Conformation and Equilibrium Rigidity of Molecules of Poly(phenylquinoxalines)

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ABSTRACT: Hydrodynamic properties (sedimentation, diffusion, and viscosity) and flow birefringence (FB) have been investigated for solutions of three samples of poly(phenylquinoxalines) (PPhQ) differing in the number of rotating bonds in the repeat unit. Parameters of the equilibrium rigidity (the Kuhn segment length) for molecules of the polymers investigated were determined. The conformational analysis of the PPhQ chains was carried out taking into account possible stereoisomeric forms of quinoxaline groups of molecules. The degree of hindrance σ^2 to intramolecular rotations in the PPhQ molecules was found to be close to those for aromatic polyamides. The experimental data of FB show that the molecules of the investigated PPhQ are not stereoregular. The conclusion that the PPhQ structure is irregular on a molecular level agrees well with the fact that these polymers have low crystallizability in spite of their high chain rigidity.

The synthesis and investigation of thermomechanical properties of poly(phenylquinoxylines) (PPhQ) were the subject of many investigations carried out in recent years.[1-6] To a great extent this is due to the high thermal and thermooxidative stability of these polymers and the possibility that materials with good technical properties can be prepared from them.

At the same time, although phenylated polyquinoxalines are readily dissolved in common organic solvents, their molecular characteristics in dilute solutions have not been widely studied. Recently, when the methods of light scattering,[7] osmometry,[8] and sedimentation[9] have been used, the molecular weights of some PPhQ samples and fractions have been determined and the dependences of intrinsic viscosities on the molecular weight of these polymers have been obtained. Moreover, an attempt has been made to carry out the conformation analysis of these molecular structures.[7]

The conformational analysis in ref 7 is based on hydrodynamic data. The authors use for interpretation the value of $[\eta]$ (the intrinsic viscosity). However, these characteristics greatly depend on the degree of branching and on the strength of the solvent. In particular, the authors ascribe the deviation from the Gaussian properties to the excluded volume effect and use the Stockmayer–Fixman procedure for finding unperturbed dimensions. Nevertheless, for macromolecules of the type of PPhQ, the deviation from the Gaussian behavior is probably due to the draining effect, and in this case it is necessary to use, for example, the theory of Yamakava and Fujii.[26]

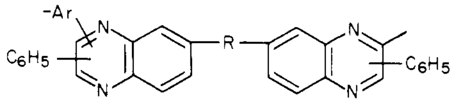
Since it is difficult to interpret uniquely the conformational properties of PPhQ by using hydrodynamic data alone, we used another method: flow birefringence (FB), in which the value of $[n]/[\eta]$ ($[n]$ is the characteristic value of birefringence) is used. It is well known from both experimental data and theoretical papers that when the chain is relatively long (the Gaussian range), the value of $[n]/[\eta]$ does not depend on the power of the solvent (if the effect of the macroform is absent), on hydrodynamic interaction, and on excluded volume effects.[10-12] It does not depend on the branching of macromolecules either, provided the branches are relatively long. This value may be obtained from photoelastic measurements in slightly swollen networks.[10,12]

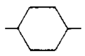
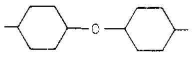
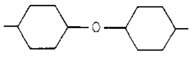
The FB method has been particularly useful in investigations of polymers with very rigid chains.[13-15]

Samples, Measurement Procedure, and the Results Obtained

Three samples of PPhQ with the same structure (Table I) were investigated.

Table I
Structure of Poly(phenylquinoxalines)



	R	Ar
I		
II		
III	O	

Polymers were synthesized by using the methods described previously.[4-6]

Polymers II and III were fractionated by the method of fractional precipitation of chloroform solutions (initial concentration $C = 0.5 \times 10^{-2}$ g/cm^3) with heptane. Polymers II and III gave 12 and 14 fractions, respectively. Measurements of viscosities of solutions required for the determination of intrinsic viscosity, $[\eta]$ (Table II), were carried out in a capillary viscometer in two solvents, tetrachloroethane and chloroform, at 21 °C. FB for all samples and fractions was measured in an instrument with an internal rotor in which the length of the optical beam is 3 cm and the gap width is 0.029 cm.

This apparatus and a compensator with the phase difference 0.033 λ (λ = 5460 Å) permitted flow birefringence Δn to be measured in the range of $C \leq 10^{-2}$ g/cm^3 and the flow rate gradients g in the range from 50 to 3000 s^{-1}. Measurements of Δn were carried out in tetrachloroethane and in chloroform at 21 °C.

The molecular weights of unfractionated polymers and fractions of polymer II were determined from the sedimentation–diffusion analysis in tetrachloroethane. Translational diffusion was investigated with a polarizing diffusometer.[16,17] The sedimentation analysis was carried out with a G 120 analytical centrifuge (MOM, Hungary) equipped with an interferometric attachment[18] at a rotor speed of 37 000 rpm. Experiments were carried out with the use of an artifical boundary in a cell with a polyamide insert. The precision of determinations of the low flotation coefficients involved was 15–20%, and the corresponding error in the determinations of M was ca. 20–30%. The measurements of D were carried out at $C = 0.06 \times 10^{-2}$ g/cm^3 and those of $[S]$ at $C = 0.08 \times 10^{-2}$ g/cm^3. The values obtained were assumed to coincide with the values at $C \to 0$. The molecular weight M was determined from

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Table II
Hydrodynamic and Optical Characteristics of PPhQ Samples and Fractions

		tetrachloroethane					chloroform	
polymer	fraction no.	$[\eta] \times 10^{-2}$ $\mathrm{cm^3\,g^{-1}}$	$[S] \times 10^{13}$	$D \times 10^7$ $\mathrm{cm^2\,s^{-1}}$	$M \times 10^{-4}$	$[n]/[\eta] \times$ $10^{10}\ \mathrm{g^{-1}}$ $\mathrm{cm\,s^2}$	$[\eta] \times 10^{-2}$ $\mathrm{cm^3\,g^{-1}}$	$[n]/[\eta] \times$ $10^{10}\ \mathrm{g^{-1}}$ $\mathrm{cm\,s^2}$
I	unfract.	1.35	0.6	1.3	6.0	140	1.20	140
II	1	1.20		1.0	12.0		1.15	85
	2	1.03	0.7	1.1	8.4		0.90	85
	3	0.77	0.5	1.6	4.1		0.66	80
	4	0.59	0.4	2.4	2.2		0.44	40
	5	0.44	0.35	2.75	1.7			
	6	0.29		4.0	0.8		0.25	60
	7	0.13	0.3	6.0	0.6		0.11	45
	unfract.	0.85	0.6	1.1	7.0	77	0.70	82
III	1	1.90			13.0	45		
	2	1.64			12.0	44		
	3	0.96			8.0			
	4	0.90			6.5	48		
	5	0.40			3.0	51		
	unfract.	1.55			11.0	45	1.22	45

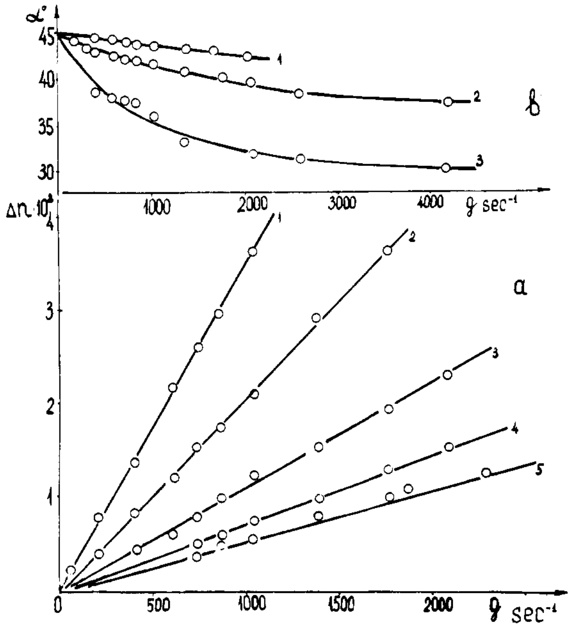


Figure 1. Values of Δn (a) and orientation angle α (b) vs. flow rate gradient g for sample 111 in tetrachloroethane: (a) concentration of solutions, fraction 5: 1, 0.82×10^{-2} g/cm^3; 2, 0.60×10^{-2} g/cm^3; 3, 0.33×10^{-2} g/cm^3; 4, 0.25×10^{-2} g/cm^3; 5, 0.16×10^{-2} g/cm^3; (b) 1, $M = 6.5 \times 10^4$ (fraction 4); 2, $M = 11.0 \times 10^4$ (unfractionated sample); 3, $M = 13.0 \times 10^4$ (fraction 1).

Svedberg's equation and the specific partial volume $\bar{v} = 0.75$ cm^3/g was determined pycnometrically.

The molecular weights M_w of sample III and its fractions were determined by light scattering with an FPS-2 instrument. All measurements were carried out at an angle of 90° and at $\lambda = 5460$ Å. Before measurements were taken, the solutions were centrifuged at 10^4 rpm. The values of CH/J were extrapolated to zero concentrations C, where H is the optical constant and J is the light scattering intensity.

The type of dependence of orientation angles α and birefringence Δn on the rate gradient indicated that the solutions under investigation exhibit true molecularity (Figure 1a,b).

The slopes of the plots of Δn vs. $g(\eta - \eta_0)$ (Figure 2) allow the determination of the value of reduced FB, $\Delta n/g(\eta - \eta_0) = [n]/[\eta]$ (Table II), for fractions and samples. Figure 3 shows that the values of $\Delta n/g(\eta - \eta_0)$ in tetrachloroethane and in chloroform coincide for each polymer.

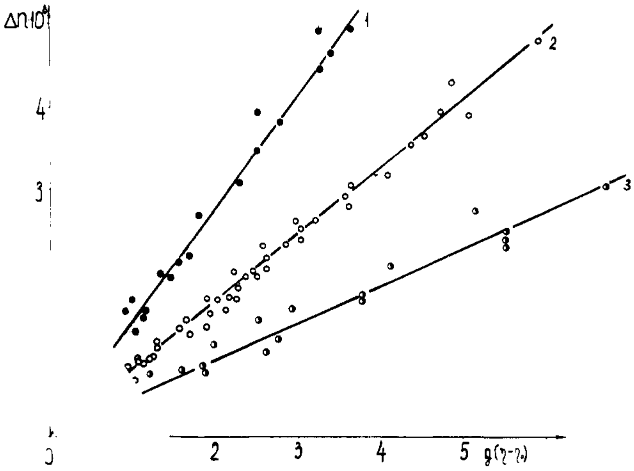


Figure 2. Value of flow birefringence Δn vs. shearing stress $g(\eta - \eta_0)$ for solutions of poly(phenylquinoxaline) fractions in tetrachloromethane and in chloroform. Numbers on the lines correspond to those of the investigated polymers.

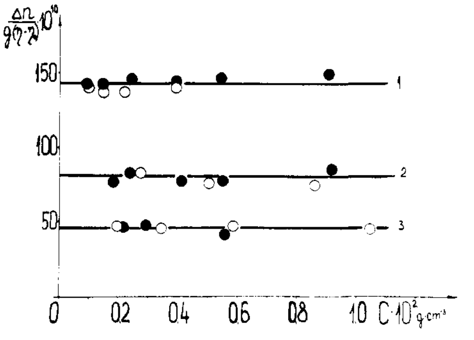


Figure 3. Reduced birefringence $\Delta n/g(\eta - \eta_0)$ vs. concentration of solution C for samples of poly(phenylquinoxalines) in two solvents: open circles, tetrachloroethane; filled circles, chloroform. Numbers on the lines correspond to those of poly(phenylquinoxalines).

Flow birefringence is high and positive because strongly anisotropic phenyl rings are incorporated in the main polymer chain. The values of M and $[\eta]$ in Table II correlate with the data for PPhQ published previously.[7-9]

Optical Anisotropy and Equilibrium Chain Rigidity[33]

At high M the value of $[n]/[\eta]$ for polymers II and III is virtually independent of the molecular weight. This

Table III
Experimental Values of Characteristic FB and Parameters of Equilibrium Rigidity of PPhQ Molecules

sample	$[n]/[\eta]\times 10^{10}$ g^{-1} cm s^2	P	S	PS	λ/l trans-trans	λ/l cis-cis	λ/l trans-cis, cis-trans	A, Å trans-trans	A, Å cis-cis	A, Å trans-cis, cis-trans
I	140	7	9.5	66.5	12.12	11.36	11.29	161	151	150
II	85	8	5.05	40.4	15.39	14.80	14.72	109	105	104
III	50	8	2.97	23.7	15.59	15.59	15.87	65	65	66

means that the role of the macroform's effect is negligible, the dynamo-optical properties of polymer molecules in this range of M correspond to those of Gaussian coils, and the value of $[n]/[\eta]$ is determined from Kuhn's equation:

$$[n]/[\eta] = B\beta A \qquad (1)$$

where A is the length of the Kuhn segment, β is optical anisotropy of the unit length of a completely extended chain (without deformation of valency angles and bonds), and B is a factor dependent on the refractive index n and the temperature T of a dilute solution:

$$B = (4\pi/45kTn)(n^2 + 2)^2$$

For chain molecules with high kinetic and equilibrium rigidity, the value of $[n]/[\eta]$ decreases with M tending to a limit $[n]/[\eta] \rightarrow 0$ at $M \rightarrow 0$.[19a] For these molecules the value of β can be determined from the initial slope (at $M \rightarrow 0$) of the curve $[n]/[\eta] = f(M)$ and also from the shape of this curve.[19] For fractions of polymer II (Table II) the decrease in $[n]/[\eta]$ with M is seen quite distinctly, but these data are not sufficient to determine the initial slope of the curve $[n]/[\eta] = f(M)$ and, correspondingly, to calculate β. Hence, to evaluate β we shall compare dynamo-optical properties of PPhQ with those of well-investigated aromatic polyamides.[14,15,20-22]

The optical anisotropy of such molecules as PPhQ mainly consisting of aromatic rings in a linear (chain) order is virtually entirely governed by the anisotropy of these rings. The same can be said about aromatic polyamides. The optical anisotropy of the phenyl ring with respect to the central axis lying in its plane is 30×10^{-25} cm^3.[20] The anisotropy of the naphthalene ring is twice as large[23] and is virtually equal to that of the nitrogen-containing quinoxaline heterocycle which forms a part of the PPhQ chain. Consequently, in calculating the anisotropy one quinoxaline ring can be taken equivalent to two phenyl rings. It should be borne in mind that the effective anisotropy Δa of the phenyl ring in the solvent medium can differ from 30×10^{-25} cm^3 owing to the effect of microform[24] which is proportional to the square of the refractive index increment dn/dc in the polymer–solvent system. However, for solutions of aromatic polyamide in sulfuric acid[20-22] and for those of PPhQ in chloroform, the values of dn/dc and refractive indices n virtually coincide. This means that for the two polymer–solvent systems being compared the values of the optical factor B in eq 1 are equal and the values of β are proportional to the number of phenyl rings per unit length in the direction of the extended chain. Hence, if we compare the value of $[n]/[\eta]$ for PPhQ with the value of $([n]/[\eta])_{TPhA}$ obtained earlier for poly(p-phenyleneterephthalamide) (PPPhTPhA),[22] we can write for the Gaussian range:

$$([n]/[\eta])/([n]/[\eta])_{TPhA} = (\beta A)/(\beta_{TPhA}A_{TPhA}) \qquad (2)$$

where $\beta = P\Delta a/\lambda$ and $\beta_{TPha} = P_{TPhA}\Delta a/\lambda_{TPhA}$. Here λ is the length of the PPhQ chain repeat unit, P is the number of phenyl rings in the PPhQ repeat unit, λ_{TPhA} and P_{TPhA} are the same values for PPPhTPhA, and A and A_{TPhA} are lengths of the Kuhn segment for the PPhQ and PPPhTPhA chains, respectively.

When we take account of the fact that $A/\lambda = S$ and $A_{TPhA}/\lambda_{TPhA} = S_{TPhA}$ where S and S_{TPhA} are the numbers of "monomer units" (repeat units of the chain) in a Kuhn segment for the PPhQ and PPPhTPhA chains, respectively, we obtain from eq 2:

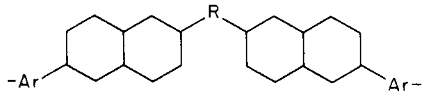
$$S = \frac{[n]/[\eta]}{([n]/[\eta])_{TPhA}}\,\frac{P_{TPhA}S_{TPhA}}{P} \qquad (3)$$

For PPPhTPhA it is known[22] that P_{TPhA} is 1, $([n]/[\eta])_{TPhA}$ is 400×10^{-10} cm s^2 g^{-1}, and S_{TPhA} is 190. The values of P for the three samples of PPhQ being studied (Table III) are known from the structural formula (Table I), and the average experimental values of $[n]/[\eta]$ for these samples are shown in Table III. Using these data from eq 3, we obtain the values of S presented in Table III. They characterize the equilibrium rigidity of chains of these PPhQ samples and the values of PS equal to the number of phenyl rings in a Kuhn segment. To determine the more usual (and more obvious) characteristics, the Kuhn segment length A, we should calculate the length of the repeat chain unit λ which in principle can depend on the stereochemical configuration of the quinoxaline chain nucleus.

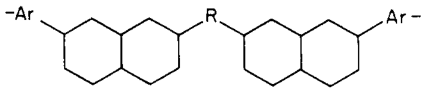
This configuration is determined by the type of bonding of the quinoxaline ring to the adjacent bonds of the main chain which takes place with the formation of cyclic structures during polycondensation.

In principle, attachment of four types can be distinguished leading to four stereoisomeric forms of the quinoxaline nucleus.

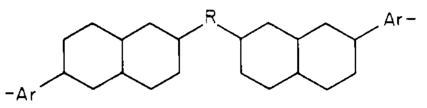
trans-trans



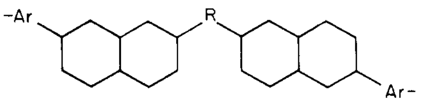
cis-cis



trans-cis



cis-trans



The two latter structures differ only when the Ar group is asymmetrical (as in samples II and III) and do not differ when Ar is symmetrical (as in sample I).

Extended conformations of molecules of the PPhQ samples investigated corresponding to the above types of

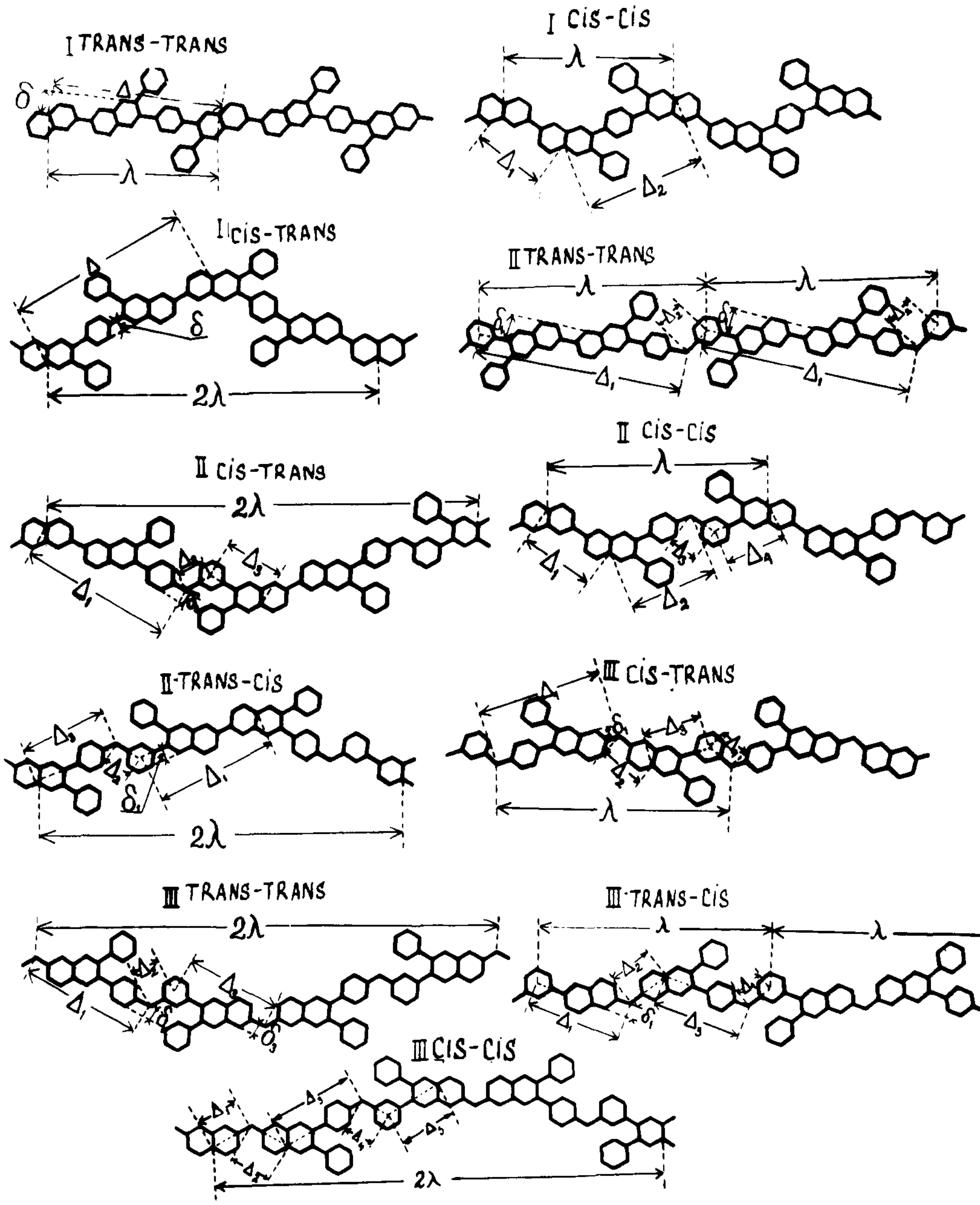


Figure 4. Extended conformations of molecules of poly(phenylquinoxalines) I, II, and III corresponding to different isomeric forms of the quinoxaline group in the chain.

bonding are shown in Figure 4. In the scheme all valency bonds in the chain are taken to be l = 1.4 Å and the angles to be 120°. The length of the repeat unit λ for each structure is shown in the figure. The numerical values of λ/l for polymers I, II, and III corresponding to different structures of the quinoxaline chain nucleus are shown in Table III. These data show that only for polymer I is a small increase (~10%) observed in the value of λ/l corresponding to the trans-trans structure as compared to those for two other types of bonding. With the exception of this case, for all three polymers the length of the repeat unit (or λ/l) is virtually independent of the stereoisomerism of the quinoxaline nucleus. Consequently, the lengths of the Kuhn segments in the last column in Table III can be reliably calculated from experimental values of S in Table III by using the relationship $A = \lambda S$. The differences in the values of A for the same polymer related to differences in the assumed values of λ/l are much lower than errors in experimental data used to determine A. Taking this into account and in accordance with Table III, it should be assumed that for PPhQ I A is 150 Å, for PPhQ II it is 104 Å, and for PPhQ III it is 65 Å.

The value of A for polymer I is greater by an order of magnitude than the values characteristic of typical flexible-chain polymers.[24,25] This makes it possible to consider polymer I as a rigid-chain polymer.[13,14] The equilibrium rigidity of polymers II and III is slightly lower because they contain a larger number of bonds about which rotation is possible. However, even for these polymers A is four- to sevenfold higher than for flexible-chain polymers. If the hydrodynamic diameter d of molecules of investigated PPhQ is taken to be 5–6 Å, the parameter of intramolecular hydrodynamic interaction d/A should be in the range of 0.04 to 0.1. This is several times lower than the value characteristic of flexible-chain polymers[24,26] even without bulky side groups. This means that in discussing hydrodynamic properties of PPhQ molecules in solution, the undrained Gaussian coil cannot serve as an adequate model. This is confirmed qualitatively by low value of the sedimentation coefficients [S] of these polymers (Table

Table IV
Virtual Bonds $\Delta_1, \Delta_2, \ldots, \Delta_\nu$ and Their Number ν in the Repeat Unit of an Equivalent Chain[a]

polymer	stereoisomeric form of QG	ν	virtual bonds	A_f, Å	σ^2
I	trans-trans	1	$\Delta = 12l$; $\delta = l3^{1/2}$	∞	
	cis-cis	2	$\Delta_1 = 5l$; $\Delta_2 = 8l$	31.4	4.8
	cis-trans trans-cis	1	$\Delta = 12.5l$; $\delta = l3^{1/2}/2$	58.4	2.6
II	trans-trans	2	$\Delta_1 = 14l$; $\Delta_2 = 2l$; $\delta_1 = l3^{1/2}$	31.7	2.9
	cis-cis	4	$\Delta_1 = 5l$; $\Delta_2 = 6l$; $\Delta_3 = 2l$; $\Delta_4 = 4l$	20.9	5.2
	cis-trans	3	$\Delta_1 = 10.5l$; $\Delta_2 = 2l$; $\Delta_3 = 4l$; $\delta_1 = l3^{1/2}/2$	27.5	3.8
	trans-cis	3	$\Delta_1 = 8.5l$; $\Delta_2 = 2l$; $\Delta_3 = 6l$; $\delta_1 = l3^{1/2}/2$	26.8	3.9
III	trans-trans	3	$\Delta_1 = 8.5l$; $\Delta_2 = 2l$; $\Delta_3 = 6.5l$; $\delta_1 = l3^{1/2}/2$; $\delta_3 = l3^{1/2}/2$	27.0	2.4
	cis-cis	5	$\Delta_1 = 3l$; $\Delta_2 = 3l$; $\Delta_3 = 6l$; $\Delta_4 = 2l$; $\Delta_5 = 4l$	18.2	3.5
	cis-trans	4	$\Delta_1 = 8.5l$; $\Delta_2 = 3l$; $\Delta_3 = 4l$; $\Delta_4 = 2l$	21.2	3.1
	trans-cis	4	$\Delta_1 = 6.5l$; $\Delta_2 = 3l$; $\Delta_3 = 6l$; $\Delta_4 = 2l$; $\delta_1 = l3^{1/2}/2$	20.7	3.2

[a] The length of the Kuhn segment A_f at free rotation and the parameter of hindrance to rotation σ^2 in PPhQ molecules for different stereoisomeric forms of the quinoxaline group (QG) in the chain.

II), which indicate the absence of strong intramolecular hydrodynamic interaction (i.e., high "draining" effect) in polymer chains.

To solve the problem whether high equilibrium rigidity of the PPhQ molecules is due to strong hindrance to rotation in their chains or is a result of geometrical properties of their structure, it is necessary to consider in greater detail the conformational analysis of these molecules.

Conformations and Hindrance to Rotation in PPhQ Molecules

Conformational properties of molecules of a PPhQ I sample depend strongly on the isomeric form of the quinoxaline nucleus. If it is the trans-trans form, then (as Figure 4 clearly shows) at any chain conformation all the valency bonds about which rotation is possible become parallel. Hence, the chain is in the "crankshaft" conformation[27] characterized by a very high degree of intramolecular orientational order and very high equilibrium rigidity. In this conformation of PPhQ molecules, the FB of their solutions should not be lower than in solutions of paraaromatic polyamides[22] and, correspondingly, the value of A should exceed at least by an order of magnitude the experimental value (Table III). Nevertheless, the experimental results sharply contradict this, showing that even if the trans-trans form of the quinoxaline nucleus exists in the PPhQ molecules, it is not the only form. This result seems quite natural since the polycondensation process of the formation of PPhQ is not "stereospecific".

If it is assumed that in the formation of the PPhQ chain all the quinoxaline nuclei acquire the cis-cis structure, it follows that, according to Figure 4, the molecule of sample I can be modeled by an equivalent chain of linear portions (virtual bonds) jointed at an angle $\alpha = 60°$ (the valency angle is 120°) of length $\Delta_1 = 5l$ and $\Delta_2 = 8l$ in each monomer unit. For this chain, with complete freedom of rotation of parts $\Delta_1, \Delta_2, \ldots \Delta_\nu$ (with the same angle α), by using the methods of statistical mechanics[28-30] it is possible to obtain for the length of the Kuhn segment A_f the expression:

$$\lambda A_f = \frac{1 + \cos^\nu \alpha}{1 - \cos^\nu \alpha} \sum_{i=1}^{\nu} \Delta_i^2 + \frac{2}{1 - \cos^\nu \alpha} \sum_{i=1}^{\nu-1} \sum_{k>i}^{\nu} \Delta_i \Delta_k (\cos)^{k-i} \alpha + \cos^{\nu-(k-i)} \alpha \quad (4)$$

where ν is the number of virtual bonds Δ_i in the part of an equivalent chain corresponding to the repeat unit of the polymer chain.

For the PPhQ I sample with the quinoxaline nucleus in the cis-cis configuration, ν is 2 and eq 4 is reduced to the form:

$$A_f = \frac{(\Delta_1^2 + \Delta_2^2)(1 + \cos^2 \alpha) + 4\Delta_1\Delta_2 \cos \alpha}{\lambda(1 - \cos^2 \alpha)} = 255l^2/\lambda$$

From this equation, by using the value of λ/l in Table III and $l = 1.4$ Å, we obtain $A_f = 31.4$ Å. Comparing this value with the experimental value of A in Tables III, we find for the degree of hindrance to rotation in the chain of PPhQ I $\sigma^2 = A/A_f = 4.8$. This value is reasonable since it corresponds to the degree of hindrance to rotation in molecules of typical flexible-chain polymers.[12,24,25,31]

However, since (as shown above) the trans-trans form cannot be the only configuration of quinoxaline groups in the PPhQ chain, there is no reason to think that the cis-cis form can be the only possible form for them. It is more probable that a statistical array of all four above forms exists and that the most adequate description of the chain conformation corresponding to this is the trans-cis (or cis-trans) configuration of the quinoxaline nucleus. Under these conditions, the PPhQ I molecule can be modeled by an equivalent chain (Figure 4) in which each monomer unit is replaced by two parallel virtural bonds each of length $\Delta/2$ about which rotation takes place and by one bond of length δ normal to the former about which no rotation exists. The angle α between the straight parts, Δ, of the two neighboring units remains 60°. For this chain we have[32]

$$\lambda A_f = \delta^2 + \Delta^2(1 + \cos \alpha)/(1 - \cos \alpha) \quad (5)$$

Substituting into eq 5 the values of $\Delta = 12.5l$, $\delta = l3^{1/2}/2$ (Table IV), $\lambda = 11.26l$ (Table III), and $l = 1.4$ Å, we obtain $A_f = 58.4$ Å. Comparing this value with the experimental value of $A = 150$ Å for the degree of hindrance to rotation, we find $\sigma^2 = 2.6$. This value is in very good agreement with the value of $\sigma^2 = 2.5$ obtained for aromatic polyamides.[21,27]

A similar conformational analysis can be carried out for PPhQ samples II and III taking into account various possible stereoisomeric structures of the quinoxaline group. The conformations of molecules and equivalent chains with virtual bonds corresponding to these structures are shown in Figure 4. Equation 4 is used to calculate A_f since in all cases the angles between the bonds, α, are 60°. In those cases (for trans-trans and trans-cis structures) when parallel virtual bonds Δ at a distance δ from each other appear in the equivalent chain, it is possible to replace them by one bond of the corresponding length without great error assuming that $\delta = 0$ since in all cases we have

$\delta^2 << \Delta^2$ (see eq 5). The parameters used in the calculations of A_f and the results obtained are shown in Table IV.

For each of these three polymers with free rotation about the valency bonds, the equilibrium rigidity decreases on passing from the trans-trans to the cis-cis form of the quinoxaline group and has an intermediate value for a mixed (cis-trans) structure in accordance with an increasing number of nonparallel rotation bonds in the chain during this transition. However, for polymer I, the corresponding decrease in A_f changes the chain conformation "catastrophically" from that of a crankshaft ($A_f = \infty$) to that of a polymer with a slightly higher rigidity ($A_f = 31.4$ Å), whereas for the two other samples (II and III) the maximum changes amount to not more than 30%. These differences show that the conformational properties of a rigid-chain polymer are very sensitive to the insertion of even a small number of flexible fragments into its chain just as it has been shown for paraaromatic polyamides.[27]

It is possible to determine the degree of hindrance to rotation in the PPhQ chains $\sigma^2 = A/A_f$ corresponding to different hypothetical stereoregular forms of the quinoxaline group by comparing the values of A_f in Table IV with experimental values of A in Table III. The values of σ^2 are given in Table IV. All of them are within the range of values characteristic of typical flexible-chain polymers.[12,24,25,31] Hence, the physical reason for high equilibrium rigidity of PPhQ chains is the specific geometrical structure of these molecules rather than the hindrance to intramolecular rotations.

However, as shown above, the experimental data on FB in solutions of PPhQ I show that there is no stereoregularity in the molecular structure of these polymers. Consequently, to describe adequately their conformational properties it should be assumed that the cis-trans and trans-cis structures of the quinoxaline group in the chain alternate statistically. The corresponding values of A_f and σ^2 in Table IV are boxed in. It can be seen that the values of A_f corresponding to cis-trans and trans-cis structures virtually coincide, and the values of the degree of hindrance are in satisfactory agreement with those of σ^2 for aromatic polyamides.[21,27]

The conclusion that the PPhQ structure is irregular at the molecular level agrees well with the fact of low crystallizability of these polymers[8] in spite of their high chain rigidity.

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(33) The equilibrium flexibility (or rigidity) of the chain characterizes the "average" conformation of a molecule in the equilibrium state in dilute solution. In modeling a chain molecule by a freely joined segment, the length of the Kuhn segment A serves as a quantitative measure of the equilibrium rigidity.