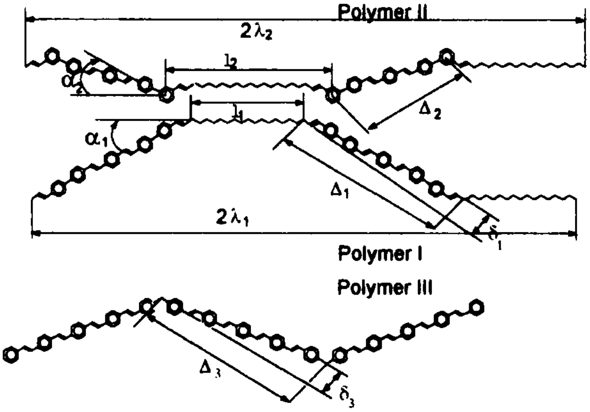


FIGURE 2 Structures of polymer repeat units in the conformation of the greatest chain stretching.

Structure III refers to polymer III investigated previously[3]. Just as in polymer I , rigid para-aromatic fragments of polymer II contain five aromatic rings separated by four ester groups. Therefore, the lengths Δ of rigid fragments in the direction of para-aromatic axes ($\Delta=30.8\cdot10^{-8}$cm), just as the displacements δ of para-aromatic axes in the direction normal to them ($\delta=4.85\cdot10^{-8}$ cm) are identical for polymers I and III. The orientations of para-aromatic axes of polymer III molecules with respect to the direction of the extended chain which are ensured by carbon atoms joining rigid fragments ($\theta=70.5°$) virtually coincide with these of para-aromatic axes of polymer I.

The transition from polymer III to polymer I is accompanied by the additional incorporation into the molecules of flexible portions of polyoxyethylene chain (POE) with the length $l_1=19.4\cdot10^{-8}$cm, which connect rigid fragments. Consequently, the fraction of rigid ester-aromatic fragments in the total chain length of polymer I is $x=(\Delta\cdot\cos\theta/2 + \delta\cdot\sin\theta/2)/\lambda_I$, equal to 0.60.

Taking into account the above considerations, chain flexibility of polymer I may be expressed by the equation

$$A_I^{-1} = x\cdot A_{III}^{-1} + (1-x)\cdot A_{POE}^{-1} \qquad (2)$$

where A_I is the Kuhn segment's length of molecules of polymer I ($A_I=26\cdot10^{-8}$ cm, the table) and A_{III} is the Kuhn segment length for polymer III ($A_{III}=80\cdot10^{-8}$ cm[3]). The solution of Eq.(3) with respect to the length of the Kuhn segment A_{POE} for the polyoxyethylene chain (fragments of which occupy the fraction $(1-x)=0.40$ with respect to the chain length of polymer I) leads to the value of $A_{POE}=13\cdot10^{-8}$ cm. This value is close to the segment Kuhn length evaluated[8] for a free oxyethylene chain ($A=(10\pm5)\cdot10^{-8}$cm).

The difference between equilibrium flexibilities of the molecules of polymers II and I, is due to differences in their structures shown in Fig.2. One of them is the decrease in the length of rigid fragments of the molecules of polymer II ($\Delta_{II}=25.6\cdot10^{-8}$ cm, $\Delta_I=30.8\cdot10^{-8}$ cm for polymers II and I, respectively). The other difference is the increase in the length of the flexible part of polymer II bonding rigid fragments of molecules. The elongation of the flexible portion is caused by the transition of two ester groups from the composition of rigid fragments of the molecules of polymer I into that of flexible fragments polymer II. In this case the virtually free motion of ester groups about the CH_2-O and CO-Ph bonds ensured a considerable increase in the flexibility of parts linking rigid fragments of molecules of polymer II.

The increase in chain flexibility of polymer II can be described quantitatively by the following additive equation

$$\lambda_{II}/A_{II} - \lambda_I/A_I = k\cdot\{(\cos\theta/2 + \delta/\Delta\cdot\sin\theta/2)^2/[(\delta/\Delta)^2 + (1+\cos\theta)/(1-\cos\theta)]\}\cdot\sigma^2 \qquad (3)$$

where k=2 is the number of ester groups included into the composition of flexible fragments of polymer II, $\delta/\Delta=0.2$ is the relative displacement of CH_2-O and CO-Ph bonds of ester groups in the direction normal to them, σ is the factor of hindrance of rotation about the same bonds, and the angle $\theta=70.5°$. The substitution into Eq.3 experimental values of A_I and A_{II} and the values of λ_I and λ_{II} found previously gives the hindrance factor $\sigma=1.1$. This value corresponds to virtually free rotation about the above bonds, which we have reported previously and which is characteristic of ester-aromatic chains[1].

Intramolecular orientational mobility of rigid mesogenic chain fragments is determined by the length and flexibility of spacers joining these fragments. At the same time the length and flexibility of spacers influence on the equilibrium-conformational parameters of the molecule, λ and A . In fact, λ increases with increasing length of flexible fragments. In turn, the increase in the length and equilibrium flexibility of these fragments results in the decreasing length of the Kuhn segment A.

Hence, the orientational mobility of rigid mesogenic fragments can be characterized by a dimentionless parameter λ/A. The values of λ/A for polymers I and II are 1.81 and 2.87 , respectively, and, as follows from the consideration of these values, they increase on passing from polymer I to polymer II.

It follows from the above considerations that the transition from para- (polymer I) to meta- (polymer II) inclusion of biphenylene fragments into the chains of polymers investigated here leads to increasing intramolecular orientational mobility of their rigid mesogenic fragments.

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