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OPTICAL ANISOTROPY AND CONFORMATION OF POLY (FLUOROALKOXYPHOSPHAZENES) IN SOLUTIONS

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Abstract Conformational and optical properties of some poly (fluoroalkoxyphosphazenes) (PAP) were investigated by flow birefringences and viscometry. Comparative research of optical anisotropy dependence of PAP moleculs on the side chain lenght were carried out. It is established that shear optical coefficient $[n]/[\eta]$ of PAP molecules essentially depends on the length and structure of the side chain.

INTRODUCTION

Polyphosphasenes (PAP) attract particular attention of researchers not only as polymers with voluable technologic properties but also as polymers exhibiting different forms of order. Phase transitions in polyphosphazenes and the effect of their side groups length have been studied systematically, and packing models for side and main chains have been considered[1].

It has been shown previously for a member of liquid crystalline polymers[2] that the mesomorphism of these polymer molecules is formed on the molecular level. This is due to the high equilibrium rigidity of the main chains (polyalkylisocyanates) or the presence of mesogenic fragments in the main or side chains (comblike polymers)[2].

The monomer units of the PAP do not contain classic mesogenic groups. Therefore, the problem of the nature of mesomorphism in these polymers requires that the properties of PAP and the conformation of their macromolecules be studied on the molecular level.

In the present work the optical and hydrodynamic properties of polyalkoxyphosphazenes (PAP) were investigated by flow birefringence and viscometry. The following samples and fractions of PAP were chosen for investigations: $[-N=P(OR)_2-]n$ differing in the structure of the side chain: $R_1=CH_2CF_3(PAP-I)$; $R_2=CH_2(CF_2)_2H(PAP-II)$;

$R_3=CH_2(CF_2)_4H(PAP-III)$.

EXPERIMENTAL DATA

The synthesis, the preparation of fractions, and their characteristics have already been described[3]. Flow birefringence (FB), Δn, was measured in ethyl acetate (EA) by a visual method in a dynamo-optimeter with an inner rotor 4cm in height along the beam path. The gap between the rotor and the stator was 0.0315 cm. Measurements were carried out at in a concentration range $(0.08\text{-}0.14)\cdot10^{-2}$ g/cm^3 and the flow rate gradients g ranged from 100 to 2000 sec^{-1} at 21°C. After special purification, the solutions were dispersed molecularly, which is confirmated by the linear slope of the dependence of the value of FB (Δn) (Fig.1, lines 1,2) and the orientation angle (Fig. 1, lines 3) for the solution on the flow rate gradient, g.

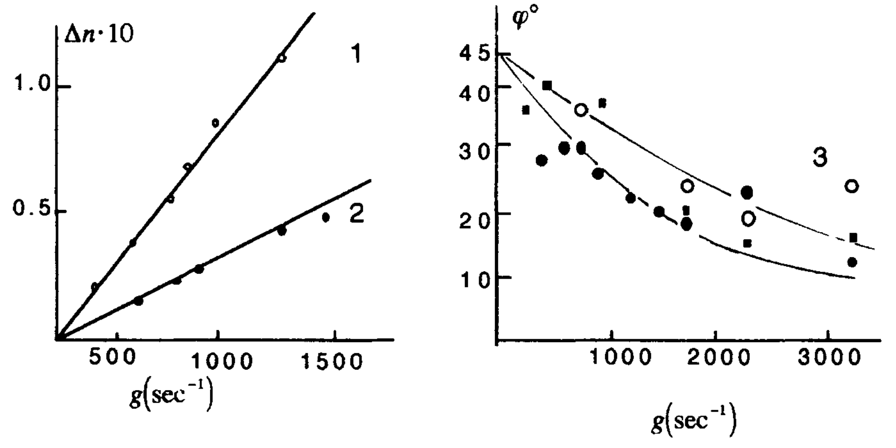

FIGURE 1. Birefringence $(\Delta n)(1,2)$ and orientation angle $(\varphi)(3)$ vs flow rate gradient (g) for PAP-I in ethyl acetate. Straight lines 1, 2 and 3: polymer concentration in solution
$C_1 = 0.32\cdot10^{-2}\, g/cm^3, C_2 = 0.18\cdot10^{-2}\, g/cm^3, C_3 = 0.14\cdot10^{-2}\, g/cm^3$.

The extrapolation of FB, Δn, to zero solution concentration and zero flow rate gradient gave shear optical coefficients $\frac{[n]}{[\eta]} = \lim_{\substack{g\to0\\ c\to0}} \Delta n / g(\eta - \eta_0)$, where η and η_0 are the viscosities of the solution and the solvent, respectively. The dynamo-optical and hydrodynamic characteristic of PAP in EA are given in Tables 1 and 2.

RESULTS AND DISCUSSION

Positive FB was detected in solutions of all the PAP samples. Special measurements have shown[4] that the refractive index increment of the PAP-ethyl acetate system is very low (dn/dc= 0.004). This fact implies that the experimental values of $[n]/[\eta]$ (Table 1) reflect the intrinsic anisotropy of PAP molecules.

Taking into account the high molecular weight M of the PAP samples it may be assumed[5] that in this range of M the values of $[n]/[\eta]$ do not depend on M. This fact makes it possible to determine the optical anisotropy of the Kuhn segment $\alpha_1 - \alpha_2$ according to the theory[5].

$$\alpha_1 - \alpha_2 = ([n]/[\eta])\left[45nkT/4\pi\left(n^2+2\right)^2\right], \tag{1}$$

were n is refractive index of the solvent, k is Boltzmann's constant and T is the temperature. The experimentally determined $\alpha_1 - \alpha_2$ values are given in the Table1.
The positive sign of FB implies that the optical polarizability of molecules is greater in the longitudinal direction α_1 than in the perpendicular derection α_2.

The optical anisotropy of the side chains, calculated with respect to their own axes, is mainly determinated by the presence of the fluorine atom, is positive, and may only be expected to decrease the anisotropy of the monomer unit.

This can be confirmed by the following experimental fact: a molecule with an optically isotropic organic main chain containing fluorine atoms in side chains exhibits slight negative anisotropy (Table 1, last line). Hence, the optical anisotropy of macromolecules PAP as whole is determined by that of the polymer backbone. The increase in the optical anisortopy of side groups with their increasing length decreases the optical anisotropy of all the molecule. The value of $\alpha_1 - \alpha_2$ decreases almost twice with increasing length of the side group. This experimental fact implies that the optical anisotropy of the main chain of the molecule containing alternating double bonds is relatively high. Long side chains only decrease the $\alpha_1 - \alpha_2$ value.

TABLE 1. Molecular characteristics of the samples of PAP in ethyl acetate.

	R	$[\eta]\cdot 10^{-2}$ cm^3/g	$M\cdot 10^{-6}$	$[n]/[\eta]\cdot$ $\cdot 10^{10}$	$(\alpha_1-\alpha_2)\cdot$ $\cdot 10^{25} cm^3$
1	$-CH_2CF_3$	6,2	18,0	13	160
2	$-CH_2(CF_2)_2H$	7,5 - 0,8	21,3 - 1,1	11	145
3	$-CH_2(CF_2)_4H$	6	9,1	8	106
4	$-CH_2-C(CH_3)-$ $O=C-OCH_2(CF_2)_2H$	a comparison		-2	-26

The molecules of polymers PAP-II and PAP-III have relatively long side chains and, in fact, they can be regarded as comblike macromolecules.

As shown by experimental data[2], a characteristic feature of comblike moleculs is the negative anisotropy of the whole molecule. However, in the case of PAP molecules, the contribution of side groups to optical anisotropy of the entire molecule is not sufficient to the attain the change in the sign of anisotropy. The high positive anisotropy of the main chain of the PAP molecule is probably due to a considerable ordering of the main chain. It is the existence of intramolecular order that is one of the main reasons determining the mesomorphism of macromolecules.

TABLE 2. Optical characteristics of the sample of PAP-II in ethylacetate.

	$M \cdot 10^{-6}$	$[\eta] \cdot 10^{-2}$ cm^3/g	$[n]/[\eta] \cdot 10^{10}$	$[x/g] \cdot 10^4$	G	D_r c^{-1}
I	1.13	0.8	10.5	-	-	-
II	5.86	3.6	10.0	2.6	0.68	320
III	9.96	5.0	-	-	-	-
IV	14.42	6.5	11.8	5.6	0.32	149
V	18.70	-	11-10	8.0	0.23	95
VI	21.13	7.5	11-12	7.9	0.27	105
n/f sample	11.40	6.0	11	5.0	0.4	173

The Table 2 gives the results of investigation of the molecular weight dependence of optical shear coefficient $[n]/[\eta]$ of PAP-II.

In the same table the characteristic values of orientation angles $[x/g] = \lim_{\substack{g \to 0 \\ c \to 0}} \left(\frac{\varphi^\circ - 45^\circ}{g} \right)$ are given. The experimental data show that in the investigated high molecular weight range the value of $[n]/[\eta]$ does not depend on M. Constant optical anisotropy is the characteristic property of molecules having the shape of a Gaussian coil.

Regardless of the model properties of particles, characteristic orientation in solution determines the orientational relaxation of the particules in flow, i.e. rotational diffusion coefficient of macromolecules D_r.

$$[x/g] = (12Dr)^{-1}. \qquad (2)$$

The coefficients D_r calculated from eq. (2) were used to evaluate the degree of the equilibrium rigidity of PAP-II molecules.

According to the theory of rotational friction of the wormlike chains[5], the plotting of the dependence of $D_r \cdot M^2/kT$ on $M^{1/2}$ makes it possible to estimate the length of the Kuhn's segment of the molecule A. The value of A for PAP-II molecules is A=(120 ± 10) Å. Hence, the main chain of PAP molecules, which contains alternating double bonds actually has limited flexibility: its rigidity is 4-5 times higher that of usual flexible chain macromolecules. The characteristic orientation angle $[x/g]$ of molecules also dependes on their molecular weight M:

$$[x/g] = GM[\eta]\eta_0 / RT \qquad (3)$$

were R is the universal gas constant and η_0 is the solvent viscosity. The coefficient G depends on the properties of the model used for discribing the hydrodynamic behaviour of the molecules. This coefficient depends on the degree of flexibility of the macromolecule and the hydrodynamic interaction in the chain. For a kinetically rigid Gaussian coil the value of G is much higher than for a flexible coil, and its dependence on hydrodynamic interaction is slight.

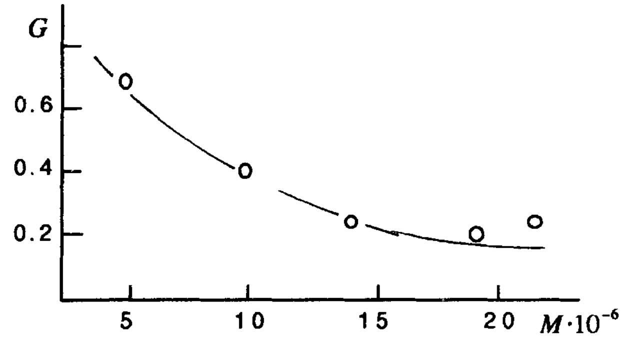

FIGURE 2. Dependence of the coefficient G vs molecular weight M for PAP-II in ethil acetate.

Fig. 2 shows the molecular weight dependence of the coefficients G calculated from eq. (3). At high M the value of G tends to the limiting value $G_{M \to \infty} = 0{,}2$ which is characteristic of nondraining Gaussian coil. The increase in G with decreasing M reflects a certain change in the conformation of PAP molecules: a specific feature of these molecules consists in an increase in coil draining with decreasing molecular weight.

The results of investigation of FB of PAP molecules (value of $[n]/[\eta]$, $\alpha_1 - \alpha_2$) and the orientation of macromoleculus in flow (valus of $[x/g], D_r$, G) reflects the specific features of molecular conformation. Alternating double bonds of the inorganic main chain increase the equilibrium rigidity of macromolecules. This fact is confirmed by the positive sign of FB and by the high Kerr effect observed for these polymers[4].

The interaction between side chain and the high molecular weight determine the hydrodynamic non-draining of molecules (strong hydrodynamic interaction - low G values). Both these features lead to the intramolecular order of chain elements. It is these features of molecular conformation which ensure orientational and polar orders, that determine the mesomorphism of PAP molecules when the interacting groups are sufficiently long.

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