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Structure and Rigidity of Molecules of Aromatic Polyamides in Solutions

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ABSTRACT: Possibilities of using dynamooptical data (flow birefringence) for the analysis of conformations and equilibrium rigidity of aromatic polyamides in solutions have been shown. It has been proved experimentally and theoretically that molecules of para-aromatic polyamides are characterized by tremendously high equilibrium rigidity. Hence, they can be used to obtain ultrahigh modulus fibers. Aromatic polyamides responsible for these properties exhibit the following structural features: the trans conformation of their amide groups and the para position of aromatic rings in their chain which imparts the "crankshaft" shape to this chain.

In recent years rigid-chain polymers have attracted great attention of research workers in the field of physicochemistry and technology of macromolecular compounds. The reason for this is the fact that up-to-date polymer materials with very valuable thermomechanical properties may be obtained on the basis of macromolecular compounds characterized by a limited chain flexibility and usually called rigid-chain polymers. Aromatic polyamides are some of the most important among these polymers.

Conjugation in Chain and Rigidity of Molecules of Aliphatic Polyamides

High thermomechanical properties of polyamide materials, such as "nylon 6" (polycaprolactam) and other aliphatic polyamides, are related primarily to their high crystallinity and ability to form intermolecular hydrogen bonds. These properties are determined in turn by the peculiar structure of their molecules containing amide groups (the source of hydrogen bonds) separated along the chain by links of five or more methylene groups CH_2 ensuring the "tactic" chain order and thus facilitating its packing in the polymer crystal.

At the same time investigations of conformational properties of molecules of aliphatic polyamides (nylon 6 and nylon 66) in dilute solutions have shown[1] that in the absence of intermolecular interactions they are typical flexible-chain polymers similar, for instance, to polyethylene. This seems quite natural since over four-fifths of nylon 6 molecule consists of the polymethylene chain, the high flexibility of which (just as for other carbochain polymers) is ensured by a considerable freedom of intrachain molecular rotations about the C–C bonds.

The situation changes greatly when the amide groups in aliphatic polyamide are very close to each other along the chain. This is the case with poly(alkyl isocyanates) (nylon 1, –CONR–), the molecules of which consist entirely of amide groups incorporated in the chain one after another in a

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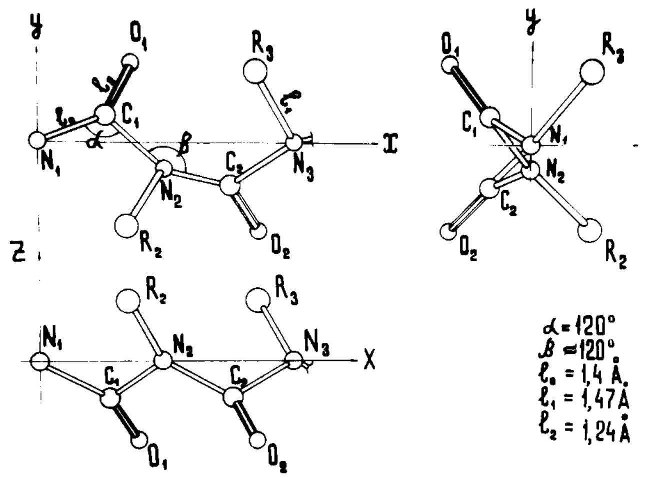


Figure 1. Structure of poly(alkyl isocyanate) chain.

"head-to-tail" order and in which the hydrogen atom on nitrogen is replaced by an alkyl radical R. Since in the amide group rotation about the C–N bond is greatly hindered (because this bond is of a quasi-conjugated type[2]), its equilibrium configuation may be a planar trans or cis form. This should lead to the coplanarity of all bonds in the main chain of poly(alkyl isocyanates). Steric interactions of the R radical with neighboring carbonyl oxygen may deflect the chain conformation from complete coplanarity,[3] but its structure retains its regularity with a high degree of order in which amide groups are incorporated in the chain in a strictly alternating succession of cis and trans configurations. The probable structure of the nylon 1 chain is shown in Figure 1 in three projections. The conjugation energy stabilizing this structure and virtually excluding a possibility of rotation about the C–N bond favors exceptionally high equilibrium and kinetic rigidity of the poly(alkyl isocyanate) chain. Thus, the length of the Kuhn segment A for poly(butyl isocyanate) molecules is 1000 Å. This corresponds to the number of monomer units in a segment $S = 500$.[4] This rigidity is revealed in specific properties of nylon 1 macromolecules in dilute solutions; these properties have been studied in detail by molecular hydrodynamic and optical methods.[4-7]

Dynamooptical Properties and Rigidity of Aromatic Polyamides in Solutions

The interest in aromatic polyamides has greatly increased recently in connection with a possibility of obtaining on their basis fibers with ultrahigh modulus and strength.[8] Some aromatic polyamides are capable of forming the mesomorphous (liquid crystalline) state in concentrated solutions thus facilitating the spinning of these fibers.[9] On the basis of this fact, by analogy with concentrated solutions of viruses and polypeptides in a helical conformation in which lyotropic mesomorphism has been revealed,[10] it could be suggested that molecules of these aromatic polyamides are characterized by a rodlike shape.

However, up to the present no quantitative data on the conformational properties and the rigidity of molecules of these polyamides have been available.

This is mainly due to the poor solubility of these polymers. The most interesting of them are molecularly soluble only in very aggressive solvents, such as concentrated sulfuric acid. Although for industrial purposes spinning solutions in less agressive solvents (dimethylacetamide) are also used, special investigations of optical properties of these solutions[11] have shown that in order to study the molecular structure and conformation of many aromatic polyamides sulfuric acid should be used since in other solvents molecular association takes place.

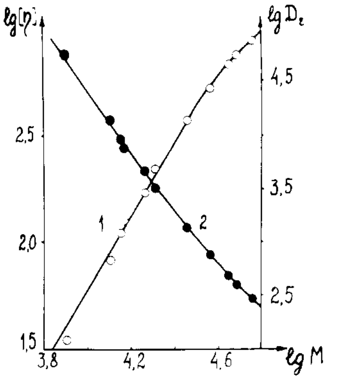


Figure 2. Coefficient of rotatory diffusion D_r (curve 1) and intrinsic viscosity $[\eta]$ (curve 2) vs. molecular weight M for samples of poly(p-phenyleneterephthalamide) (PPPhTPhA) in sulfuric acid.

Another difficulty in investigations of aromatic polyamides on a molecular level is related to the impossibility of using for the most interesting of them (those with the most rigid chains) such a classical method of conformational analysis as sedimentation in an ultracentrifuge.

Flow birefringence (FB) proved the most effective method for quantitative characterization of conformational properties and equilibrium rigidity of the chain of aromatic polyamides. However, in this case, too, in order to apply this method successfully it was necessary to develop a special apparatus resistant to agressive solvents.[12]

The main values determined in FB measurements[13] are the orientational angle α formed by the optical axis of the anisotropic solution and the flow direction and the value of flow birefringence itself Δn. The characteristic orientational angle is given by $[\chi/g] = \lim_{g\to 0, c\to 0} [(\pi/4 - \alpha)/g]$ where g is the rate gradient corresponding to the orientational angle α. According to the FB theory, the value of $[\chi/g]$ is directly determined by the coefficient of rotatory diffusion D_r of a rigid macromolecule:[13]

$$[\chi/g] = (12D_r)^{-1} \qquad (1)$$

The value of D_r is related to the intrinsic viscosity $[\eta]$ and the molecular weight M of dissolved macromolecules by the equation

$$[\eta]D_rM\eta_0 = FRT \qquad (2)$$

where η_0 is the viscosity of the solvent and R is the gas constant. The F coefficient depends, although slightly, on the shape of the particles and for the two limiting conformations of the chain molecule, the straight rod and the Gaussian coil, it is $2/15$ and $1/4$, respectively.

Thus, if we take into account eq I, eq 2 permits the determination of the molecular weight of the polymer from experimental values of $[\chi/g]$ and $[\eta]$.

This method has been used in investigations of several aromatic polyamides. As an example of the results obtained, Figure 2 shows dependences of D_r and $[\eta]$ on M for samples of poly(p-phenyleneterephthalamide) (PPPhTPhA) in sulfuric acid.[14] In an analytical form the dependence of $[\eta]$ on M may be expressed by the equation $[\eta] = K_\eta M^a$ where $K_\eta = 9.4 \times 10^{-6}$ and $a = 1.7$ in the range of M from 0.8×10^4 to 4×10^4; $K_\eta = 1.46 \times 10^{-2}$ and $a = 1$ in the range of M from 4×10^4 to 6×10^4. Similar investigations of fractions of poly(m-phenyleneisophthalamide) (PMPhIPhA) in sulfuric acid lead to the dependence of $[\eta]$ on M in which $K_\eta = 6.52 \times 10^{-3}$ and $a = 0.86$ in the range of M from 3.4×10^4 to 26×10^4. A much greater value of a for PPPhTPhA than for PMPhIPhA qualitatively indicates that molecules of para-aromatic polyamides exhibit a higher equilibrium rigidity than those of the meta derivatives.

Quantitative information concerning the equilibrium rigidity of chains of these polymers may be obtained from the dependence of the characteristic value of birefringence $[n] = \lim (\Delta n/g\eta_0 c)_{g\to 0, c\to 0}$ on molecular weight (c is the solution concentration). The following expressions are used for this purpose:

$$[n]/[\eta] = (2\pi/135nkT)(b_0/F)(n^2 + 2)^2(\gamma_1 - \gamma_2) \qquad (3)$$

$$[n]/[\chi/g] = (8\pi N_A/45n\eta_0)b_0(n^2 + 2)^2(\gamma_1 - \gamma_2)/M \qquad (4)$$

Here N_A is the Avogadro's number, n is the refractive index of the solution, b_0 is the coefficient which for molecules with an extended shape virtually amounts to unity. The value of $\gamma_1 - \gamma_2$ is the difference between the two main optical polarizabilities of the molecule. According to the theory of the anisotropy of wormlike chains it is given by:[15]

$$\gamma_1 - \gamma_2 = \Delta a(M/M_0)\varphi(x) \qquad (5)$$

Here Δa is the anisotropy of the monomer unit in the chain; $\Delta a = \beta\lambda$ where β is the average anisotropy of the unit chain length. Function $\varphi(x)$ is given by

$$\begin{aligned}\varphi(x) &= (6/5)[1 - (1 - e^{-x})/x]/ \\ &\quad \{x - 0.8[1 - (1 - e^{-x})/x]\} = 1 - (5/9)x \\ &\quad + (85/324)x^2 - (170/1458)x^3 + \ldots \qquad (6) \\ x &= L/a = 2M/M_0S\end{aligned}$$

Here S is the number of monomer units in the Kuhn segment and M_0 is the molecular weight of a monomer unit.

Figure 3 shows results obtained from PPPhTPhA samples in sulfuric acid. Full curves represent the theoretical dependence of $[n]/[\eta]$ (curve 1) and $[n]/[\chi/g]$ (curve 2) on M plotted from eq 3–6. The points are experimental data. Good agreement of experimental points with theoretical curves ensures reliable determination of two molecular characteristics: the anisotropy of the monomer unit Δa and the number of units S in a segment (and, consequently, its length A). For PPPhTPhA we obtain $\Delta a = 41.5 \times 10^{-25}$ cm^3 (this coincides with the value of Δa found earlier for poly(p-benzamide) (PPBA) from measurements of magnetic birefringence).[11] The experimental value of S is 200 ± 20, hence, the length of the Kuhn segment A = 1300 ± 130 Å.

Similar investigations were carried out with solutions of several other polyamides, such as PMPhIPhA, PPBA (dashed curve in Figure 3), and the poly(p-amide hydrazide)(PPAH). Their results are shown in Table I which includes the structural formulas of the polymer as well as the limiting value of $[n]/[\eta]$ characterizing the optical anisotropy of the Kuhn segment, its length A, and the number of monomer units in a segment S. The "monomer unit" in polymers **2–4** is assumed to be the amide group with the neighboring phenyl ring, and in polymer **5** it is assumed tentatively that the identity period includes three monomer units. The error in the determination of A is about 10% of the measured value.

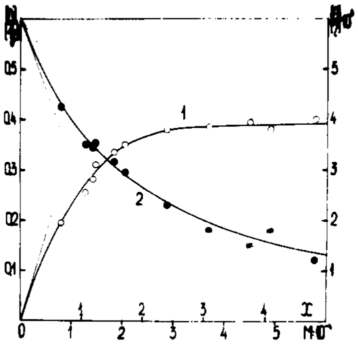


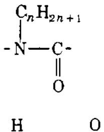
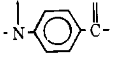
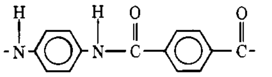
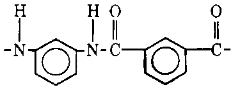
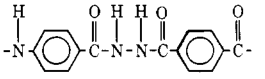
Figure 3. $[n]/[\eta]$ vs. M (curve 1) and $[n]/[\chi/g]$ vs. M (curve 2) for PPPhTPhA samples in sulfuric acid. Full curves are theoretical dependences corresponding to eq 3–6. Points are experimental data.

Structure of the Amide Group in Chains of Aromatic Polyamides

Data in Table I show that the character of the incorporation of aromatic rings into the chain of aromatic polyamides is of primary importance for the conformational properties of their molecules. Meta derivatives are typical flexible-chain polymers ($S \approx 8$) whereas molecules of para-atomatic polyamides are characterized by very high equilibrium rigidity exceeding hundreds of times that of flexible-chain polymers and approaching the rigidity of the nylon 1 chain. Moreover, the structure of the amide group should also greatly affect the formation of these properties. This group is rigidly coplanar and in principle may be either in the trans or in the cis configuration (as we have seen, this is observed for poly(alkyl isocyanates), Figure 1). In order to decide which of these structural forms predominates in chains of aromatic poly-

Table I

Limiting Value of Reduced Anisotropy [n]/[η] of Solutions of Some Polyamides, Length of the Kuhn Segment *A*, and the Number of Monomer Units *S* in the Segment

Polymer	Report unit	$[n]/[\eta] \times 10^{10}$, g^{-1} cm s^2	*A*, Å	*S*
(1) Nylon-1 in tetrachloromethane	 $-\mathrm{N}(\mathrm{C}_n\mathrm{H}_{2n+1})-\mathrm{C}(=\mathrm{O})-$	300	1000	500
(2) PPBA in H_2SO_4		650	2100	320
(3) PPPhTPhA in H_2SO_4		400	1300	200
(4) PMPhTPhA in H_2SO_4		27	50	8, 4
(5) PPAH in dimethyl sulfoxide		280	800	160

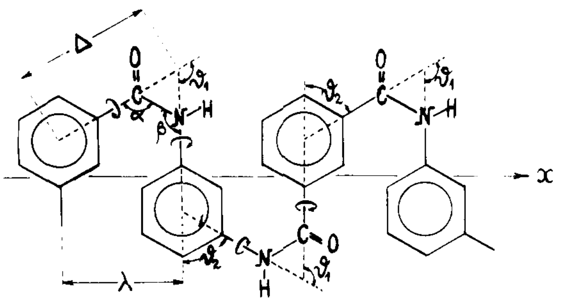


Figure 4. Conformation of PMPhIPhA chain when the amide group is in the cis configuration.

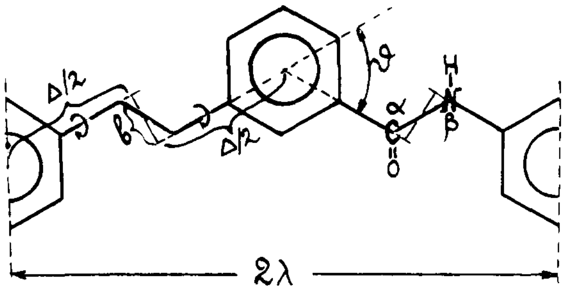


Figure 5. Conformation of an extended PMPhIPhA chain when the amide group is in the trans configuration.

amides, it should be taken into account that in contrast to nylon 1, amide groups in their chains are separated by phenyl rings about which rotation is possible. Hence, an aromatic polyamide molecule may be replaced by an equivalent chain of straight links joined at the same angles and performing a more or less hindered rotation through these angles. Moreover, the configuration of this equivalent chain depends both on the structure of the amide group and on the character of the incorporation of aromatic rings into it.

Figure 4 shows an extended conformation of the chain of the meta-aromatic polyamide PMPhIPhA with the amide group in the cis configuration. In this case the equivalent chain consists of links of length Δ joined successively at angles $\vartheta_1 = 120°$ and $\vartheta_2 = 60°$. It can be shown that when rotation in the chain is free (unhindered), the number of monomer units in the Kuhn segment is given by[16]

$$S_f = \left(\frac{\Delta}{\lambda}\right)^2 m \frac{(1 + \cos\vartheta_1)(1 + \cos\vartheta_2)}{1 - \cos\vartheta_1 \cos\vartheta_2} \qquad (7)$$

Here λ is the projection of the monomer unit along the direction of the extended chain (the x axis in the figure) and m is the number of rotational axes (rotating links) in the monomer unit. In the case under consideration (Figure 4) $\Delta = \lambda/\cos 30°$, $m = 2$, and from eq 7 we find $S_f = 8/5 = 1.6$. The experimental value for this polymer (Table I) is 8.4. This means that the cis structure of the amide group in the PMPhJPhA molecule may agree with experimental data only if it is assumed that the degree of hindrance to rotation about the C_{ar}–C_{al} and C_{ar}–N bonds is $\sigma^2 \equiv S/S_f = 8.4/1.6 = 5.2$.

When the amide group is in the trans configuration, the extended PMPhlPhA chain adopts the conformation shown in Figure 5. Here every monomer unit also has two rotational bonds; nevertheless, when angles α (at carbon) and β (at nitrogen) in the amide group are equal, these bonds are parallel. Hence, the polymer molecule may be replaced by an equivalent chain in which each monomer unit consists of two parallel links each of length Δ/2 about which rotation is possible and of one link b normal to them about which rotation is impossible. For this chain[17]

$$S_f = (b/\lambda)^2 + (\Delta/\lambda)^2(1 + \cos\vartheta)/(1 - \cos\vartheta) \qquad (8)$$

where the value of λ is the same as in eq 7 and ϑ is the angle between axes of rotation of two neighboring monomer units. In this case (Figure 5) $\vartheta = 60°$, $(b/\lambda)^2 = 1/25$, and $(\Delta/\lambda)^2 = 16/15$ and from eq 8 we obtain $S_f = 3.3$. Comparing this value to the experimental value of $S = 8.4$, we obtain the degree of hindrance $\sigma^2 = S/S_f = 2.5$. This value is half that found assuming the cis structure of the amide group in PMPhIPhA chains. However, both values of σ^2 (5.2 and 2.5) are within the limits of values characteristic of flexible-chain polymers.[13] This shows that rotations about the C_{ar}–C_{al} and C_{ar}–N valence bonds in aromatic polyamides are relatively weak but does not indicate which of the two structures of the amide group predominates, cis or trans.

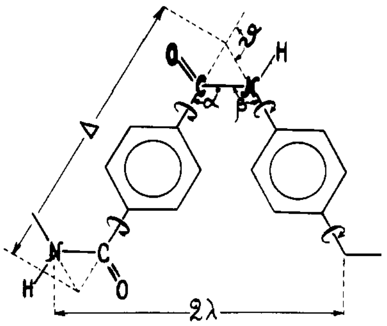


Figure 6. Conformation of the PPPhTPhA chain when the amide group is in the cis configuration.

In order to solve this question, the molecular conformation of the simplest para-aromatic polyamide PPPhTPhA should be considered. It is shown in Figure 6 in the form of the cis structure of the amide group. Here, just as in Figure 4, the molecule is modeled by a chain of straight links of equal length Δ, but in contrast to PMPhIPhA, only one rotational bond exists in the PPPhTPhA monomer unit (m = I) and here $\Delta = 2\lambda$. Furthermore, the angle between any pair of neighboring rotational bonds ϑ is 120°. Taking this into account and using eq 7 we find $S_f = 4/3$. If a possible degree of hindrance σ^2 over the ranges found above is taken into account, then the number of monomer units in the Kuhn segment of the PPPhTPhA chain is given by $S = (4/3)(5.2) = 7$ or $S = (4/3)(2.5) = 3.3$. Both these values of S sharply contradict experimental data which lead to the value of $S = 200$ for PPPhTPhA in H_2SO_4 (Table I). This means that the cis configuration of the amide group shown in Figure 6 does not correspond to the actual structure of the PPPhTPhA chain and should be rejected. The instability of this form is probably produced by steric interactions of neighboring phenyl rings in the chain. But for the same reasons the trans form of the amide group in the PMPhIPhA chain should be considered as a stable structure rather than the cis form (Figure 5).

Hence, the degree of hindrance to internal rotations in molecules of these aromatic polyamides should be taken as $\sigma^2 = 2.5$.

"Crankshaft" Conformation

When the amide group exhibits the trans configuration which should be considered as the only configuration possible for the PPPhTPhA chain, the conformation of this chain markedly depends on whether valence angles α and β in the amide group may be considered equal. If we assume that α is equal to β, then, as is clearly shown in Figure 7, irrespective of the degree of hindrance rotation about the N–C_{ar} and C_{ar}–C_{al} axes, directions of these axes in all monomer units coincide. As a result the PPPhTPhA chain exhibits a conformation like a "crankshaft" in which all axes of rotation are

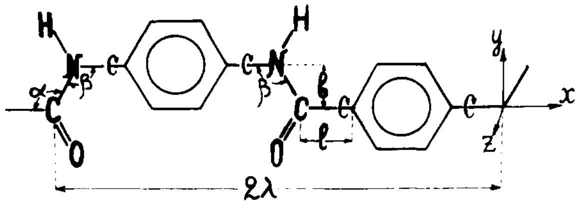


Figure 7. Conformation of the PPPhTPhA chain when the amide group is in the trans configuration.

mutually parallel but do not lie on one straight line. Formally, when the chain is relatively long, this conformation can be described by eq 8 assuming that ϑ is 0. In this case S_f is ∞ corresponding to the conformation of an infinitely rigid rod-like molecule. In fact, the geometrical dimensions of the "crankshaft" in the direction of axes of rotation (the x axis in Figure 7) increase proportionally to the degree of polymerization K so that at $\alpha = \beta = 120°$ the length L of the molecule is $L = K\lambda = 4.5lK$ where l is the length of each valence bond in the chain ($l \approx 1.4$ Å).

Transverse dimensions of the macromolecule may be characterized by projection of its elements on the YZ plane. Evidently, the picture obtained depends on the character of internal rotations about axes normal to the YZ plane.

If these rotations are assumed to be randomly disordered, then the shape of the "crankshaft" equivalent to the PPPhTPhA chain is similar to that shown in Figure 8a. Here the origin of x, y, z coordinates coincides with the middle of the chain consisting of links λ (about which rotation takes place) bonded by links b normal to them (about which rotation is impossible). Evidently, $b = l \sin \alpha = l\ (3/2)^{1/2}$ (see Figure 7) although for clarity links λ and b in Figure 8 are shown equal. When random disorder and complete rotational freedom exist (random changes in azimuths $\Delta\varphi$ on passing from one monomer unit to another), the projection of the equivalent chain on the YZ plane is represented by a chain of freely joined links of length b and the middle of this chain is at the origin.

In order to characterize qualitatively transverse dimensions of the "crankshaft" representing, for example, the PPBA molecule, it is possible to use the value $(\bar{r}^2)^{1/2}$ where r is the distance from the origin of the yz coordinates for the most distant element along the chain. Evidently, when the chain is relatively long and the rotation is free, then $\bar{r}^2$ is $Kb^2/2$, and taking into account the above factor of hindrance $\bar{r}^2 = \sigma^2Kb^2/2$ correspondingly:

$$(\bar{r}^2)^{1/2} = l(7.5\ K/8)^{1/2} \approx lK^{1/2}$$

Hence, transverse dimensions of the molecule are proportional to (degree of polymerization)$^{1/2}$. The degree of asymmetry of the molecule p can be characterized by the ratio $p = L/(\bar{r}^2)^{1/2} = 4.5K^{1/2}$ which shows that the conformation of the model under consideration does not correspond to a constant diameter since in this series p increases proportionally to K. However, for values of $K \geq 50$ (used in experiments in ref 12, 14, and 18) p is greater than 30. This justifies the modeling of hydrodynamic properties of molecules of the para-aromatic polyamide by those of a thin straight rod in the phenomenon of flow birefringence in which the shape asymmetry of the particle is represented by the coefficient $b_0 = (p^2 - 1)/(p^2 + 1)$ in eq 4.

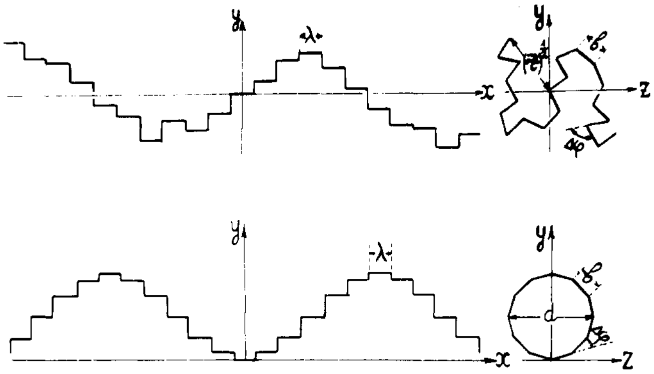


Figure 8. "Crankshaft" conformation of para-aromatic polyamide chain: (a, top) randomly disordered internal rotations; (b, bottom) regular change in rotational azimuth along the chain.

The low degree of hindrance, $\sigma^2 = 2.5$, obtained experimentally in investigations of equilibrium properties of molecules does not necessarily mean that rotation is close to "true free rotation". In principle, it may correspond to the existence of high-potential barriers hindering rotation only in the case when the potential curve of hindrance $U(\varphi)$ is relatively symmetrical. Under these conditions the PPBA molecule should behave as a kinetically rigid system modeled by a "crankshaft" with a series of rigid "crank" portions distributed uniformly along the rotational azimuths φ. In this case the passing from one monomer unit to another (i.e., movement along the x axis by the length λ) is accompanied by rotation of the link b through a constant azimuthal angle $\Delta\varphi$ and the chain acquires the conformation of a regular helix shown in two projections in Figure 8b. Evidently, the number of monomer units in a turn of the helix is $n = 2\pi/\Delta\varphi$, its pitch is $\lambda n = 2\pi\lambda/\Delta\varphi$, and its diameter $d = b$ (sin $(\Delta\varphi/2)$ characterizes transverse dimensions of the molecular model. Hence, the degree of asymmetry of the molecule $p = K\lambda/d = K\lambda \sin (\Delta\varphi/2)b$ expressing λ and b by l at $\alpha = \beta = 120°$, we find $p = 3(3)^{1/2}K \sin (\Delta\varphi/2)$, i.e., p increases proportionally to molecular weight in accordance with a homologous series of rigid helices with a constant diameter. In this case even for a helix with a very great number of turns in a period $n = 20$ (a "thick" helix) at $K = 50$, the degree of asymmetry p is greater than 20. Thus, the character of internal rotations (free or symmetrically hindered rotations) does not significantly affect the equilibrium geometrical shape of the PPPhTPhA molecules. In all cases it is close to that of a thin straight rod the length of which is proportional to the degree of polymerization. The question which of the two mechanisms prevails in molecules of para-aromatic polyamides should be solved by investigations of kinetic properties of these molecules in dilute solutions.

As to the optical properties of the chain shown in Figures 7 and 8, irrespective of the hindrance to internal rotation they correspond to a system with a maximum orientational-axial intramolecular order in which the difference between the two main polarizabilities of the molecule is $\gamma_1 - \gamma_2 = \gamma_x - (\gamma_y + \gamma_z)/2 = K\Delta a$, i.e., it is proportional to the degree of polymerization (Δa is the mean anisotropy of the monomer unit at the x,y,z axes). It is just the chain conformation similar to a "crankshaft" that explains unique magnetooptical properties of molecules of para-aromatic polyamides.[11,12,14]

Structure and Equilibrium Flexibility of Molecules of Para-Aromatic Polyamides

Experiment shows that although the rigidity of these polymer chains is great, it is finite. Their flexibility is shown by the fact that a quite appreciable deviation of $\gamma_1 - \gamma_2$ from proportionality to M (i.e., to K) is observed with increasing degree of polymerization (Figure 3).

This fact may be attributed to a slight difference between the configuration of the amide group and that shown in Figure 7 caused by its deformation during thermal motion of the chain and by inequality of its valence angles α and β. The first source of chain flexibility exists in poly(butyl isocyanate)

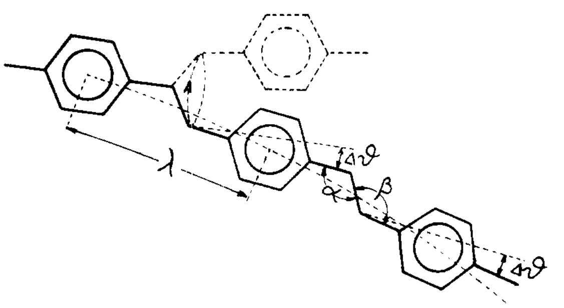


Figure 9. Conformation of para-aromatic polyamide chain when angles α and β at carbon and nitrogen atoms of the amide group are unequal.

molecules and leads to the number of monomer units in the Kuhn segment $S_1 = 500$ (Table I). This value exceeds the experimental value $S = 200$ obtained for PPPhTPhA. Differences between the values of S and S_1 can be attributed to the second mechanism of flexibility existing in PPPhTPhA chains and caused by inequality of angles α and β. In fact, this inequality leads to the appearance of a finite angle $\Delta\vartheta = \beta - \alpha$ between the neighboring rotational bonds. This causes chain curving (Figure 9) and requires description of its conformation in terms of a persistent model. According to this model

$$\cos \Delta\vartheta = \exp(-\lambda/a_f) = \exp(-2/S_f) = 1 - 2/S_f + \ldots \qquad (9)$$

where a_f and S_f are the persistent length and the number of monomer units, respectively, in the Kuhn segment for a persistent model with completely free rotation.

Assuming that these two mechanisms of flexibility of PPPhTPhA chains are additive, we can find the value of S_2 (determined by the finite value of angle $\Delta\vartheta$) from the equation

$$1/S_2 = 1/S - 1/S_1 \qquad (10)$$

which leads to $S_2 = 330$. Substituting $S_f = S_2/\sigma^2 = 330/2.5 = 132$ into eq 9, we find $\beta - \alpha = \Delta\vartheta = 10°$. This value agrees with the limits of possible values of $\Delta\vartheta$ = 6–12° according to the literature.[19] Thus, experimentally determined equilibrium flexibility of PPPhTPhA molecules can be quantitatively interpreted within the limits of the molecular structure under consideration.

The "crankshaft" conformation is characteristic of all aromatic polyamides containing phenyl rings in the para position. Consequently their chains exhibit high optical anisotropy and equilibrium rigidity (Table I). However, quantitative differences in the equilibrium rigidity of different para-aromatic polyamides greatly exceed experimental errors and, hence, are related to differences in their molecular structure.

Thus, the rigidity of the PPBA chain ($S = 320$) greatly exceeds that of PPPhTPhA molecules. The only difference in the molecular structure of these two polymers is the incorporation into the chain of all amide groups in the "head-to-tail" order for PPBA and in the alternating order for PPPhTPhA. It seems possible that the dipole-ordered structure of the PPBA chain favors its greater geometrical and optical order. It also cannot be ruled out that in the PPBA molecule conjugation in the carbonyl–nitrogen system is transferred through each phenyl ring increasing the degree of hindrance to rotation about para-aromatic axes. The qualitative evaluation of the latter effect from eq 9 and 10 with angle $\Delta\vartheta = 10°$ and the value of $S_1 = 500$ shows that the value of $S = 320$ found experimentally for PPBA corresponds to the degree of hindrance $\sigma^2 = 6.8$, the value characteristic of typical flexible chain polymers.[13]

PPAH chains are more flexible than chains of two other para-aromatic polyamides investigated (Table I). Their structure is characterized by the hydrazide bond N–N in the repeat unit. Since rotation about the N–N bond is much more free than about the amide bond C–N, this is sometimes regarded as the reason for greater coiling of the PPAH chains as compared to PPPhTPhA.[20] Nevertheless, it should be borne in mind that the bond N–N in the "crankshaft" chain is parallel to all para-aromatic axes about which rotation is not less free ($\sigma^2 = 2.5$) than that about the N–N bond. Moreover, as we have seen, the character of hindrance to these rotations does not appreciably affect the equilibrium rigidity of para-aromatic polyamides. Consequently, greater flexibility of PPAH molecules cannot be accounted for by lower hindrance to rotation about the hydrazide bond as compared to the amide bond.

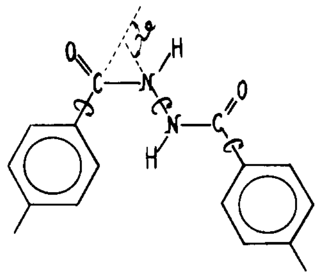


Figure 10. The cis form of the amide group in the PPAH chain.

It may be of greater importance that the presence of the hydrazide group increases the distance along the chain between phenyl rings adjoining this group. This decreases steric interactions between them and increases a possibility of one or another amide group exhibiting cis configuration (Figure 10). If this actually occurs, a rotational bond appears in the corresponding unit of the PPAH chain directed at an angle of 120° to the chain and the latter exhibits a sharp turn at this angle. Evidently, the presence of these "defective" units should lead to a sharp decrease in the equilibrium rigidity of PPAH molecules. If we ascribe the difference in flexibilities of PPPhTPhA and PPAH to this mechanism, then this difference may be expressed quantitatively by the equation

$$1/S_{\mathrm{PAH}} - 1/S_{\mathrm{TPhA}} = \frac{\delta}{\sigma^2}\frac{1 - \cos\vartheta}{1 + \cos\vartheta} \qquad (11)$$

Here $S_{\mathrm{PAH}} = 160$ is the number of monomer units in the PPAH segment, $S_{\mathrm{TPhA}} = 200$ is the same in the PPPhTPhA segment, $\vartheta = 120°$ is the angle of the turn of the chain, $\sigma^2 = 2.5$ is the degree of hindrance to rotation in the PPAH chain, and δ is the ratio of the number of amide groups in cis configuration in the PPAH chain to the number of all amide groups in it. Substituting numerical values into eq 11, we obtain $\delta = 1 \times 10^{-3}$. Thus, in order to explain different rigidities of the PPPhTPhA and PPAH chains it is sufficient to assume that 0.1% of all amide groups in the PPAH chain are in the cis configuration.

The above data show that incorporation into the polymer molecule of atomic groups changing the direction of chain rotation leads to increasing equilibrium chain flexibility. In accordance with this, the limiting case or the structure with the highest possible equilibrium rigidity is the chain in which all rotational axes are mutually parallel. Molecules of para-aromatic polyamides represent just this case.

All these molecules are characterized by a regular successive alternation of bonds with relatively free rotation and those with a fixed (an immobilized) coplanar trans structure. These peculiarities of structure of para-aromatic polyamides are responsible for their unique ability to form lyotropic liquid crystals and for the properties of fibers with a ultrahigh modulus which are based on them.[8]

A similar situation is well-known in the field of thermotropic liquid crystals in which normal aliphatic acids even with a long alkyl chain are not nematogenic whereas in aliphatic diene acids a stable nematic mesophase is readily established.[21]

The analogy between molecules of para-aromatic polyamides and liquid crystalline systems may be extended further. As is clearly shown in Figure 7, PPPhTPhA molecules (and other similar polyamides) exhibit a highly organized intramolecular uniaxial orientational long-range order (along the x axis) as well as a coordination (transitional) long-range order along the x coordinate, whereas neither orientational nor translational long-range order is observed in the normal plane (yz). It is known that this type of ordering is characteristic of the smectic mesophase. Hence, we have many reasons to characterize PPBA molecules as molecules with an intramolecular quasi-smectic order. Para-aromatic polyamides clearly illustrate that the intramolecular structure and organization of the polymer not only determine its supermolecular structure but also ensure the principal properties of materials manufactured from them.[8]

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Functional Polymers. 4.[1] Polymers of 2,4-Dihydroxy-4′-vinylbenzophenone, New Polymeric Ultraviolet Absorbers

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ABSTRACT: The synthesis of 2,4-dihydroxy-4′-vinylbenzophenone was accomplished in five steps, with an overall yield of 15%, starting with p-ethylbenzoic acid. Pure 2,4-dihydroxy-4′-vinylbenzophenone was polymerized with azobis(isobutyro)nitrile as initiator; radical copolymerizations with methacrylic acid and styrene were also accomplished. In polymerizations with azobis(isobutyro)nitrile, no interference of the phenol groups of 2,4-dihydroxy-4′-vinylbenzophenone was observed. In copolymerization with styrene using benzoyl peroxide as initiator, the molecular weight of a copolymer containing 3 mol % 2,4-dihydroxy-4′-vinylbenzophenone was found to be significantly higher than that of styrene homopolymer prepared under identical conditions. This effect was also observed in the polymerization of styrene in the presence of a model compound, 2,4-dihydroxy-4′-ethylbenzophenone.

Polymers carrying reactive functional groups have been shown to be of value in a variety of uses. Among these polymers are materials which have ultraviolet-absorbing groups attached to the polymer chain.[2a] We have recently reported the synthesis of several 5-vinylsalicylic acid derivatives, which were homopolymerized and copolymerized with acrylic monomers.[2b] The present paper describes the synthesis and polymerization of another important UV absorber, 2,4-dihydroxy-4′-vinylbenzophenone.

In recent years a number of polymerizable 2-hydroxybenzophenones have been prepared. The most important route to these compounds utilizes the 4-hydroxyl group of 2,4-dihydroxybenzophenone to attach this unit to a reactive monomer capable of free-radical, coordination, or ring-opening polymerization. Acrylates, methacrylates, and unsaturated epoxide compounds have been employed as polymerizable substrates.[3-16] Allyl bromides, p-chloromethylstyrene, and epichlorohydrin have been used as substrates for displacement of halogen, yielding polymerizable ether derivatives of 2,4-dihydroxybenzophenone.[17-20] A Claisen rearrangement of 2-allyloxybenzophenone has been used to prepare 3-allyl-2-hydroxybenzophenone, which was copolymerized with ethylene with partial deactivation of the initiator (vanadium chloride and butyllithium).[21]

More recently, a first attempt to prepare 2-hydroxy-4′-vinylbenzophenone derivatives was made.[22,23] This type of monomer is very desirable because it may be expected to undergo copolymerization with acrylic monomers and with styrene derivatives, and because it contains no chemically sensitive linkages. The preparation of 2-methoxy-4′-vinyl-

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