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Flow Birefringence of Polyamides and Polyesters in Acid Solutions

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FLOW BIREFRINGENCE OF POLYAMIDES AND POLYESTERS IN ACID SOLUTIONS

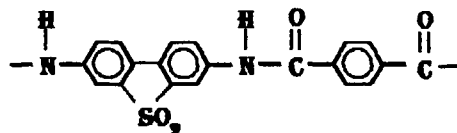
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Abstract Flow birefringence and viscometry of dilute acid solutions of polyamide and polyester are used for investigations of hydrodynamical, optical and conformational characteristics of their molecules. Quantative data on the equilibrium rigidity of the molecules are compared with those obtained before for the molecules with similar structure.

INTRODUCTION

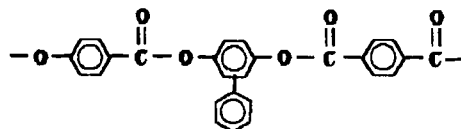
In recent years great attention has been paid to the new materials with liquid crystalline, thermo-mechanical and fibre making properties. High equilibrium rigidity of the macromolecules often determines lyotropic or thermotropic mesomorphism in a concentrated solution or bulk. It was shown in cellulose and its derivatives¹ that cycles in the main chains brings macromolecules to the high rigidity. The extreme rigidity of synthetic polyisocyanates² is connected with quasiconjugation along the chain. As our investigations have shown^{3,4} the high rigidity of aromatic polyamides is due to the para-position of phenylene ring and trans-configuration of amide groups - the "crankshaft" conformation. For fibre strength modification different heterocycles were introduced in polyamide molecules⁵. Poly(biphenylsulfone terephthalamide) (PPhSTPhA) investigated in the present work has the structure:



This copolyamide differs from poly(para-phenylene terephthalamide) (PPPhTPhA) by the presence of dibenzothiophene sulphone⁶ and as is the case for most of para-polyamides is soluble only in sulphuric acid. In concentrated solution this poly-

mer forms lyotropic liquid-crystalline mesophases.

Another polymer for our studies is para-aromatic polyester with the following structure:



This thermotropically mesogenic phenyl-substituted para-aromatic polyester is soluble in mixture of acids (14.4% monochloroacetic + 35.5% dichloroacetic + 50.1% trichloroacetic) acid.

EXPERIMENTAL DETAILS

Some samples of PPhSTPhA marked in the Table 1 by asterisk are the result of thermal degradation (heating temperature 70-105°C for 100 hours in sealed ampoules)⁷. Intrinsic viscosity $[\eta]$ and flow birefringence (FB) were measured in 96% sulphuric acid ($\eta_s = 22 \cdot 10^{-2}$ ps, $\rho = 1.843$ g/cm³). The values of $[\eta]$ given in the Table 1 were determined in Ostwald viscometer at a solvent flow time $\tau_0 = 62.4$ s. FB Δn was measured by a previously described method³ in a teflon dynamo-optimeter with an inner rotor (height =

TABLE 1 Hydrodynamical and optical characteristics of PPhSTPhA

$[\eta] \cdot 10^{-2}$ cm ³ /g	$[\eta]/[\eta] \cdot 10^{10}$ cm s g ⁻¹	$[\chi/g] \cdot 10^5$ s ⁻¹	$M_\eta \cdot 10^{-4}$	$M_{\text{vis}} \cdot 10^{-4}$	G
9.0	460	35	5.25	5.76	0.64
8.0	460	30	4.68	5.55	0.71
7.0	450	23	3.80	4.86	0.82
6.5	450	23	4.12	5.24	0.70
4.25	460	12	2.57	4.18	0.99
4.0*	440	7.5	2.40	2.78	0.71
1.95*	340	1.8	1.78	1.37	0.65
1.00*	280	0.66	0.78	0.98	0.80
0.48*	200		0.47		
0.36*	170		0.39		
0.15*	167		0.22		
0.09	130		0.16		
0.06*	45		0.12		

6 cm, gap = 0.055 cm). The ratio of dynamo-optical constants $[\eta] = \lim_{\substack{g \rightarrow 0 \\ c \rightarrow 0}} \frac{\Delta n}{g \eta_o c}$ to $[\eta]$ gi-

ves the shear optical coefficient $[\eta]/[\eta]$ (Table 1) which characterizes the optical properties of dissolved macromolecules. The FB orientational angles, φ , dependence on flow rate gradient, g , were observed. Values of the characteristic orientation angle

$\left[\frac{\chi}{g} \right] = \lim_{\substack{g \rightarrow 0 \\ c \rightarrow 0}} \frac{45^\circ - \varphi}{g}$ are given in Table 1. High $[\eta]/[\eta]$ values and its dependence on $[\eta]$

make it possible to use the theory of optical and hydrodynamic properties of kinetically-rigid worm-like chains¹.

The molecular weights M_η were determined from experimental $[\eta]$ values using Equation (1) obtained for PPPhTPhA⁴

$$[\eta] = M^2 * (48 + 0.42 M^{1/2})^{-3} \quad (1)$$

and $M_{[\chi/g]}$ we calculated using Equation (2) and the experimental $[\chi/g]$ and $[\eta]$ values

$$[\chi/g] = GM * [\eta] \eta_o / RT \quad (2)$$

where G is a model coefficient¹.

The experimental dependence of $[\eta]/[\eta]$ on M (Figure 1) can be written¹ as following

$$[\eta]/[\eta] = B\beta AM / (M + M_S) \quad (3)$$

where A is a Kuhn segment length and β is an optical anisotropy of unit length; $B = 4\pi(n^2 + 2)^2 / 45nkT$ is an optical coefficient (n is refractive index of solvent, k is Boltzmann constant and T is absolute temperature); M_o , M_L , and M_S are molecular weight of monomer unit, unit of chain length, and Kuhn segment.

When $M \rightarrow \infty$ Equation (3) comes to

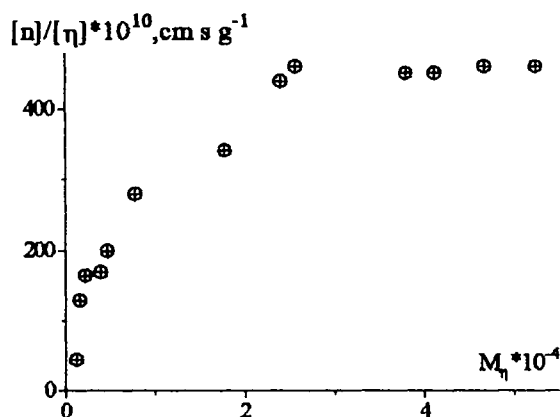
$$[\eta]/[\eta]_\infty = B\beta A \quad (3a)$$

and when $M \rightarrow 0$ Equation (3) comes to

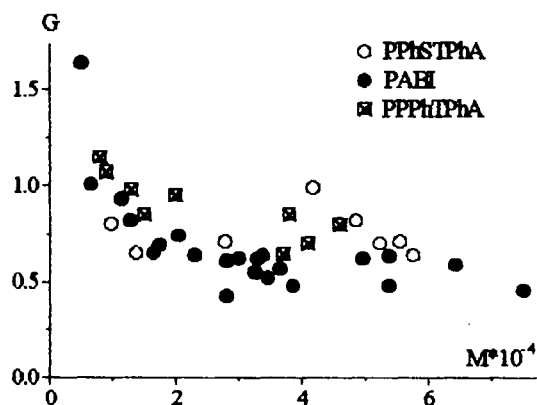
$$\partial([\eta]/[\eta])/\partial M = B\beta/M_L \quad (3b)$$

The ratio of Equations (3a) to (3b) is equal to $M_S = 8 * 10^3 = M_o * S$; $M_o = 376$ and $S = 21$ (S -- number of monomer units in Kuhn segment).

The analyses of λ , the length of monomer unit projection on the molecular axis

FIGURE 1 Dependence of $[\eta]/[\eta]$ on M for PPhSTPhA

makes it possible to select $\lambda = (16.8 \pm 0.2) \cdot 10^{-8}$ cm. For this λ the Kuhn segment length A for PPhSTPhA is $(350 \pm 10) \cdot 10^{-8}$ cm and optical anisotropy of the monomer unit $\Delta a = 310 \cdot 10^{-25}$ cm. Comparing $M[\eta]$ and $[\chi/g]$ in Equation 1 and 2 one can obtain G values. The values for polyamidobenzimidazole (PABI) and PPPhTPhA investigated before and PPhSTPhA at high M are $G = 0.75 \pm 0.05$ so in agreement with

FIGURE 2 Dependence of G on M of poly-para-amides

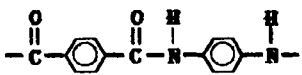
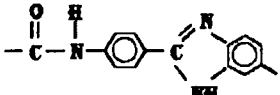
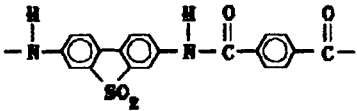
theory this G value reflects coil-draining of polyamide molecules.

For rigid-chain aromatic polymers^{4,5} the dependence of $[n]/[\chi/g]$ on $[n]/[\eta]$ can be linear:

$$[n]/[\chi/g] = RT(\eta_s G) [\beta \beta/M_L + (AM_L)^{-1} [n]/[\eta]] \quad (4)$$

Using the intercept, $(BRT/\eta_s G) \cdot \beta M_L$, and slope, $\partial([n]/[\chi/g])/\partial([n]/[\eta]) = -RT(\eta_s G)AM_L$, one can calculate $\beta = 20 \cdot 10^{-17} \text{ cm}^2$ and $A = (340 \pm 10) \cdot 10^{-8} \text{ cm}$.

TABLE 2 Optical and conformational properties of para-aromatic polyamides

POLYMER	$([n]/[\eta])_\infty \cdot 10^{10}$ cm s g	$\beta \cdot 10^{17}$ cm ²	$A \cdot 10^8$ cm	σ cN/tex	ΔE , GPa
	400	17	300	290	
	360	18	290		30
	520	19	345	310	40

From Table 2 we see the increase in equilibrium rigidity of PPhSTPhA molecules over that of PAB and PPPhTPhA which is caused by introduction of a heterocycle none distorting "crankshaft" but increasing the length of the rigid-chain part. This agrees with the change in fibre strength and elastic modulus.

Another fibre making para-aromatic polymer - polyester III (Table 3) is soluble only in the mixture of chloroacetic acids. Experimental results by flowbirefringence and intrinsic viscometry make it possible to know the molecular weights of the samples from the equation $[\eta] = K_\eta M^\alpha$ ($K_\eta = 0.00129$ and $\alpha = 1.22$)¹⁰ and to calculate the equilibrium rigidity from Equation (3a), on the assumption $\beta = 8.3 \cdot 10^{-17} \text{ cm}$, so $A = (230 \pm 20) \cdot 10^{-8} \text{ cm}$.

Comparing the polyesters from Table 3 we can say that the main contribution to the rigidity of polyesters is an ester group with trans-structure and quasiconjugation

along the chain so that the molecular order in the *para*-aromatic esters chains depends on their regularity and position of phenyl side group.

TABLE 3 Optical and conformational properties of *para*-aromatic polyesters

STRUCTURE	$[\eta]/[\eta]^* \cdot 10^{-10}$ $\text{cm}^2 \text{s}^2 \text{g}^{-1}$	$\beta \cdot 10^{17}$ cm^2	$A \cdot 10^8, \text{cm}$	Ref.
	130	8.1	200 ± 20	8
	150	8.1	220 ± 20	9
	160	8.3	230 ± 20	This work
	240	8.6	350 ± 20	10

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