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Semirigid Chain Molecules

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The problem of the extent to which the hydrodynamic and optical behaviour of chain molecules in solutions can be used for the observation and the quantitative assessment of their rigidity and of the internal ordering of their structures is examined. The general theoretical positions are illustrated by experimental results for a series of polymers, the molecules of which have a rigid chain structure. There is a bibliography of 106 references.

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I. INTRODUCTION

A characteristic property of chain molecules of polymers is their flexibility, that is, their ability to change conformation under the influence of thermal motion or under the action of deforming forces. This property explains the rubberlike behaviour of high-molecular-weight elastomers in the temperature range above their glass points. In solutions such flexible chain molecules have the conformation of a statistical coil which in Θ conditions (an "ideal" solvent) can be regarded as a "gaussian" coil.

The properties of solutions of flexible chain molecules have been the subject of detailed and thorough study by many investigators and have been described in several reviews and monographs [1-10].

In connection with the development of the synthesis of polymers suitable for the creation of high-strength and thermally stable fibres, films, and other materials for special purposes, the need for a study of the morphological and conformational properties of the macromolecules of such polymers has become increasingly evident in recent years.

The chemical structure of these macromolecules shows that many of them, despite their chain structure, should have limited flexibility, occupying a position intermediate between the absolutely rigid submicroscopic species (such as viruses or globular proteins) and the ideally flexible chain molecules of many synthetic polymers.

The classical examples of such "semirigid" chain molecules are the molecules of natural celluloses, and also of polypeptides and nucleic acids in helical conformation. Until comparatively recently our practical information about rigid chain molecules was limited to these examples. However, in recent years various investigators synthesised new polymers, the macromolecules of which show the properties characteristic of semirigid chain molecules.

II. THEORETICAL PRINCIPLES

1. Conformation and Rigidity of the Molecular Chain

The estimation of the rigidity or flexibility of a macromolecule can be approached in various ways, leading to two concepts: thermodynamic (equilibrium) and kinetic (non-equilibrium) flexibility. The opinion about the equilibrium flexibility of the chain is divided on the basis of a study of the equilibrium conformation (dimensions and geometric form) which the macromolecule adopts in various media.

Information about kinetic flexibility has been obtained by investigating the rate of occurrence of the processes which convert the macromolecule from one conformation into another.

Although there are grounds for assuming that for a definite molecular structure both types of flexibility are interconnected, the extent and nature of this relation in each individual instance requires special study.

The first of the two above-mentioned types of flexibility—equilibrium flexibility (and the corresponding rigidity) of chain molecules will be examined below. A quantitative measure of the equilibrium rigidity of a molecular chain could be the length of a statistical segment A (Kuhn and coworkers [10]) or the persistent length of the chain $a = A/2$ (Porod [11]).

The length A is determined from two conditions [10]. The first is the equality $L = NA$, where N is the number of segments in the chain and L its contour length, that is, the length of the chain at its greatest extension without destroying the valence angles and bonds; when an ordered secondary structure is present in the molecules (for example, the α-helix type) the retention of this structure during the extension must be borne in mind. The second condition is formulated as follows: at long chain lengths ($L \gg A$) and in the absence of higher order interactions [12] it is modelled by a gaussian chain, that is, the mean square distance between its ends $\overline{h^2}$ is proportional to its contour length $\overline{h^2} = NA^2$. The combination of these two conditions leads to the equation

$$A = \overline{h^2}/L \qquad (1)$$

valid for a gaussian chain.

When the contour length L is insufficient for satisfying the conditions $L \gg A$, $N \gg 1$ (which for rigid chain molecules, where A is large, can occur at rather high values of L, that is, in the range of rather large molecular weights), then the molecular chain is not gaussian and relation (1) is not satisfied.

In this instance an effective method of describing the conformational properties of a molecule is the model of a "persistent" or "wormlike" chain [11]—a three-dimensional line of constant curvature. This curvature is characterised by the parameter a—the persistent length (correlation length) [11-15]; a is determined by the relation

$$a = -\Delta L / \ln \overline{\cos \Delta\theta},$$

where $\Delta\theta$ is the angle between the tangents to the segment of the wormlike chain at its initial and final points. The bar denotes an average over all the conformations of the

chain corresponding to the given values of L and h. Hence a is a measure of the equilibrium rigidity of the chain, increasing with decrease in the convolution of the latter.

For persistent chains instead of formula (1) the theory[11,16] leads to the relations:

$$\overline{h^2}/L = A[1-(1/x)(1-e^{-x})], \quad (2)$$

$$6\overline{R^2}/L = A\{1-(3/x)[1-(2/x)\{1-(1/x)(1-e^{-x})\}]\}, \quad (3)$$

where $\overline{R^2}$ is the radius of gyration of the molecules, $x = L/a = 2L/A$. Equations (2) and (3) are applicable in any range of values of parameter x, that is, to chain molecules of any length under the condition of no effects of long-range order interactions (action at a distance).

In the limit, when $x \to 0$, from Eqns. (2) and (3) it follows that $h = L$ and $\overline{R^2} = L^2/12$, that is, the conformation of the molecule is similar to a linear bar. On the other hand, when x is large Eqns. (2) and (3) correspond to the properties of gaussian chains—Eqn. (2) is equivalent to Eqn. (1), and (3) gives $\overline{R^2} = \overline{h^2}/6$.

The variation of $\overline{h^2}/LA$ and $6\overline{R^2}/LA$ with x according to Eqns. (2) and (3) is shown by curves *1* and *2* in Fig. 1.

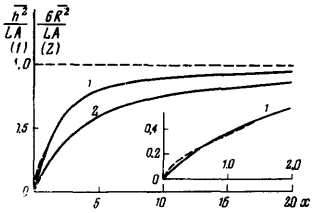


Figure 1. Variation of the statistical dimensions of a persistent (wormlike) chain with its contour length L. *1*) $\overline{h^2}/AL$ as a function of the parameter $x = L/A$. Continuous curve: according to theory[11]; broken curve: according to theory[17]. *2*) $6\overline{R^2}/AL$ as a function of $x = L/A$ according to theory[16].

For comparison with experimental results it is convenient to make the substitution $L = P\lambda$ in Eqns. (2) and (3) where P is the degree of polymerisation and λ the projection of the monomeric unit on the direction of the molecular chain. Instead of Eqn. (2) we obtain:

$$\overline{h^2}/P = S\lambda^2[1-(S/2P)(1-e^{-2P/S})] \quad (2')$$

where S is the number of monomeric units in the segment.

On plotting the experimental values of $\overline{h^2}/P$ as a function of P, a curve like curve *1* in Fig. 1 is obtained. Its initial slope gives λ^2, whereas the asymptotic level $S\lambda^2$ allows S to be determined and correspondingly $A = S\lambda$. The value of S can also be determined from the form of the curve, by its departure from the asymptotic limit at a given value of P (this departure is determined by the value of the parameter S/P). Similar results can be obtained from the experimental dependence of $6\overline{R^2}/P$ on P.

The advantage of the above wormlike model is its universality, since in it the flexibility of the molecular chain is determined without any a priori hypotheses about the mechanism of this flexibility (restricted or free rotation around the valence bonds, rotational isomerism defects of the secondary structure, etc.). On the other hand, starting from the experimental data on the dimensions of the molecules ($\overline{h^2}$ or $\overline{R^2}$) and the degree of their polymerisation P this theory not only allows the rigidity of the molecular chain to be estimated but also makes possible judgements about its conformation since the projection of the monomer λ is also determined in this.

On the other hand it can be shown that, for example, for a molecular chain with restricted rotation the persistent model leads to the same results as the calculation of $\overline{h^2}$ by the method of statistical mechanics in the rotational isomer approximation. Flory[18] recently developed such a method for application to chains of any length and used it for calculating the molecular dimensions of certain polymers[17,19]. The results are given as a plot of $\overline{h^2}/nl^2$ against n ($1 < n < \infty$), where n is the number of valence bonds in the chain with a valence angle of $\pi - \theta$ between neighbouring bonds, and l the length of the chain. This can be easily converted into the relation $\overline{h^2}/AL = f(x)$ on taking into account that in this instance

$$x = 2n\cos^2\frac{\vartheta}{2}/\lim_{n\to\infty}(\overline{h^2}/nl^2), \qquad A = l\lim_{n\to\infty}(\overline{h^2}/nl^2)/\cos\vartheta/2$$

and

$$L = nl\cos\vartheta/2.$$

The curve $\overline{h^2}/Al = f(x)$ for the polyethylene chain (from Flory and Jernigan's results[17]) is shown in Fig. 1 (broken curve). In the range $0.5 < x < \infty$ it coincides with curve *1* determined by Eqn. (2). The difference in the models is noticeable only for extremely short chains for which $x < 0.5$ and $n < 3$, that is, in the range of molecular weights without practical significance.

It should be borne in mind that all the relations examined, (1)–(3), characterising the skeleton rigidity of the chain (short-range action), assume the absence of effects of long-range action in the molecule and therefore strictly speaking are applicable only to chain molecules, which are found in a Θ-solvent.

In thermodynamically good solvents owing to the effects of the excluded volume (action at a distance) the dimensions of the molecular coils are increased and the molecular chains are no longer gaussian[12]. In the range of molecular weights where under Θ conditions relation (1) is obeyed, in good solvents it is not satisfied and can be replaced[1] by Eqn. (4):

$$\overline{h^2} = N^{1+\varepsilon}\cdot A^2 = A^{1-\varepsilon}L^{1+\varepsilon} \quad (4)$$

where $0 < \epsilon < 0.2$ and ϵ does not depend on L.[12]

Kurata and coworkers[20] concluded that in very good solvents the parameter ϵ can reach the value 1/3. From Eqn. (4), the effect of the excluded volume leads to an increase in $\overline{h^2}/L$ with increase in L, that is, it brings about a departure from gaussian properties of the same nature as the short-range action (rigidity of the chain) describable by Eqns. (1)–(3). However, the departure from gaussian properties due to the rigidity of the chain appears in the range of low molecular weights and disappears at higher molecular weights. On the other hand these departures due to action at a distance increase steadily with the molecular weight and therefore will appear in the range of high molecular weights. This circumstance allows (at least in principle) the effects of short-range and long-range action to be distinguished from the form of the dependence of $\overline{h^2}/L$ on L.

The effects of long-range action (non-ideality of the solutions) show the decisive influence on the conformation of flexible chain molecules and were considered in detail for such molecules in several monographs[1,4-8,12]. On the other hand, for rigid-chain polymers the excluded volume

effect, even in good solvents, is expressed relatively weakly and in several instances it cannot be taken into consideration.

In accordance with Eqns. (2) and (3) the study of the conformational properties and rigidity of the persistent chains requires the experimental determination of their molecular weights (degrees of polymerisation P) and radius of gyration $\overline{R^2}$. The first characteristic is readily determined by one of the well-known methods [1].

The determination of $\overline{R^2}$ is a much more complex task. A direct method which can be employed for this is the study of the angular asymmetry of light scattering by the polymer in solution [1]. However, it must be remembered that these measurements are usually accompanied by considerable experimental errors, since they must be made in the range of comparatively low molecular weights (where departure from gaussian properties occurs), in which the degree of asymmetry of light scattering is slight and is easily quenched by the presence of a minute amount of dust, the formation of molecular associates, or traces of the non-dissolved polymer, and also by other accidental factors. Therefore although there have been investigations (chiefly with cellulose derivatives) in which the dimensions and rigidity of the molecules were determined by the asummetry of light scattering method using the theoretical relations (2) and (3), their results are not always reliable and sometimes difficult to explain [21-23].

Another method of determining the rigidity of a molecular chain is the direct measurement of its persistent length $a = A/2$ using small-angle scattering of X-rays [24]. This method has as yet had only limited value since as well as the complexity of the experimental technique it is applicable only to polymers the scattering ability of which differs markedly from that for the pure solvent. In this connection it is the rule that in studying the conformation of molecules in solutions hydrodynamic methods are more widely employed.

2. Hydrodynamic Properties of Chain Molecules

The rigidity of a molecular chain is usually judged from its hydrodynamic properties in solutions by examining the variation of the sedimentation coefficient $[S]$, diffusion coefficient D, and characteristic viscosity $[\eta]$ with the molecular weight M.

This relation can be most simply represented in the form of Mark–Kuhn empirical expressions (M–K):

$$[\eta] = K_\eta \cdot M^\alpha, \tag{5}$$

$$D = K_D \cdot M^{-\beta}, \tag{6}$$

$$[S] = K_s \cdot M^{1-\beta}. \tag{7}$$

In measurements under Θ-conditions, that is, in the absence of the excluded volume effect, high values of α and β show the appreciable influence of the flowability effect, that is, the "loose" structure of the molecular coil and therefore can serve as an index of the increased rigidity of the molecular chain.

However, in non-ideal solvents the volume effects lead to osmotic distention of the coil and to a corresponding increase in the indices α and β, that is, they act in the same direction, as increased rigidity of the chain. Therefore to find the true ("skeleton") rigidity of the molecular chain the influence of the volume effects should be excluded.

For flexible chain polymers, the molecules of which are coiled in rather compact tangles even in good solvents, the hydrodynamic interaction inside the tangle is great and the flow effect is almost absent. For such molecules the influence of the volume effects can be excluded by extrapolation of the hydrodynamic properties to the range of low molecular weights using the effects of the excluded volume [12,25]. Eqn. (8) can be applied to the viscosimetric results for this purpose [26]:

$$[\eta]/M^{1/2} = (LA/M)^{3/2} \cdot \Phi + 0.51\,\Phi \cdot B \cdot M^{1/2}. \tag{8}$$

When using sedimentation or diffusion results, Eqn. (9) [27] or (10) [28] can be employed:

$$(DM^{1/2})^{-1} \equiv (1-\bar{v}\rho)\,M^{1/2}/[S]\,RT = (\eta_0 P_0/kT)\,[(LA/M)^{1/2} + 0.2\,BM^{1/2}], \tag{9}$$

$$(DM^{1/2})^{-3} = (\eta_0 P_0/kT)^3\,[(LA/M)^{3/2} + 0.51\,BM^{1/2}]. \tag{10}$$

Here $\Phi = 2.8 \times 10^{23}$, $P_0 = 5.11$, B is the parameter of the thermodynamic polymer–solvent interaction, η_0 the solvent viscosity, and L the contour length of the molecule.

On plotting the left part of Eqns. (8), (9), or (10) as a function of $M^{\frac{1}{2}}$, the intercept on the ordinate axis of the curve yields the undisturbed dimensions of the molecular chain and the corresponding rigidity, determined by the quantity A. However, this method is inapplicable for rigid-chain polymers, since for them the flow effect usually (although not always) plays a significant part.

Fortunately, for rigid chain molecules the excluded volume effect does not play a significant part, even in thermodynamically good solvents and can be neglected in the first approximation. Under such conditions the theory of the hydrodynamic properties of wormlike chains developed by Kuhn [29] and by Hearst and Stockmayer [30] (K-S) can be used for estimating the rigidity of the chain. At sufficiently high molecular weights when the molecule can be modelled by a gaussian chain, the K-S theory leads to the expressions

$$M/[\eta] = \Phi^{-1}\{(M/LA)^{3/2} M^{1/2} + 0.93\,[\ln(A/d) - 1.43]\,(M/L)^2 A^{-1}\}, \tag{11}$$

$$DM/RT = (1.843/3\pi\eta_0 N_A)\,(M/LA)^{1/2} M^{1/2} + (3\pi\eta_0 N_A)^{-1}\,(M/L)\,[\ln(A/d) - 1.43]. \tag{12}$$

Apart from the quantities L and A, which characterise the conformation and rigidity of the chain, Eqns. (11) and (12) contain the diameter d of the wormlike model, which must be allowed for in the correct description of its hydrodynamic properties.

On plotting the left part of Eqns. (11) or (12) as a function of $M^{\frac{1}{2}}$, the value of M/LA can be found from the slope of the straight line obtained, that is, the chain rigidity can be estimated. A/d and consequently the chain diameter d can be found from the intercept on the ordinate axis.

Eqns. (11) and (12) show that in the range of extremely large molecular weights when the first term on the right-hand side (dependent on M) is much greater than the second, the variation of the viscosity and diffusion coefficients with molecular weight is described by Eqns. (5)–(7) with indices $\alpha = \beta = 0.5$. Besides it must be borne in mind that in non-ideal solvents an increase in M is accompanied by an increase in the part played by the excluded volume effects; this leads to values of α and β exceeding 0.5. This effect is evidently observed in solutions of high-molecular-weight desoxyribonucleic acid [31,32].

At moderate values of M and considerable rigidity of the chain the part played by the second term on the right-hand side of Eqns. (11) and (12) becomes appreciable and there is a corresponding increase in the index α in Eqn. (5) to values approaching unity (cellulose derivatives, DNA).

Finally, for extremely rigid chain molecules in the range of low molecular weights, when the chain length $L \leq A$, but

much greater than the diameter d (slightly curved fine rods), theory[30] leads to the expression:

$$[\eta] = 2\pi N_A L^3 [45\,(M/L)\,(\ln\,(L/d) - 1.03)]^{-1} \cdot [1 - f\,(L/A)] \qquad (13)$$

from which it follows that the index in Eqn. (5) lies between 1 and 2. This is actually realised, for example, for polypeptide molecules in helical conformation[33]. Hence high values of the exponent in Eqn. (5) were obtained for these well-known rigid chain polymers.

However, this is by no means a general rule, since for gaussian chains the values of α and β are determined by the intramolecular hydrodynamic interaction, which depends on the diameter d as well as the degree of convolution L/A of the chain.

Thus from Eqns. (11) and (12) if the diameter of the molecular chain is d and is comparable with the length of the segment A—for example, $A \simeq 4d$ and $\ln(A/d) = 1.43$—then the indices α and β in Eqns. (5)–(7) will be close to 0.5, irrespective of the rigidity of the chain. A similar situation occurs, for example, for oligomers with flexible chain molecules[34-37]. As will be shown below, it can also occur with some rigid chain polymers where the segment length A is considerable (graft polymers)[38].

From what has been said above, the viscosity and translational friction for chain molecules and their dependence on the molecular weight can vary considerably. They are determined by the main parameters of the chain—diameter, contour length, and segment length, and also depend on the thermodynamic interaction of the molecules with the solvent. Consequently in several instances use of hydrodynamic properties alone seems insufficient for the quantitative determination of the rigidity, conformation, and internal structure of macromolecules.

The information obtainable becomes much more complete when a study of the hydrodynamic properties of the solutions is supplemented by an investigation of their dynamo-optical and electro-optical properties.

3. Dynamo-optical Properties of Chain Molecules[39]

The segment length A or the persistence length $a = A/2$, being a measure of the equilibrium rigidity of the main chain of the molecules, reflects to a certain extent another important property, the orientation order in the molecule. However, optical anisotropy is a more direct and much more sensitive measure of the orientation ordering of the structure of the molecule.

The optical anisotropy of a chain molecule of a polymer is measured by the difference between two of its principal polarisabilities $\gamma_1 - \gamma_2$ in directions parallel to and perpendicular to the vector h joining the ends of the chain.

For the simplest model—a gaussian chain[29]—the optical anisotropy of the molecule in the equilibrium conformation is independent of its contour length, that is, the molecular weight, and close to the anisotropy of the segment $\alpha_1 - \alpha_2$:

$$\gamma_1 - \gamma_2 = \frac{3}{5}(\alpha_1 - \alpha_2) \qquad (14)$$

The difference in polarisability of the segment $\alpha_1 - \alpha_2$ depends on the anisotropy of a monomeric unit $a_\parallel - a_\perp$ and the number of monomeric units S constituting the segment:

$$\alpha_1 - \alpha_2 = S\,(a_\parallel - a_\perp)\ . \qquad (15)$$

Therefore molecules with high rigidity (that is, having a high value of S) are characterised by high optical anisotropy.

On the other hand it has been shown that the swelling of molecules in good solvents, which greatly alters their dimensions and hydrodynamic properties, has hardly any effect on their optical anisotropy[1,39,40]. Therefore anisotropy can serve as a measure of the true skeletal rigidity of the molecular chain, irrespective of the effects of excluded volume, that is, the thermodynamic interaction of the molecule with the solvent.

It is very important that the anisotropy of the monomeric unit $\alpha_\parallel - \alpha_\perp$, and also the anisotropy of the molecule, can be either positive or negative, depending on the degree and nature of the ordering of the valence bonds of the monomeric unit relative to the direction of the main chain. Therefore optical anisotropy is a measure of the axial orientation order in the arrangement of the structural elements of the molecule—both of the main chain and also its lateral groups.

In a system having a uniaxial orientation order the degree of this order Q is known[41] to be given by:

$$Q = \frac{1}{2}(3\overline{\cos^2\theta} - 1) \qquad (16)$$

where θ is the angle of the departure of the longitudinal axis of the structural element (segment) from the direction of preferential orientation (that is, from the direction of the vector h in the molecule). $\overline{\cos^2\theta}$ is a quantity obtained by averaging over all the orientations of the segments in the molecule, at given values of $\bar{h}^2$ and L.

From Eqns. (15) and (16) there is a simple relation between the degree of orientation order Q and the anisotropy of the molecule:

$$Q = (\gamma_1 - \gamma_2)/P\,(a_\parallel - a_\perp) \qquad (17)$$

where P is the degree of polymerisation.

Experimentally, the anisotropy of the molecule described by a gaussian chain can be determined by measuring the double refraction Δn in flow in solution of the polymer being studied and a calculation by Kuhn's formula[10]:

$$\Delta n/\Delta\tau = \Delta n/g\,(\eta - \eta_0) = [n]/[\eta] = [4\pi\,(n_S^2+2)^2/45kTn_s]\,(\alpha_1 - \alpha_2). \qquad (18)$$

Here $\Delta\tau = g(\eta - \eta_0)$ is the effective shear stress in flow with a velocity gradient of g, $[n]$ is the characteristic birefringence of the solution, with $[n] = (\Delta n/g\eta_0 c)_{c \to 0}$ where c is the concentration.

When the refractive index of a polymer n_k differs from that of a solvent n_S, an additional positive anisotropy of the molecule arises, owing to the optical interaction of parts of the chain with one another—the "form effect"[39,42].

The overall form effect can be divided into two parts—the "macroform" effect and the "microform" effect. The first of these is due to the interaction of parts rather far apart along the chain (optically long-range action) and is determined by the asymmetry of the form of the macromolecular coil as a whole. The double refraction of the macroform for a gaussian chain equals:

$$([n]/[\eta])_f = [0.058\,\Phi\,(n_s^2+2)^2(n_k^2 - n_s^2)^2/\pi\rho^2 N_A RTn_s^3]\,(M/[\eta]) \qquad (19)$$

where Φ is the Flory coefficient, and ρ the density of the polymer. For a given polymer–solvent system the macroform effect is proportional to $M/[\eta]$ and therefore increases with the molecular weight.

The "microform" effect is due to the optical interaction of parts of the molecule which are neighbours along the chain. Unlike the macroform effect, the double refraction of the microform for a gaussian chain is independent of the molecular weight but proportional to the molecular weight

of a segment $M_S = A(M/L)$ and consequently increases with the rigidity of the chain:

$$([n]/[\eta])_{fs} = [(n_s^2+2)^2 (n_k^2 - n_s^2)^2/180\pi RTn_s^2\rho](L_2 - L_1)_s \cdot M_s \quad (20)$$

where $(L_2 - L_1)$ is the coefficient of the asymmetry of the form of the segment.

The principal role in the total, experimentally observable form effect for flexible chain molecules is taken by the macroform anisotropy, Eqn. (19), whereas for molecules with high skeletal rigidity of the chain it is the macroform anisotropy, Eqn. (20). Therefore for rigid-chain molecules the experimental measurement of the microform effect is an independent method of determining the skeletal rigidity of the molecular chain.

A characteristic feature of the macroform effect is its marked decrease with increase in the concentration of the solution[1,43]. On the other hand, the quoted value of the microform birefringence $[\Delta n/g(\eta - \eta_0)]_{fs}$ varies little with concentration[39,42]. Therefore a study of the concentration dependence of the form birefringence can enable the relative parts of its macro- and micro-constituents to be estimated and information obtained about the rigidity of the polymer investigated.

If the contour length L of a chain molecule is not very great in comparison with the segment length A (that is, the condition $h \ll L$ is not satisfied), it can no longer be regarded as a gaussian chain and Kuhn's formula (14) is inapplicable.

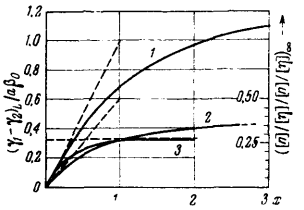


Figure 2. Variation of the optical anisotropy of the persistent length $(\gamma_1 - \gamma_2)_L$ and reduced birefringence of the solution $[n]/[\eta]$ with the parameter $x = L/a$. *1)* $(\gamma_1 - \gamma_2)_L/a\beta_0$ as a function of x; *2)* $\cdot [n]/[\eta]_L / [n]/([\eta])_{x\to\infty}$ as a function of x; *3)* $(\gamma_\parallel - \gamma_\perp)_L/a\beta_0$ as a function of x.

In this instance the difference in the principal polarisabilities $(\gamma_1 - \gamma_2)_L$ of molecules of length L is calculated by the theory of persistent anisotropy[44], which yields the relation

$$(\gamma_1 - \gamma_2)_L = \frac{3}{5}(\alpha_1 - \alpha_2)(1 - e^{-5x/6}) = a\beta_0 x\left[1 - \frac{5}{12}x + \frac{25}{216}x^2 - \frac{125}{5184}x^3 + \ldots\right], \quad (21)$$

where $x = L/a$, $a = A/2$, and $\beta_0 = (\alpha_1 - \alpha_2)/A$ is the anisotropy of unit length of the chain.

In distinction from the gaussian chains the anisotropy of a persistent chain increases with its length L (and consequently, the molecular weight), tending (at $x \to \infty$) to a limiting value of $\frac{3}{5}(\alpha_1 - \alpha_2)$ corresponding to the anisotropy of a gaussian chain. The corresponding dependence is shown in curve *1*, Fig. 2, where the ratio $(\gamma_1 - \gamma_2)_L/a\beta_0$ is represented as a function of the parameter x. The initial slope of the curve is evidently 1, the limiting value equals 6/5.

On plotting the values of $(\gamma_1 - \gamma_2)_L$ as a function of the contour length L of the molecule, then according to Eqn. (21), the initial slope of the curve determines the value of β_0, whereas the asymptotic limit gives a value of $\frac{6}{5}a\beta_0$.

It must be remembered that according to theory—Eqn. (21)—the decrease in molecular anisotropy with chain shortening is determined solely by the parameter $x = L/a$, and not by the absolute length of the segment A. Consequently, this phenomenon should occur not only for rigid but also for flexible chain molecules in the range of rather low molecular weights (oligomers). In reality the decrease in flow anisotropy with decrease in molecular weight was observed experimentally in oligomers with flexible chain molecules[37] although their hydrodynamic behaviour exhibited no special features.

This phenomenon is of special significance for rigid-chain molecules (large A) since then it should be observed in the range of rather high molecular weights and can serve as a direct proof of increased skeletal rigidity of the chain.

In accordance with Eqn. (21) and unlike the gaussian coils, Eqn. (18), the flow birefringence $([n]/[\eta])_L$ in solution of persistent chains should increase with the molecular weight, tending to a limiting value of $([n]/[\eta])_\infty$ as $x \to \infty$, determinable by Eqn. (18).

For rigid wormlike chains ($A \gg d$) in the range of low x ($x < 3$) this increase is determined by the formula:

$$([n]/[\eta])_L = (4\pi/45\,kTn_s)(\gamma_1 - \gamma_2)_L \cdot F(x) \cdot (n_s^2+2)^2, \quad (22)$$

where $F(x)$ is a tabulated[44] function reflecting the change in the geometric asymmetry of the molecules with increase in length, and the value of $(\gamma_1 - \gamma_2)_L$ is determined by Eqn. (21).

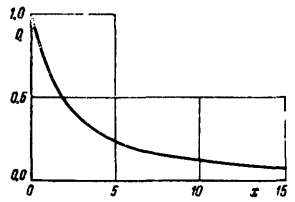


Figure 3. Variation of the degree of intramolecular orientation ordering Q with the parameter $x = L/a$ for a persistent chain.

The variation of $([n]/[\eta])_L/([n]/[\eta])_\infty$ with x, according to Eqn. (22), is represented by curve *2* of Fig. 2. The initial slope of the curve obtained is 0.5, the asymptotic limit is 1.

A comparison of the experimental dependence of the birefringence on the molecular weight with the theoretical (22) enables the anisotropy of unit length β_0 and the persistence length $a = A/2$ of the molecular chain to be determined.

Eqn. (21) also enables the change in the degree of intramolecular orientation order Q with increase in chain length to be presented clearly. On combining Eqns. (21), (17), and (14) and taking into account that $P/S = x/2$, we obtain:

$$Q = (6/5x)(1 - e^{-5x/6}). \quad (23)$$

Fig. 3 shows the dependence of Q on x according to Eqn. (23). With increase in x the degree of ordering falls sharply from values close to unity to values close to zero.

Values of $Q \simeq 1$ are characteristic of systems with an almost perfectly ordered structure, which occurs, for example, in ideal three-dimensional single crystals.

Less perfect, but nevertheless extremely high, orientation order is observed in liquid crystalline (mesomorphic) systems; thus for a nematic mesophase the value of Q lies in the range 0.4–0.7.[41]

As the graph in Fig. 3 shows, the same level of orientation ordering in the structure of chain molecules can be achieved in the range of molecular weights where x does not exceed a few units. Several examples can now be given (see below) of extremely rigid chain molecules for which this range corresponds to molecular weights of tens and even hundreds of thousands.

For such "crystal-like" polymeric molecules the degree of intramolecular orientation order corresponds to the level of the supermolecular organisation of the nematic mesophase.

However, for most flexible-chain polymers even at $P \simeq 10^3$, Q has an order of magnitude of 0.01 and this decreases with a further increase in molecular weight. Such a low degree of orientation order can be observed and measured only by using such sensitive quantities as the optical anisotropy of the molecule determinable from the stream birefringence.

These features of the optical properties of rigid-chain molecules, predicted by theory, are independent of both excluded volume effects and of hydrodynamic interaction in the molecular chains. Therefore the use of these properties as characteristics of rigidity and the degree of ordering of the structure of a molecule is not complicated by a need to allow for the thermodynamic quality of the solvent and a flow effect.

4. Electro-optical Properties

In examining the order of the structure of macromolecules a distinction must be made between orientation axial order and orientation dipole order. Many chain molecules contain polar groups or bonds and in the presence of a coaxial order in the mutual orientations of these groups the macromolecule should have a high total dipole moment. However, for flexible chain molecules this is usually not observed. One of the reasons can be the mutual compensation of the local and group moments in their vector addition. The main reason is the flexibility of the macromolecule, which results in local polar groups of the molecule in an external electric field being orientated practically independently of one another. Here the dipole polarisation of the molecule in an electric field is simply equal to the sum of the polarisation of its polar units and does not differ much from the polarisation of a liquid monomer of equal mass.

For rigid-chain molecules the situation can be significantly different. Owing to the rigidity of the molecular structure the orientations of the polar groups of the molecule in an electric field are independent of one another but are mutually correlated to a greater or less extent with the molecular chain or its parts (segments). Therefore if the vector sum of the local group moments is not equal to zero, that is, if their orientation-polar ordering inside the molecule is realised, the latter can have a significant dipole moment and under the action of an electric field it rotates as a rigid particle.

Note that these properties of the molecule depend not only on its equilibrium rigidity but also to a considerable extent on its kinetic rigidity.

In solutions of such polar rigid-chain molecules a high birefringence is produced in an electric field E (the Kerr effect). The value of Δn and the sign of the birefringence depend on the magnitude and sign of the optical anisotropy of the molecule $\gamma_1 - \gamma_2$ and also on its dipole moment μ and the angle θ formed by the axis of the dipole with the optical axis of the molecule[45]:

$$\lim_{\substack{c\to 0\\ E\to 0}} (\Delta n/cE^2) = \frac{\pi N_a}{15n}\left(\frac{n^2+2}{3}\right)^2\left(\frac{\varepsilon+2}{3}\right)^2 \cdot \frac{\gamma_1-\gamma_2}{M}\left(\frac{\mu}{kT}\right)^2 (3\cos^2\vartheta - 1). \quad (24)$$

Here c is the concentration, n the refractive index, and ϵ the dielectric constant of the solution.

An experimental study of this effect and a comparison of the results with those on flow birefringence enables information to be obtained about the value and direction of the molecular dipole and additional conclusions to be drawn about the conformation, rigidity, and ordering of the structure of the molecule.

On modelling a semirigid molecule by a persistent chain the value of its dipole moment μ can be linked[11,46] with the contour length $L = ax$ by the theoretical relation:

$$\overline{\mu^2} = (\mu_0 S)^2 (x - 1 + e^{-x})/2 \quad (25)$$

or

$$\overline{\mu^2}/L = (\mu_s^2/A)[1 - (1 - e^{-x})/x], \quad (26)$$

where μ_0 is the component of the dipole moment of the monomeric unit along the axis of the molecule, S the number of monomeric units in its segment, and μ_S the dipole moment of the segment.

An experimental study of the variation of the dipole moment μ with the molecular weight M and a comparison of this relation with the theoretical one—Eqns. (25) and (26)—enables the persistent length a to be found and hence the rigidity of the molecule to be estimated from electro-optical results.

In a periodic electric field solutions of rigid-chain polar molecules exhibit a dependence of the Kerr effect on frequency, which shows the existence of relaxation in the dipole orientation process. A study of the frequency dependence enables the rotational mobility of the molecules to be determined and additional information to be obtained about their conformation and rigidity.

III. SOME EXPERIMENTAL RESULTS

1. Cellulose and Its Derivatives

As shown above, cellulose and its derivatives have for long been the best known, "classical" example of chain molecules with high skeletal rigidity. This property follows directly from the geometry of the molecular chain (Fig. 4).

The monomeric unit is a glucoside ring with two adjacent valence bonds OC_1 and OC_4, around which rotation is possible. In calculating the statistical dimensions of the chain its monomeric unit can be denoted[47] by an equivalent "effective" unit consisting of two parallel bonds $b = 2.7$ Å, around which rotation takes place and one bond $d = 1.45$ Å (normal to the first two) around which there is no rotation. On using this scheme it can be shown that for a sufficiently long chain with completely free rotation around bonds OC_1 and OC_4 (that is, "bonds" b) the mean square distance between its ends $\overline{h_f^2}$ is[47]:

$$\overline{h_f^2} = P[d^2 + (2b)^2(1 + \cos\vartheta)/(1 - \cos\vartheta)], \quad (27)$$

where P is the number of monomeric units in the chain, and $\pi - \theta$ is the valence angle between the neighbouring bonds OC_1 and OC_4.

On substituting the values of b and d and assuming $\theta = 70°$ we obtain $\overline{h_f^2} = 62P \times 10^{-16}$ cm^2, and for the length of a segment of the cellulose chain with completely free rotation:

$$A_f = \overline{h_f^2}/P\lambda = \overline{h_f^2}/P\left(2b\cos\frac{\theta}{2} + d\sin\frac{\theta}{2}\right) = 12 \text{ Å}.$$

This value of A_f corresponds with the number of monomeric units in the segment $S_f = 2.5$.

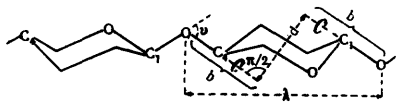


Figure 4. Conformation of the cellulose chain. λ = projection of the monomeric unit on the chain direction; $b = 2.7$ Å is the length of the "effective bond" around which rotation is possible; $d = 1.45$ Å is the length of the "effective bond" around which rotation is impossible.

For a carbochain polymer not containing rings in the chain under the condition of free rotation an analogous calculation gives[1]:

$$A_f = l(1 + \cos\theta)/(1 - \cos\theta)\sin\theta/2,$$

which for $\theta = 70°$ and $l = 1.54$ A leads to the value $A_f = 3.8$ Å.

Hence even when there is completely free rotation the segment length of the cellulose chain should be more than three times as great as the segment length of a flexible carbochain polymer.

An analogous conclusion can be reached by considering the possible conformations of another linear polysaccharide—amylose. However, here the theoretical values are less definite since spiral structures can be formed with amylose[48].

The real polymeric chains in a Θ-solvent have the undisturbed dimensions $(\overline{h_\Theta^2})^{\frac{1}{2}}$, which owing to restricted rotation exceed the chain dimensions in free rotation:

$$\overline{h_\Theta^2}/\overline{h_f^2} = \sigma^2,$$

where σ is the rotation restriction factor. Many flexible carbochain polymers are characterised by values of σ lying in the range $\sigma^2 \simeq 4-5$, which corresponds with segment lengths of $A = A_f\sigma^2 \simeq 15-20$ Å.[1,25,49]

The problem of the value of the restriction factor σ for cellulose derivatives has been the subject of discussion recently. The method with the best theoretical basis for determining σ is the direct measurement of the undisturbed radius of gyration of the molecule $\overline{R^2}$ from the asymmetry of its light scattering in solutions. There are considerable experimental difficulties in such measurements for polysaccharides[21-23] and evidently for this reason they are rather few. Some examples are given in Table 1. The values of $A = S\lambda$ were calculated from the experimental values of $\overline{R^2}/P = \frac{1}{6}S\lambda$, obtained in the range of limitingly large values of P, Eqns. (3) and (2′). Here the values of λ were taken as 5.15 and 3 Å for cellulose and anylose chains respectively (the value $\lambda = 3$ Å corresponds to a helical model of the amylose chain[48,50]). Corresponding values of the restriction factor $\sigma = (A/A_f)^{\frac{1}{2}}$ are given here.

The value of A for polysaccharides is an order of magnitude greater than the corresponding values found by the light scattering method for most of the flexible carbochain polymers[1]. The rotation restriction factor σ in polyglucose chains is, according to the light scattering results, at least twice the value of σ for flexible chain polymers[1,25,49].

Table 1. Segment length A, number (S) of monomeric units in the segment, and rotation restriction factor for molecular chains of some derivatives of polysaccharides obtained from measurements of the asymmetry of light scattering.

Polymer	Solvent	10^8A, cm	S	σ	Reference
Cellulose trinitrate	acetone	230	44	4.4	51
	acetone	235	45	4.4	52
	acetone	233	44	4.4	53
	ethyl acetate	234	44	4.4	54
	isopentyl acetate	216	42	4.25	53
	dioxan	220	43	4.3	53
	nitrobenzene	58	11.2	2.2	53
Cellulose tricarbanilate	dioxan–methanol mixture (Θ-solvent)	268	52	4.7	55
Amylose tricarbanilate	dioxan–methanol mixture (Θ-solvent)	414	80	5.8	55
Amylose acetate	nitromethane	100	19	2.9	56

Conclusions about the high rigidity of the molecules of cellulose derivatives[51-56] also agree with hydrodynamic properties of their solutions. Thus the index α in the Mark–Kuhn equation (5) for many of them is close[49] to unity, which is usually connected with the flow effect, whereas the excluded volume effect (ideality of the solvent) is less important[53,55].

At the same time it was noted in several studies[53,57-60] that certain properties of the solvent and the temperature have a pronounced influence on the undisturbed dimensions (that is, the skeletal rigidity) of the molecules of the cellulose derivatives.

In recent years another point of view on the rigidity of molecules of cellulose derivatives has been advanced, based on the use of viscosimetric results for the determination of their unperturbed dimensions[25]. Here it was suggested that the high value of the index α in Eqn. (5) and the large molecular dimensions observable experimentally in polysaccharides are the consequence not of their increased rigidity but of the exceptionally marked influence of the volume effects, since modern theories in principle admit a value of $\epsilon = \frac{1}{3}$ in Eqn. (4) and correspondingly $\alpha = 1$ in Eqn. (5) owing to the non-ideality of the solution[20]. A second a priori assumption, which is made in this is the postulation of almost complete non-flowability of molecules of cellulose derivatives in solutions, like the molecular coils of flexible chain polymers. On starting from this assumption the undisturbed dimensions of the molecules are determined from the viscosimetric results of the extrapolation of the latter into the range of low molecular weights, using Eqn. (8). The unperturbed dimensions and the restriction factor σ, obtainable as a result of such a

procedure are close to the corresponding values for flexible carbochain polymers and on this basis it is concluded that the molecular chains of cellulose and its derivatives do not exhibit a high rigidity[25,61-64].

Recently Flory[65] criticised this viewpoint by observing that in addition to an unproven neglect of the flow effect in molecules of cellulose derivatives it also ignores the departure from gaussian behaviour of their chains in the range of low molecular weights—factors, the presence of which makes the use of formula (8) quite improper. The reality of the pronounced influence of flow on the hydrodynamic properties of molecules has been demonstrated for several polysaccharides[66,67].

The departure from gaussian behaviour in the range of low molecular weights for polysaccharide chains has been shown in several papers[51-55] by the direct determination of their dimensions by the method of asymmetry of light scattering in solutions. This gave the dependence of the dimensions on the molecular weight which corresponded at least qualitatively to Eqns. (2) and (3) and to the theoretical curve (Fig. 1) for rigid wormlike chains.

Unlike flexible chain molecules[34-36], the dependence of the viscosity $[\eta]$ on the molecular weight M in the range of low M for cellulose derivatives also has features which show the absence of gaussian properties[68].

What has been stated above gives grounds for considering that the characteristic parameters of the rigidity of polysaccharide molecules found by direct measurements (Table 1) are much more reliable than the corresponding quantities obtained by use of model theories and making several doubtful assumptions[25,61-63].

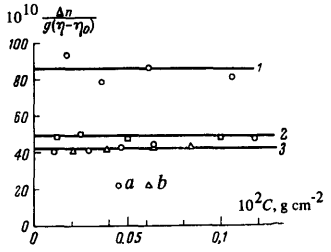


Figure 5. Reduced birefringence of solutions of cellulose monophenylacetate in various solvents depending on the concentration[69]: *1*) in ethyl acetate; *2*) in cyclohexanone; *3*) *a*) in bromoform; *b*) in acetophenone.

Because of the discussion and existence of two opposite viewpoints it is extremely important to obtain data on the rigidity of cellulose molecules by other methods free from model assumptions of hydrodynamic theories and independent of the thermodynamic properties of the solution. As already stated, a study of the dynamo-optical properties of the solutions can be such a method.

Usually the value of the flow birefringence and the corresponding optical anisotropy of a segment are appreciably greater for cellulose derivatives than for flexible-chain polymers[1], which by itself is a qualitative index of the high skeletal rigidity of polysaccharide chains.

In solutions of cellulose derivatives where the refractive index of the polymer n_k differs from the refractive index of the solvent n_s a very high form effect is observed.

It is characteristic that the reduced birefringence $\Delta n/\Delta\tau$ is here independent of concentration (see Fig. 5) unlike the marked concentration dependence of the form birefringence for solutions of flexible-chain polymers[1,43].

Another characteristic feature of the form effect, observable in solutions of cellulose derivatives, is the extremely weak dependence of the reduced birefringence $\Delta n/\Delta\tau = [n]/[\eta]$ on molecular weight (Fig. 6), whereas for flexible-chain polymers the value of $[n]/[\eta]$ increases sharply with the molecular weight (Fig. 7).

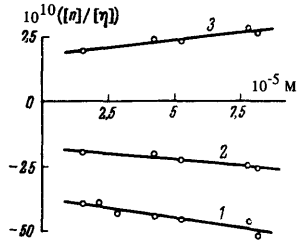


Figure 6. Variation of the reduced anisotropy of solutions of cellulose nitrate with the molecular weight[70]. *1*) $[n]/[\eta]$ for fractions of cellulose nitrate in cyclohexanone ($n_k - n_s = 0$, proper anisotropy); *2*) $[n]/[\eta]$ for the same fractions in butyl acetate ($n_k - n_s$, total birefringence); *3*) $[n]/[\eta]$ corresponding to the microform effect, calculated by subtracting the ordinate of curve *1* from the ordinate of curve *2*.

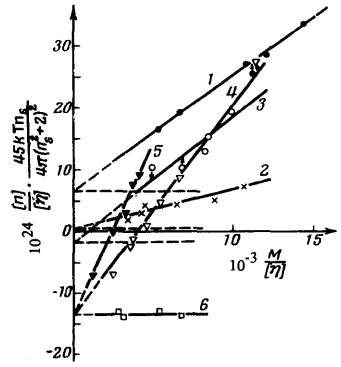


Figure 7. Variation of the quantity

$$x = \frac{[n]}{[\eta]}\cdot\frac{45kTn_s}{4\pi(n_s^2+2)^2},$$

which forms part of Eqns. (18) and (19) with $M/[\eta]$ for solutions of certain flexible-chain polymers[1]. *1*) Polyisobutene in hexane; *2*) polydimethylsiloxane in toluene; *3*) poly(butyl methacrylate) in ethyl acetate; *4*) polystyrene in dioxan ($n_k - n_s = 0.18$); *5*) polystyrene in butanone ($n_k - n_s = 0.22$); *6*) polystyrene in bromoform ($n_k - n_s = 0$).

Both the first and the second feature show that the form birefringence observable in solutions of cellulose derivatives (unlike flexible chain molecules) is an effect of the chain microform and determinable by Eqn. (20).

In accordance with Eqn. (20) the experimentally found variation of $[n]/[\eta]$ with the refractive index of the solvent n_S is a parabolic curve (Fig. 8). The minimum of the parabola gives the proper anisotropy of the segment $\alpha_1 - \alpha_2$. From the remaining points of the curve, using Eqn. (20), the molecular weight of the segment $M_S = A(M/L)$ can be calculated and hence its length A. The values thus obtained for certain cellulose esters are given in Table 2.

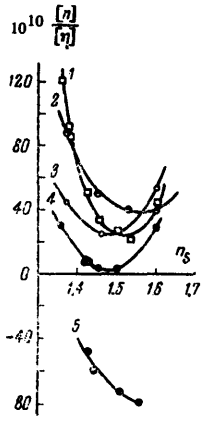


Figure 8. Variation of the reduced birefringence $[n]/[\eta]$ of solutions of cellulose esters with the refractive index of the solvent: *1*) cyanoethyltritylcellulose[73]; *2*) monophenylacetylcellulose[69]; *3*) ethyl cellulose[71]; *4*) cyanoethylacetylcellulose[72]; *5*) cellulose benzoate[69].

For specimens 3, 4, and 5 with large lateral substituents $(L_2 - L_1)_S = 2$ is taken for calculating A, for the other specimens $(L_2 - L_1)_S = 2\pi$.

As Table 2 shows, the segment lengths A and the corresponding values of σ obtained by measuring the flow birefringence have magnitudes close to the values of A and σ found by the light scattering method (Table 1). Similar results are given by an investigation of the photoelasticity of gels of cellulose derivatives in various solvents[72,73].

Hence the dynamo-optical properties of solutions and gels of cellulose derivatives are not only a qualitative but also a quantitative index of the high skeletal rigidity of their molecular chains.

This rigidity is determined not only by the presence of rings in the chain—a high value of $\bar{h}_f^2$ in Eqn. (27) and hence of A_f—but also by the higher (than for carbochain molecules) value of the restriction factor σ. It is very probable that a significant part in the retardation of intramolecular rotation is played by the hydrogen bonds established between the oxygen, hydrogen, and nitrogen atoms forming part of the lateral substituents of the polyglucose chain.

For polysaccharide molecules containing ionogenic groups the skeletal rigidity can be increased even more, owing to the electrostatic interaction of these groups.

A decrease in the ionic strength of the solution and an increase in the dissociation of the ionogenic groups is accompanied by the uncoiling of the chain of the polyion due to the electrostatic repulsion of its charged parts. During this there is an increase in both the characteristic viscosity of the solution (owing to the increase in the size of the molecular coils), and in its characteristic flow birefringence $[n]$. However, $[n]$ increases more rapidly than $[\eta]$ and therefore the ratio $[n]/[\eta]$ increases. This shows that in a polyelectrolytic uncoiling of a molecular chain of a polyion (unlike its osmotic swelling in a strong solvent) there is an increase in the segment anisotropy $\alpha_1 - \alpha_2$, Eqn. (18), and consequently also in the segment length A.

Table 2. Optical anisotropy and parameters of the rigidity of various cellulose esters from the flow birefringence.

Polymer	Degree of substitution	$(\alpha_1 - \alpha_2)\cdot 10^{25}$, cm^3	$10^8 A$, cm	s	$(\alpha_\parallel - \alpha_\perp)\cdot 10^{25}$, cm^3	$\sigma = \left(\frac{\bar{h}_0^2}{\bar{h}_f^2}\right)^{1/2}$	Reference
Cellulose nitrate	2.60	−300	260	50	−12	4.7	70
Ethyl cellulose	2.60	310	180	35	18	3.9	71
Cellulose benzoate	3.0	−900	270	52	−36	4.8	69
Cellulose phenylcarbanilate	1.9	−1100	180	35	−60	3.9	69
Monophenylacetyl cellulose	2.5	440	250	49	18	4.6	69
Cyanoethylacetyl cellulose	1.7	15	250	49	0.7	4.6	72
	0.9						
Cyanoethyltritylcellulose	2.0	220	280	54	8	4.9	73
	1.0						

In other words, polyelectrolytic uncoiling of the chain is accompanied by an increase in its skeletal rigidity.

This is shown by Table 3, which gives the results of viscosimetric and dynamo-optical investigations of aqueous solutions of the sodium salt of a specimen of a sulphite ester of cellulose (Na-SC with a lateral substituent $-SO_3Na$, molecular weight $M = 10^5$) at various ionic strengths I.

Table 3. Hydrodynamic, optical, and conformational characteristics of the molecule of the sodium salt of sulpho-ester of cellulose at various ionic strengths of the solution[74].

I, M	$[\eta]$, cm^3 g^{-1}	$10^{10}\frac{[n]}{[\eta]}$	$10^{25}(\alpha_1 - \alpha_2)$, cm^3	$10^{25}\frac{\alpha_1 - \alpha_2}{[\eta]}$, g	$10^8 A$, cm
0.200	290	46.6	634	2.19	195
0.150	290	47.4	645	2.22	195
0.100	310	50.0	680	2.19	216
0.010	500	72.0	980	1.96	330
0.005	610	96.7	1320	2.16	410
0.001	870	127.0	1730	2.00	575

From Table 3, clearly the value of the ratio $(\alpha_1 - \alpha_2)/[\eta]$ is approximately the same for different ionic strengths and is equal to 2.1×10^{-25}. Because of the identity

$$\alpha_1 - \alpha_2 \equiv \beta_0 A$$

and Eqn. (1), we have

$$\bar{h}^2/[\eta] = 2.1 \cdot 10^{-25} \ (L/\beta_0).$$

for all ionic strengths. This signifies that (since for a particular chain molecule L/β_0 is independent of its convolution) in the polyelectrolytic uncoiling of the Na-SC chain the characteristic viscosity $[\eta]$ increases in proportion to $\bar{h}^2$, which is characteristic for hydrodynamically flowing gaussian coils. Therefore the assumption about the non-flowability of molecules of ionogenic derivatives of cellulose made in some studies[20,61,62] is untenable.

Judging by the structure of substituent groups, it can be expected that the proper segment anisotropy Na–SC in the range of high ionic forces ($I = 0.2$), when the polyelectrolytic effects are suppressed is close to the proper anisotropy of an ethylcellulose segment[71] $(\alpha_1 - \alpha_2)_i = 310 \times 10^{-25}$ cm^3. The fact that in aqueous salt solutions at $I = 0.2$ the observed anisotropy $(\alpha_1 - \alpha_2)$ is 634×10^{-25} cm^3, that is, is 634/310 = 2.05 times the value of $(\alpha_1 - \alpha_2)_i$, shows that half the birefringence thus observable is due to the microform effect. Starting from this and using Eqn. (20) the segment length A can be calculated. The values of A obtained at various ionic strengths (Table 3) show the increase in the skeletal rigidity of the chain during its polyelectrolytic uncoiling.

2. Molecules with a Regular Secondary Structure

a. Deoxyribonucleic acid (DNA). DNA, like cellulose derivatives, can be regarded as a classic example of a polymer with semirigid chain molecules. The generally accepted model of the molecule is the rigid double-helix structure proposed by Watson and Crick[75], maintained by hydrogen bonds, which "reinforce" the purine and pyrimidine bases of the DNA chain.

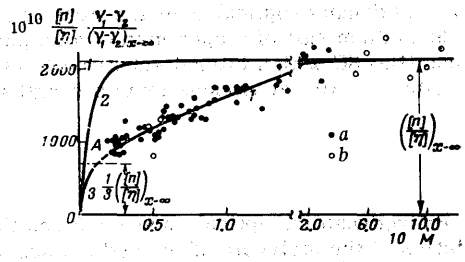


Figure 9. Flow birefringence $[n]/[\eta]$ and optical anisotropy of the DNA molecule as a function of molecular weight M. *1*) The curve of $[n]/[\eta] = f(M)$ drawn according to the experimental points; *a*) DNA fragment obtained by treatment of the DNA solutions; *b*) fragments obtained by ultrasonic destruction; *2*) curve for the variation of the relative anisotropy of the molecule $(\gamma_1 - \gamma_2)_L/(\gamma_1 - \gamma_2)_{x \to \infty}$ with $x = L/a$; *3*) initial part of the theoretical curve *2* of Fig. 2.

The application of the hydrodynamic theory of wormlike chains to the experimental results on sedimentation, Eqn. (12), leads to the values of the segment length A = 700–900 Å,[30–32] which is two to four times the value obtained for cellulose derivatives (Tables 1–3). The optical anisotropy of the DNA molecule found from the flow birefringence is very high and negative in sign. This corresponds to the high degree of orientation order of the base, the plane of which is perpendicular to the axis of the molecule.

The optical anisotropy increases with the molecular weight of DNA[76] in accordance with the theory of persistent chains[44] (Fig. 9). A comparison of the experimental curve with the theoretical one, Eqn. (22), leads to the value A = 600 Å.[76]

b. Polypeptides $-\overset{\overset{O}{\|}}{C}-CHR-\overset{\overset{H}{|}}{N}-$ Polypeptides in a helical conformation are a good example of a rigid-chain molecule with a very high rigidity. The most complete information about the hydrodynamic, optical, and electrical properties of molecules was obtained for poly-γ-benzyl-L-glutamate (PB-L-G).

The high rigidity of spiral molecules is best shown by the high value of the exponents α and β in the Mark-Kuhn equations (5)–(7).[33,46,78]

Experimental results on diffusion and sedimentation have been used for the quantitative determination of rigidity. Fig. 10 shows the variation of the sedimentation coefficient $[s]$ or the quantity DM/RT with the square root of the molecular weight $M^{\frac{1}{2}}$. According to Eqn. (12) the slope of the straight line obtained leads to a value of 2200 Å for the segment length A.[33,46] The flow birefringence in solutions of α-spiral polypeptides is very high and increases with the molecular weight (Fig. 11). Use of this relation and the theory of persistent anisotropy[44], Eqns. (21) and (22), lead to values for the anisotropy and length of the segment of respectively $\alpha_1 - \alpha_2 = 20\,000 \times 10^{-25}$ cm^3 and A = 2400 Å.

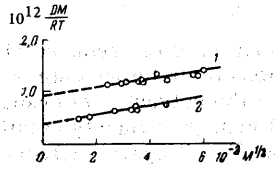


Figure 10. Variation of DM/RT with $M^{\frac{1}{2}}$ for poly-γ-benzyl-L-glutamate (*1*) and poly(butylisocyanate) (*2*).

These values agree with the hydrodynamic values and show the high degree of intramolecular orientation ordering Q, determined from Eqn. (23).

A comparison of the curves in Figs. 3 and 11 shows that in the molecular weight range investigated the value of Q for the PB-L-G molecules varies in the range 0.35–0.8, that is, it corresponds with the level of the orientation order characteristic for the nematic mesophase. Therefore the PB-L-G molecules are typical examples of a "crystal-like" molecule.

In an electric field a high birefringence arises in the PB-L-G solutions, showing the high degree of orientation-dipole order in the molecule. The positive sign of the Kerr effect shows that the total dipole moment of the molecule is directed along its axis, being the sum of the local moments of the C=O...H–N group joined by hydrogen bonds.

A comparison of the dynamo-optical and electro-optical results, Eqns. (22) and (24), enables the segment length A to be determined. The value A = 1400 Å thus obtained[46] is less than that found from the results of measurement of diffusion, sedimentation, and flow birefringence.

This fact shows that the processes in the orientation of polar polypeptide molecules in mechanical and electric fields cannot be identified. There is evidently a significant difference in the degrees of the axial and polar correlations of the units of the polypeptide helix chains.

The high value of the optical anisotropy and dipole moments are characteristic only for polypeptide molecules in

a helical conformation maintained by hydrogen bonds. When the latter are broken in strong solvents, in addition to the breakdown of the spiral structure the crystal-like orientation ordering is also destroyed and furthermore there is almost complete disappearance of the large optical effects observable in mechanical and electrical fields. An illustration is given by Figs. 12 and 13, which show the changes in birefringence in flow and in an electric field and the viscosity of the PB-*L*-G solution during the spiral–coil intramolecular conformational transformation[104].

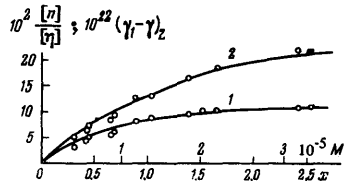


Figure 11. Variation of the reduced anisotropy of the solution $\Delta n/g(\eta - \eta_0) = [n]/[\eta]$ (*1*) and $\gamma_1 - \gamma_2$ (*2*) with the molecular weight for fractions of poly-γ-benzyl-*L*-glutamate in dichloroethane.

3. Polymeric Molecules with Rings in the Main Chain

The rigidity of the spiral conformation of polynucleotides or polypeptides is maintained by hydrogen bonds formed by intramolecular cyclic parts of the chain and leading to a "lattice" structure of the molecule.

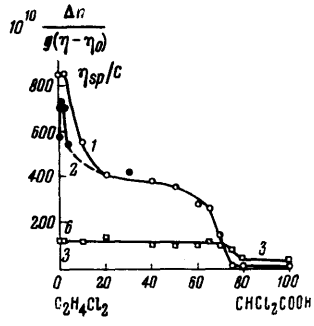


Figure 12. Variation of the optical anisotropy (*1* and *2*) and viscosity (*3*) of a solution of poly-γ-benzyl-*L*-glutamate during the destruction of the helical structure of the molecule. Solvent: *1*) dichloroethane—2% dimethylformamide with the addition of dichloroacetic acid; *2*) dichloroethane with the addition of dichloroacetic acid.

It could be expected that the same result can be reached for synthetic chain polymers by the introduction of heterocycles, some atoms of which enter the main chain of the polymer.

Although a large number of polymers with heterocycles in the chain have been obtained in recent years[79-82], quantitative data about the conformation and rigidity of such molecules in the solutions are very few. One of the probable reasons for this is the poor solubility of such polymers in ordinary solvents.

Detailed quantitative data about the properties of the solutions were obtained for polymers of *N*-substituted maleimides[83], which are readily soluble in organic solvents and occupy a sufficiently wide range of molecular weights[84].

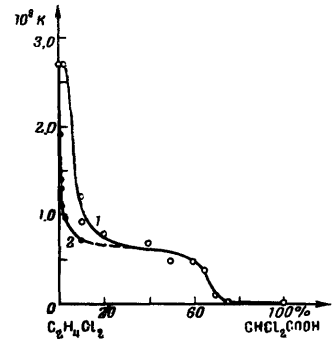
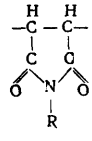


Figure 13. Variation of the Kerr constant (K) of a solution of poly-γ-benzyl-*L*-glutamate during the destruction of the helical structure of the molecule. Solvent: *1*) dichloroethane–dimethylformamide with the addition of dichloroacetic acid; *2*) dichloroethane with the addition of dichloroacetic acid.

a. Poly-*N*-isobutylmaleimide[84] (PIBMI)



As follows from the structural formula of this polymer, the presence of imide rings halves the number of single bonds around which rotation in the main chain is possible. In accordance with this, increased rigidity of the molecular chain can be expected. The rigidity of the chain was determined from the experimental results on sedimentation, diffusion, and viscometry. To rule out the influence of volume effects and to determine the undisturbed dimensions of the molecule, the hydrodynamic results were extrapolated to limitingly small molecular weights in accordance with Eqns. (8) and (10). Such a construction is shown in Fig. 14 for fractions of PIBMI in butyl acetate. The intercepts made by the straight lines on the ordinate axis give for the length of the Kuhn segment the value A = 35–40 Å, which is twice the value usually obtained for flexible chain volumes without rings in the chain[1].

However, the doubling of the rigidity due to cyclisation of the chain is not high enough for the molecule concerned to be classified as semirigid from its behaviour in solution. Thus the values of the indices $\alpha = 0.65$ and $\beta = 0.59$ in the M–K formulae (5–7) for PIBMI molecules (which are greater than 0.5) are due to the excluded volume effects and hence are unconnected with the increased rigidity of the chain. In accordance with this the anisotropy of the molecules and the reduced birefringence $[n]/[\eta]$ for PIBMI solutions in the investigated range of molecular weights

corresponds to the Kuhn equations (14) and (18) for gaussian chains and does not depend on the molecular weight[84].

Hence to reduce the flexibility of the chain to a value characteristic for semirigid chain molecules the fraction of the cyclised chains should be appreciably greater than one-half. Complete cyclisation of all the chains gives the limitingly rigid structure of the "staircase" polymer.

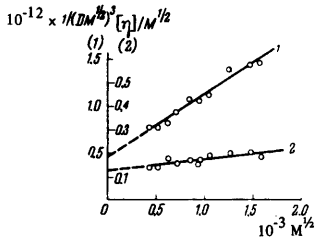
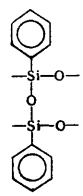


Figure 14. Variation of the quantities $(1/DM^{\frac{1}{2}})^3$ (*1*) and $[\eta]/M^{\frac{1}{2}}$ (*2*) with $M^{\frac{1}{2}}$ for fractions of poly-*N*-isobutylmaleimide in butyl acetate.

b. Staircase polyphenylsiloxane [85].



This polymer has been obtained by several investigators [86,87]. Fig. 15 shows the probable structure of its molecule. Here the cyclisation is effected by transverse Si–O bonds, which strengthen the two siloxane chains. Study of the hydrodynamic properties of fractions of one of the specimens in solutions leads to M–K dependences (5)–(7), in which the indices greatly exceed 0.5 ($\alpha = 0.88$, $\beta = 0.63$). [85]

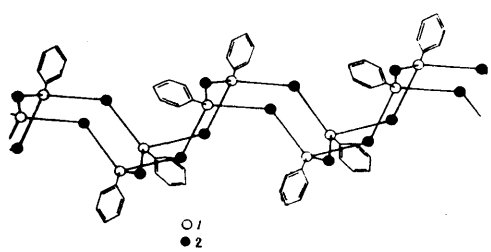


Figure 15. Structure of the molecule of staircase polyphenylsiloxane: *1*) silicon atoms; *2*) oxygen atoms.

This is due to the considerable skeletal rigidity (the flow effect) whereas the role of the excluded volume effects is small and cannot be considered.

In accordance with this the rigidity of the chain can be determined by constructing the variation of $[s]$ with $M^{\frac{1}{2}}$ and of $M/[\eta]$ with $M^{\frac{1}{2}}$ shown in Fig. 16 for one of the specimens of a staircase polymer. The slopes of the straight lines obtained lead, by use of the theory—Eqns. (11) and (12)—to values of A = 200 Å for the segment length. This value is ten times the value of A for the chain molecules of a staircase polyphenylsiloxane without rings in the chain. [1] The considerable rigidity of the molecule of the staircase polymer is quite adequate for the appearance of properties characteristic for semirigid chain molecules in the molecular weight range investigated.

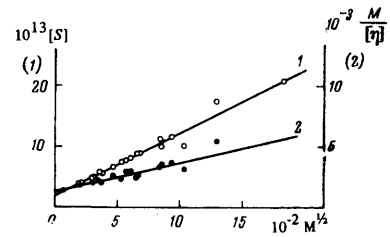


Figure 16. Variation of the quantities $[s]$ (*1*) and $M/[\eta]$ (*2*) with $M^{\frac{1}{2}}$ for fractions of staircase polyphenylsiloxane.

These properties are shown clearly in the optical behaviour of the solutions. In these there is great negative flow birefringence (which corresponds to the sign of the anisotropy introduced by the lateral phenyl radicals), the reduced value of which increases with the molecular weight (see Fig. 17) in complete agreement with the theory of the anisotropy of persistent chains—Eqns. (21) and (22).

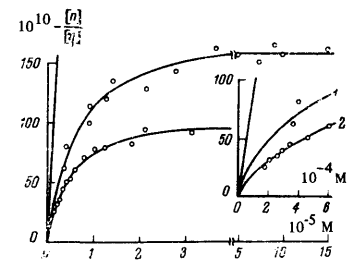


Figure 17. Variation of the reduced birefringence $[n]/[\eta]$ with the molecular weight M for fractions of two specimens of staircase polyphenylsiloxane: *1*) specimen 1; *2*) specimen 2. The experimental points correspond with the following values of the persistent length and anisotropy: for specimen 1) a = 90 Å, $\alpha_1 - \alpha_2 = -1.8 \times 10^{-22}$ cm^3; for specimen 2) a = 50 Å, $\alpha_1 - \alpha_2 = 1 \times 10^{-22}$ cm^3.

The segment length A, estimated from the initial slope and the asymptotic limit of the experimental curves of Fig. 17, is 180 Å, which agrees with the values obtained from hydrodynamic results.

The anisotropy of the segment, determinable from the asymptote of curve *1*, Fig. 17, is $\alpha_1 - \alpha_2 = -1800 \times 10^{-25}$ cm^3, which is 20 times the anisotropy of linear isotactic metaphenylsiloxane without rings in the chain [88].

At the same time the fractions $\Delta\alpha$ introduced into the anisotropy of the molecule by a single phenyl ring are almost the same for staircase and linear single-chain polyphenylsiloxanes ($\Delta\alpha = -20 \times 10^{-25}$ cm^3). This indicates that transverse oxygen bridges, which strengthen the double chain molecule of the staircase polymer and greatly increase its skeletal rigidity, are without any significant effect on the rotational mobility of the lateral phenyl groups.

Although the rigidity of the molecule of a staircase polymer is great, it is completely terminal and close, for example, to the rigidity of the chains of the cellulose esters. At a molecular weight of about 100 000 the molecule is already a gaussian coil in several of its properties, that is, considerable rigidity appears. A comparison of the curves of Figs. 17 and 3 shows that for the fractions investigated the degree of intramolecular ordering Q lies in the range from 0.2 to 0.005, that is, considerably below the level of organisation of a smectic mesophase.

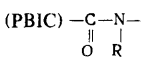
It should be noted that in the example of a staircase polymer we encounter a mechanism for chain rigidity which is greatly different from that for linear chain molecules without a secondary structure. Here the flexibility is due not to restricted rotation around valence bonds (or rotational isomerism) but to microdeformations of the macromolecular "lattice" in its thermal vibrations. However, local defects of the intramolecular lattice probably play some part in this. An illustration of this is provided by curve *2* of Fig. 17, which shows the relation $[n]/[\eta] = f(M)$ for the fractions of a specimen of cyclolinear polyphenylsiloxane obtained under somewhat different conditions than for specimen *1*. Although this polymer undoubtedly has a staircase structure, which appears in its hydrodynamic and optical properties, the presence of local defects in the structure of the molecule diminishes its rigidity and anisotropy to the values $A = 100$ Å and $\alpha_1 - \alpha_2 = -1060 \times 10^{-25}$ cm^3 respectively.

The rigidity of the molecule of a staircase polymer can be markedly decreased by the creation of "chemical" defects in its lattice, for example, by the introduction of single bonds into the molecular chain. Such partial "decyclisation" of the molecule leads to a partly staircase structure[89,90]. The poly-(*N*-isobutylmaleimide) considered above can evidently serve as an example of a "semistaircase" polymer.

The conformational properties of the molecules of other possible partial-staircase polymers have not been studied.

4. Molecules with Resonance Interaction in the Chain

The presence of additional intramolecular bonds (hydrogen or chemical), which "cyclise" the structure and thus ensure its rigidity is characteristic of all the above polymers with rigid chain molecules. Until comparatively recently it could have been thought that these structural properties are a necessary condition for the existence of semirigid chain molecules. However, the synthesis of polyisocyanates[91,92] and the study of the properties of their solutions[93-96] shows this to be incorrect. It was shown that the molecules of certain polyalkylisocyanates in solution have exceptionally high rigidity and ordering of the structure. The polybutyl isocyanate



where R = C_4H_9, was investigated in the most detail.

Solutions of this polymer in non-polar solvents are characterised by high values of the exponents α and β ($\alpha = 1.2$; $\beta = 0.85$) in the Mark–Kuhn equations (5)–(7).

To illustrate the great rigidity of the PBIC molecule, the viscosimetric results obtained for it can be treated[96] using the main formulae of the theory of viscosity of solutions of rigid ellipsoids:

$$[\eta] = \bar{v}\nu(p); \quad H^3 = 6p^3\bar{v}M/\pi N_A \,. \qquad (28)$$

where $p = H/d$; H and d are respectively the long and short axes of the ellipsoid modelling the molecule, $\bar{v}$ and M the partial specific volume and molecular weight of the polymer, and $\nu(p)$ the viscosity increment, a function of the asymmetry p of the ellipsoid, tabulated by Simha[1].

The values of $d = H/p$ and H/Z calculated by Eqn. (28) and the experimental values of $[\eta]$, $\bar{v}$, and M are shown in Fig. 18 as functions of the degree of polymerisation Z. The decrease in H/Z and the increase in d with increase in Z show the considerable flexibility of the chain and the departure of its form (with increase in Z) from rod-shaped. However, the limiting values of $H/Z = 2 \times 10^{-8}$ cm and $d = 11 \times 10^{-8}$ cm agree reasonably with the length and diameter of the monomeric unit of the molecular chain of PBIC.

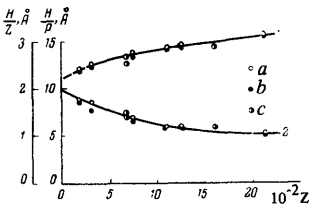


Figure 18. Variation of the quantity $H/p = d$ (*1*) and H/Z (*2*) with the degree of polymerisation Z for poly(butyl isocyanate) fractions in various solvents: *a*) benzene[93]; *b*) tetrahydrofuran[93]; *c*) benzene[96].

It follows from this analysis that in a range of molecular weights of a few tens of thousands (Fig. 18) the form of the PBIC molecule is close to a straight rod.

An analysis of the results on diffusion and sedimentation using the theory of wormlike chains—slope of the straight line *2* in Fig. 10, and Eqn. (12)—leads[96] to the enormous segment length A of 3000 Å, which surpasses even the segment length of the helical polypeptide molecules. The results on flow birefringence, which is very high and positive in solutions of polybutyl isocyanate, lead to similar conclusions.

The use of the microform effect, Eqn. (20), enables the segment length to be determined; the value obtained $A = 2600$ Å is close to the value found from hydrodynamic data. The anisotropy of the segment is great ($\alpha_1 - \alpha_2 = 9000 \times 10^{-25}$ cm^3) and its magnitude is close to the anisotropy of helical polypeptide molecules.

In PBIC solutions there is also an extremely large positive electrical birefringence[96], which shows the existence in the molecule not only of axial but also of polar orientation ordering.

The pronounced frequency dependence of the Kerr effect (Fig. 19) is also proof of high rigidity (both equilibrium and kinetic) and of the ordering of the structure; it can be

used for determining the orientation relaxation time and the geometric parameters of the molecule[96].

The effect of the saturation of the electrical birefringence observed in strong fields (Fig. 20) shows the high value of the molecular dipole and can be used for determining the dipole moment μ of the molecule[96]. The values obtained are close to the values of the dipole moments of the polypeptide molecules in the helical conformation. Similar results are obtained from a comparison of the dynamo-optical and electro-optical results[96].

The values of the dipole moments of the molecules μ obtained from measurements of the dielectric properties of the solutions[95] can also be used for determining the segment length. Having constructed a plot of μ^2/L against L, we obtain the curve of Fig. 21. In accordance with theory—Eqn. (26)—the initial slope gives the square of the dipole moment of unit length of the persistent chain $(\mu_S/A)^2$. The ratio of the asymptotic limit to the initial slope gives the segment length A. The value found by this method, A = 3000 Å, agrees with the value obtained from hydrodynamic results.

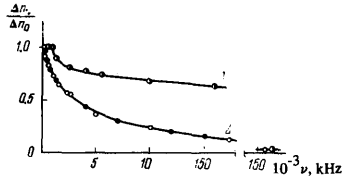


Figure 19. Variation of the relative value of the electric birefringence $\Delta n_\nu/\Delta n_0$ with the frequency ν for solutions of poly(butyl isocyanate) in tetrachloromethane: *1*) $M = 1.6 \times 10^5$; *2*) $M = 0.66 \times 10^5$.

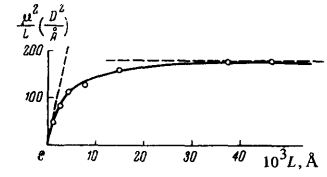


Figure 21. Variation of μ^2/L with L for poly(butyl isocyanate) in benzene.

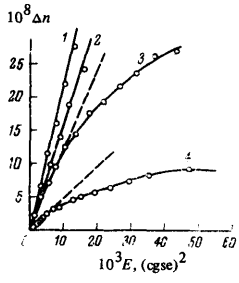


Figure 20. Variation of the electric birefringence with the square of the field strength E^2 for solutions of poly(butyl isocyanate) and poly(tolyl isocyanate) in bromoform (c = 1.77 g dl^{-1}); *3*) and *4*) poly(tolyl isocyanate) in tetrachloromethane (specimen 3; $M = 1.6 \times 10^5$, $c = 0.6 \times 10^{-3}$ g dl^{-1}); (specimen 4: $M = 0.66 \times 10^5$, $c = 0.7 \times 10^{-3}$ g dl^{-1}).

Table 4 summarises the molecular characteristics of PBIC. All these experimental results taken together show that the conformation of the PBIC molecule in weakly polar solvents corresponds to the wormlike chain model. The rigidity and ordering of its structure determined by various methods are very great and close to the rigidity and ordering of the molecules of synthetic polypeptides having an α-helical secondary structure. On taking into account the value found above for A and using Fig. 3 it is clear that for the fractions shown in Fig. 18 the value of Q lies in the range $0.4 \leq Q \leq 0.9$. Hence the PBIC molecules are crystal-like molecules with a very high degree of orientation order. Similar properties were observed in the polymers of other substituted alkyl isocyanates—polyhexyl isocyanate[94] and poly(chlorohexyl isocyanate)[96].

The chemical structure of the molecules of polyisocyanates are similar to the structure of polypeptide molecules, but the hydrogen atom in them is replaced by a side chain and the CHR group is absent from the main chain. The first feature (the absence of an N–H bond) rules out the possibility of the formation of a rigid α-helix conformation, since there are no intramolecular hydrogen bonds.

Table 4. Structural characteristics of molecules of some rigid-chain polymers.

Polymer	Mechanism of rigidity	10^{-5}M	$10^8 A$ cm	$10^{25}(a_1 - a_2)$ cm^3	$10^{23}(a_\parallel - a_\perp)$ cm^3	$10^{18}\mu$ cgse	Q
Polystyrene (for comparison)	restriction of rotation	1—100	20	—140	—18	—	$5 \cdot 10^{-3}$—$3 \cdot 10^{-5}$
Polybutylmaleimide	semistaircase structure	1.9—34	40	160	10	—	$8 \cdot 10^{-3}$—$4.4 \cdot 10^{-4}$
Polyphenylsiloxane	staircase structure						
Specimen 1		0.36—33.5	180	—1800	—25	—	$0{,}42$—$4.8 \cdot 10^{-3}$
Specimen 2		0.17—3.11	100	—1060	—25	—	$0{,}34$—0.02
Deoxyribonucleic acid	secondary helical structure	0.2—110	800	—40000	—200	—	$0{,}41$—$8.5 \cdot 10^{-3}$
Poly-γ-benzyl-*L*-glutamate	secondary helical structure	0.4—3.4	2400	20000	17	150—370	0.88—0.41
Poly(butyl isocyanate)	resonance interaction of the chain	0.2—2.0	3000	9000	7	253—2900	0.89—0.40
Phenylmethacrylic ester of cetyloxybenzoic acid	interaction in side-chains	18	65	—2700	—100	30	$3.1 \cdot 10^{-3}$
Graft copolymer of styrene and methyl methacrylate	interaction in side-chains	2.0—50	100	750		—	0.12—$0.48 \cdot 10^{-3}$

The second feature can have a decisive importance in the stabilisation of the rigidity of the molecular chain. Actually, since the peptide bonds in the polyisocyanate molecule are not separated by CHR groups, the coplanarity of all the bonds inside one peptide group (–CO–NR–) can be extended to each neighbouring pair of peptide groups, ensuring a rigid conformation of the whole chain. Here the resonance interaction of each nitrogen atom is extended to both carbonyl groups adjacent to it, giving the C–N bonds the rigidity of conjugated bonds[94].

Of the two possible planar structures of the chain (Fig. 22) the more probable is the *cis*-form, since it alone ensures the presence of a molecular dipole moment parallel to the axis of the molecule, and, corresponding to this, the agreement of the signs of the electrical and dynamic birefringences[96].

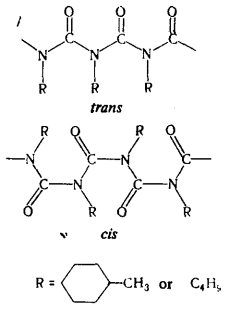


Figure 22. *trans*- and *cis*-conformations of polyisocyanate chains.

Hence poly(alkyl isocyanates) are unique instances when the exceptionally high rigidity of the conformation and the high degree of intramolecular ordering of the chain molecule are due not to the secondary structure but to the true skeletal rigidity of its single-track chain.

In addition to giving rise to these properties the structure of the side-radical at the nitrogen atom plays an important part. Thus replacing an aliphatic by an aromatic radical (tolyl isocyanate)[96] leads to the breakdown of the unique structure of the molecule. The reason for this can be sought both in the weakening of the resonance interaction in the nitrogen–carbonyl system owing to the effect of conjugated bonds of the aromatic ring and in the steric repulsion of neighbouring tolyl side-groups.

5. Molecules with Chain Side-radicals

The effect of the size and structure of the side-groups on the conformation of the polymeric molecules and the rigidity of their main chains has been studied repeatedly. Although in principle such an influence should occur the effects observable experimentally always appear insignificant[1].

Some new information about this problem was obtained recently in connection with the study of the conformational and optical properties of chain molecules having a "comb-shaped" structure. The latter is inherent to molecules with sufficiently long (linear) side-radicals or can be obtained by the grafting of one chain polymer on to another. However, in every instance the side-groups should be much shorter than the main chain.

A new approach to the study of the conformations of such molecules consists in the application of the theory of persistent anisotropy to the optical properties of the side-groups and in the calculation of their optical anisotropy in the axes of their primary element[38,44].

On drawing a tangent to the initial element of the persistent chain of length L and denoting the polarisability of the chain in the directions parallel and perpendicular to it by $\gamma_{\parallel}$ and $\gamma_{\perp}$ respectively, then for the difference $(\gamma_{\parallel} - \gamma_{\perp})_L$ the theory gives

$$(\gamma_{\parallel} - \gamma_{\perp})_L = \frac{1}{3} a\beta_0 (1 - e^{-3x}) = a\beta_0 x \left(1 - \frac{3}{2}x + \frac{3}{2}x^2 - \right.$$
$$\left. - \frac{9}{8}x^3 + \frac{27}{40}x^4 - \frac{27}{80}x^5 + \ldots\right). \quad (29)$$

The symbols in Eqn. (29) agree with those used in Eqn. (21).

The dependence of the ratio $(\gamma_{\parallel} - \gamma_{\perp})_L / a\beta_0$ on the parameter x is shown in curve *3* of Fig. 2. The initial slope and asymptotic limit of the curve are respectively 1 and 1/3.

A comparison of curves *3* and *1* of Fig. 2 shows that the anisotropy of the gaussian chain (at $x \to \infty$), calculated using the axes of its primary element is 5/18 of the anisotropy calculated using the axes of vector h.

The application of Eqn. (29) to the anisotropy of the side-chain of the comb-shaped molecules shows that the contribution Δb_L introduced by the side radical to the anisotropy of the monomeric unit of the molecule is:

$$\Delta b_L = -S^* \cdot \Delta a (1 - e^{-6n/S^*})/12 \quad (30)$$

where n and S^* are the numbers of valence bonds in the side-chain and in its segment respectively, Δa the anisotropy of the part of the side-chain containing one valence bond.

Hence from the contribution made by the side-chain groups to the anisotropy of the whole molecule the anisotropy and flexibility of these groups can be studied by the above method.

a. Poly-α-alkenes $-\overset{R}{\underset{|}{C}}H-CH_2-$ $(R = C_nH_{2n+1})$

tematic experimental results on the dependence of the anisotropy of molecules on the number n of methylene groups in its side-radicals have been obtained for a number of poly-alkenes[97]. It was shown that in several poly-α-alkenes the lengthening of the side-group is accompanied by a monotonic rise in the negative anisotropy of the segment of the molecule $\alpha_1 - \alpha_2$. This increase can be caused both by increase in rigidity of the main-chain (an increase in A or S) and also by an increase in the negative contribution introduced into the anisotropy of the monomeric unit of the molecule by its side-group with lengthening of the latter.

If the change in the rigidity of the main-chain in the lengthening of the side-group is neglected (which is true only for the lower homologues of the series), then the experimentally obtained dependence can be represented in the form $\Delta b_L = 2.73 \times 10^{-25} n$ cm^3. On the other hand if it is assumed that the flexibility of the lateral hydrocarbon chain of the molecule of the poly-alkene equals the flexibility of the polyethylene chain, then assuming that $S^* = 16$,[1] from Eqn. (30) we obtain the theoretical relation $\Delta b_L = -7.3 \times 10^{-25}(1 - e^{-3n/8})$. Both relations are shown in Fig. 23.

The theoretical curve shows that owing to the flexibility of the side-chain with increase in its length (that is, n) the anisotropy of Δb_L should reach an asymptotic limit determinable from the degree of flexibility of the side-groups.

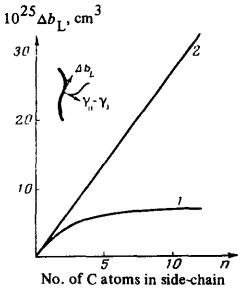
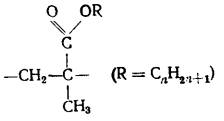


Figure 23. Contribution Δb_L introduced by the side-group to the anisotropy of the monomeric unit of a poly-α-alkene molecule as a function of the number (n) of carbon atoms in the side-chain. *1*) Theory of non-interacting chains with a flexibility equal to the flexibility of a polyethylene chain $\Delta b_L = 7.3 \times 10^{-25}(1 - e^{-3/8n})$ as follows from Eqn. (30); *2*) $\Delta b_L = 2.73 \times 10^{-25} n$ (see experimental results of Ref. 3).

However, in the range of values of n studied the experimental relation shows no tendency to saturation. This shows that the rigidity and orientation ordering of the side-groups of poly-α-alkenes greatly exceed the values which can be obtained from the experimental investigation of the conformational and optical properties of the individual hydrocarbon chains in the solution.

b. Poly(alkyl methacrylates).



A study of the conformation and optical anisotropy of the molecules of several poly(alkyl methacrylates) leads to similar conclusions[28]. Unlike the poly-α-alkenes, in addition to optical data results for this series were also obtained about the statistical dimensions and rigidity of the main-chain[28,98,99]. Consideration of these results can include more quantitative results than in the previous instance.

The experimental results on the rigidity of the main-chain and the anisotropy of the molecules of the poly(alkyl methacrylates) are given in Table 5. Up to $n = 8$ the length of the side-group has little effect on the rigidity of the main chain (the number of monomers S in its segment is close to 7–8). With a further growth of the side-chain the rigidity of the main chain increases considerably and at $n = 16$ is already twice that of molecules of the usual flexible chain polymers. This increase must evidently be regarded as the result of the interaction of long side-radicals of the molecule.

A much steeper expression of the increase in the negative anisotropy of the molecular segment $\alpha_1 - \alpha_2$ occurs with lengthening of the side-groups. Fig. 24 gives corresponding experimental values of the anisotropy of the monomeric unit of the molecule $a_\parallel - a_\perp$ as a function of the number $Z = n + 2$. The points lie satisfactorily along the theoretical curve (30) (where n is replaced by Z) under the condition $S^* = 60$ (continuous line). The broken line shows the theoretical relation corresponding to $S^* = 16$, that is, under the condition that the flexibility of the side-chain equals the flexibility of a polyethylene chain.

Table 5. Number of monomeric units S in the segment, segment anisotropy $\alpha_1 - \alpha_2$, and anisotropy of the monomeric unit $a_\parallel - a_\perp$ of the molecules of some esters of poly(methacrylic acid). n is the number of carbon atoms in the alkyl side-chain of the molecule.

Polymer	n	S	$10^{25}(\alpha_1 - \alpha_2)$ cm^3	$10^{25}(a_\parallel - a_\perp)$ cm^3
Poly(methyl methacrylate)	1	7.0	−2	−0.2
Poly(butyl methacrylate)	4	6.7	−14	−2.1
Poly(hexyl methacrylate)	6	8.6	−40	−4.6
Poly(octyl methacrylate)	8	7.9	−47	−5.9
Poly(cetyl methacrylate)	16	19	−170	−8.9
Poly(phenylmethacrylic ester of cetyloxybenzoic acid)	16	26	−2500	−100

Hence the rigidity of the side-chains of poly(alkyl methacrylates), in the range n investigated (up to $n = 16$) is four times the rigidity of chain vinyl polymers of similar structure. This result shows the presence of significant orientation ordering in the side-chains of the macromolecules, considerably surpassing the conformational ordering of the ordinary gaussian chains. The reason for this ordering is evidently to be sought in the interaction of regularly constructed alkyl radicals, which leads to the formation of an intramolecular structure with a short-range orientation order in the positions of the side-chains. This effect is all the greater the longer the side-chains, just as lengthening assists the crystallisation of the polymer in bulk.

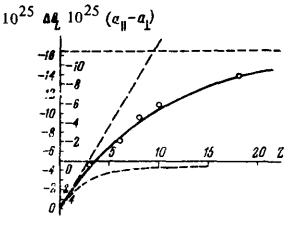


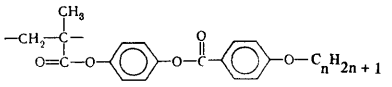
Figure 24. Variation of the anisotropy of the monomeric unit of the alkyl esters of poly(methacrylic acid) with the number of valence bonds $Z = n + 2$ in the side-chain. Continuous curve: theoretical relation according to Eqn. (30) at $\Delta a = 3.3 \times 10^{-25}$ cm^3 and $S^* = 60$. The broken curve is obtained from the equation at $\Delta a = 3.3 \times 10^{-25}$ cm^3 and $S^* = 16$.

A natural consequence of this effect is also a decrease in the flexibility of the main-chain.

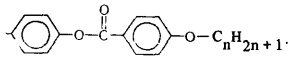
c. Polyphenyl methacrylic esters of alkyloxybenzoic acids. Convincing proof that the observable increase in the orientation order both in the main- (increase in S) and in the side- (increase in $a_\parallel - a_\perp$) chains

is the consequence of the interaction of the side-groups is given by the conformation properties of the polyphenyl methacrylic ester of alkyloxybenzoic acids (PPMEAOBA).[100]

These polymers, which have a structure of the form:



can be regarded also as esters of polymethacrylic acid where the hydrogen in the side-group is replaced by the radical:



Hence the main-chains of these macromolecules do not differ from those examined above and the lateral substituents are distinguished by the presence of groups instrumental in the formation of a liquid-crystal phase, that is, a state with a clearly expressed orientation ordering[101].

The structural characteristics of macromolecules of one of these polymers—polyphenylmethacrylic ester of cetoxybenzoic acid (PPMECOBA) ($n = 16$ in the C_nH_{2n+1} group) are given in Tables 4 and 5.

The presence of strongly interacting side-groups increases the rigidity of the main-chain of the polymer ($S = 25$). However, its optical properties are completely unique. The negative segment anisotropy of the molecule is more than an order of magnitude greater than the anisotropy of poly(cetyl methacrylate) and comparable only with the anisotropy of "crystal-like" molecules—polyisocyanate or poly-γ-benzyl-L-glutamate and the anisotropy of the monomer $a_{\parallel} - a_{\perp}$ is even appreciably greater than the anisotropy of the monomeric unit of these molecules. The last fact shows that the extremely high anisotropy of the molecule is due not so much to the rigidity of its main-chain (which is much less than for crystal-like molecules) as to the extremely perfect orientation order in its side-groups.

It is also remarkable that this order is not only axial but also polar—solutions of PPMECOBA give a high negative birefringence in an electric field. The use of these experimental results and Eqns. (18) and (24) gives a value of $\mu = 30 \times 10^{-18}$ cgse for the component of the dipole moment along the axis of the molecule. Significantly, these unique properties are combined with properties characteristic for flexible chain polymers: unlike the crystal-like molecules the dimensions of the PPMECOBA molecule are sensitive to the thermodynamic nature of the solvent and can change markedly as the latter is changed. All these facts show that in PPMECOBA molecules there is orientation ordering of a mesomorphic type, in which the side-chains of the molecule form a mobile liquid-crystalline structure.

d. Graft copolymers. Similar, although less perfect, structures are evidently formed in other macromolecules of the comblike type—graft polymers. They have quite specific optical properties, demonstrated by the example of graft polymers of styrene and alkyl methacrylates[38,102,103].

The optical anisotropy of the molecules of a graft copolymer can be many times greater than the anisotropy of the graft homopolymers. It is positive, that is, opposite in sign to the negative anisotropy of the chain of graft polystyrene, although the mass of the polystyrene in the graft copolymer exceeds 90%.

An analysis of these experimental results together with the hydrodynamic properties of the molecules [see Eqns. (11), (12), and 30)] enables the rigidity of both the main chain of the copolymer and also the chains of the graft copolymers to be determined[38]. Here the observable properties can be explained not only qualitatively but also quantitatively by the existence in the graft polymer of an intramolecular structure with a high degree of orientation order.

It is characteristic that despite the high rigidity of the main-chain of the graft polymer ($A = 100$–200 Å) the exponent in the M–K equations (5)–(7) for this polymer are close to the values $\alpha = \beta = 0.5$. This fact is explained by the high value of the diameter d of the wormlike chain, modelling the graft polymer molecule, in complete agreement with theory, Eqns. (11) and (12).

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The facts considered above show that the structural features of macromolecules leading to the appearance in them of properties characteristic for "semirigid" chains can be extremely varied (see Table 4).

Apart from the true skeletal rigidity of the single-track chain—poly(alkyl isocyanates)—additional interactions of quite different origins are possible in the molecules; however, these can be classified as "short-range actions". These interactions lead to increased rigidity of the molecular conformation. They include both purely chemical and also hydrogen bonds, leading to the formation of regular rings in the chain (staircase and partly staircase polymers, derivatives of polysaccharides, secondary helical structures of polypeptides and polynucleotides).

Furthermore, the rigidity and ordering of the conformation can be considerably increased by van der Waals interaction of the side-radicals and electrostatic repulsion of the ionogenic groups of the chain[74,105,106].

There is no doubt that the list of molecular structures which can be classified as semirigid is not limited to the examples considered above. However, in selecting the subjects for discussion we considered only those examples in which the morphological properties of the molecule have been investigated quantitatively and in sufficient detail for forming a definite opinion.

From these examples clearly the semirigid molecules cannot be regarded as a class of polymer with a definite chemical structure. This terminology should rather be applied to all the group of structures which exhibit a certain combination of physicochemical properties, which has been discussed above.

The most characteristic of these properties are a high degree of intramolecular ordering and a high value for the persistence length of the wormlike chain modelling the macromolecule.

In the range of low and moderate molecular weights these properties appear as a departure from the regularities characteristic for gaussian chains—in a specific dependence on the molecular weight of such parameters as the radius of gyration of the molecule, their optical anisotropy and dipole moments. The hydrodynamic behaviour of the semirigid chains corresponds to the conformation of a slightly bent rod.

In the range of high molecular weights the semirigid chains are already gaussian, but for these large radii of gyration, segment anisotropy (proper and microform) and dipole moments are characteristic. Considerable flow capability of the molecules is a characteristic of the hydrodynamic behaviour (when the chain diameter is not too large).

The combination of all these parameters (or some of them) can be used for the experimental observation and as a quantitative characteristic of equilibrium rigidity and the ordering of the structure of the molecular chain.

Hence we consider that the above information can be useful in two respects. Firstly, it contains various examples of those structural features of a polymer which can be responsible for its molecule having properties characteristic for semirigid chains. Secondly, it shows that the hydrodynamic, dynamo-optical, and electro-optical properties of chain molecules in solutions are reliable criteria for a quantitative appraisal of their rigidity and the internal degree of order of the structure.

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