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CONFORMATION AND PHYSICAL PROPERTIES OF SEMI-RIGID CHAIN MOLECULES IN SOLUTION*

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1. INTRODUCTION

IT IS known that the characteristic property of the chain molecules of polymers is their flexibility, i.e. their ability to change conformation under the action of thermal motion or of deforming forces.

It is this property that accounts for the rubber-like behaviour of high molecular weight elastomers at temperatures higher than their glass transition point.

In solutions these flexible chain molecules have the conformation of a statistical coil which, in the θ condition, can be regarded as the "Gaussian" coil.

The solution properties of flexible chain molecules have been thoroughly investigated by many scientists and have been described elsewhere.(1, 2)

In recent years in connection with the development of syntheses of polymers suitable for manufacturing fibres, films and other special materials having high strength and thermal stability, the necessity of studying the morphological and conformational properties of macromolecules becomes more and more pressing.

Taking into consideration the chemical composition of these molecules, one may expect that many of them although having a chain structure should possess limited flexibility and so occupy an intermediate position between absolutely rigid submicroscopic particles (as, for example, viruses or globular proteins) and ideally flexible chain molecules of most synthetic polymers.

Molecules of cellulose derivatives and also those of polypeptides and nucleic acids in helical conformation may be considered as a classical example of such "semi-rigid" chain molecules.

Up to comparatively recently, our practical knowledge about stiff-chain molecules was limited to these examples.

Nevertheless during recent years various investigators have synthetized new polymers the molecules of which have exhibited properties characteristic of semi-rigid chain molecules.

The present paper is concerned with the problem as to what extent hydrodynamic and optical behaviour of chain molecules in solutions may be used for detection and quantitative characterization of their rigidity and internal order of their structure.

General theoretical conclusions are illustrated by experimental data obtained in investigating some polymers with molecules having stiff-chain structure.

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* Main lecture.

2. GENERAL THEORETICAL CONSIDERATION

(*a*) *Hydrodynamic properties*

As we know, the length of statistical segment A (Kuhn(3)) or the persistence length of the chain $a = A/2$ (Porod(4)) can serve as a quantitative measure of the equilibrium rigidity of the molecular chain.

One of the commonest methods of determining the rigidity of chain molecules on the basis of their hydrodynamic solution properties is to use the dependence of the sedimentation $[S]$ and diffusion $[D]$ coefficients and intrinsic viscosity $[\eta]$ on the molecular weight M.

The simplest method of representing these dependencies is in the form of empirical expressions of Mark–Kuhn (M–K):

$$[\eta] = K_\eta \cdot M^\alpha \tag{1}$$

$$D = K_D \cdot M^{-\beta} \tag{2}$$

$$[S] = K_S \cdot M^{1-\beta}. \tag{3}$$

When the measurements are performed in θ solutions, i.e. without the excluded-volume effect, high α and β values show a considerable influence of the draining effect, in other words they indicate that the molecular coil has a "loose" structure. Therefore these high α and β values may serve as an indication of high rigidity of the molecular chain.

Nevertheless the volume effects in nonideal solvents cause osmotic coil expansion and a corresponding increase in the α and β values, i.e. they act in the same direction as the increased chain rigidity. Hence, in order to find true ("skeletal") rigidity of the molecular chain the excluded-volume effect should be eliminated.

In the case of flexible-chain polymers whose molecules are comparatively compact coils even in thermodynamically good solvents, the hydrodynamic interaction within the coil is very great and draining effects are negligible. For these molecules, the excluded-volume effects may be eliminated by extrapolation of hydrodynamic properties to the region of low molecular weights on the basis of the theory of these effects.(5, 6)

For this purpose one may apply Eqn. (4) to viscometric data.(7)

$$[\eta]/\mathrm{M}^{\frac{1}{2}} = (LA/\mathrm{M})^{\frac{3}{2}}\phi + 0{\cdot}51\phi B\mathrm{M}^{\frac{1}{2}}. \tag{4}$$

When sedimentation or diffusion data are used, one can apply Eqn. (5):(8)

$$(D\mathrm{M}^{\frac{1}{2}})^{-1} \equiv (1 - \bar{v}\rho)\mathrm{M}^{\frac{1}{2}}/[s]RT = (\eta_0 P/kT)[(LA/\mathrm{M})^{\frac{1}{2}} + 0{\cdot}2B\mathrm{M}^{\frac{1}{2}}] \tag{5}$$

or (6)(9)

$$(D\mathrm{M}^{\frac{1}{2}})^{-3} = (\eta_0 P/kT)^3[(LA/\mathrm{M})^{\frac{3}{2}} + 0{\cdot}51B\mathrm{M}^{\frac{1}{2}}] \tag{6}$$

where $\phi = 2{\cdot}8 \times 10^{23}$ cgs, $P = 5{\cdot}11$, B is the parameter of thermodynamic polymer–solvent interaction, η_0 is the solvent viscosity, L is the contour length of the molecular chain.

If the left part of Eqns. (4), (5) or (6) is plotted as a function of the square root of M, the intercept on the ordinate permits an estimate of the unperturbed dimensions of the molecular chain and its rigidity determined by the A value.

Nevertheless, this method is not applicable to rigid-chain polymers since usually (though not always) the draining effect plays an important part for these polymers.

It is fortunate that in many cases the excluded-volume effect for rigid-chain molecules is not very important even in thermodynamically good solvents and, to a first approximation, it can be considered negligible. In these conditions one can use the theory of hydrodynamic properties of worm-like chains worked out by Kuhn,(10) Stockmayer and Hearst(11) (K–S) for determining the chain rigidity. In the range of comparatively high molecular weights, when the molecule can be considered as a Gaussian chain, the K–S theory gives the equations:

$$M/[\eta] = \phi^{-1}\{(\mathrm{M}/LA)^{\frac{3}{2}}\mathrm{M}^{\frac{1}{2}} + 0{\cdot}93[\ln(A/d) - 1{\cdot}43](\mathrm{M}/L)^2A^{-1}\} \tag{7}$$

$$D\mathrm{M}/RT = (1{\cdot}843/3\pi\eta_0N_A)(\mathrm{M}/LA)^{\frac{1}{2}}\mathrm{M}^{\frac{1}{2}} + (3\pi\eta_0N_A)^{-1}(\mathrm{M}/L)[\ln(A/d) - 1{\cdot}43]. \tag{8}$$

Apart from the L and A values characterizing the conformation and the rigidity of the chain, Eqns. (7) and (8) contain the diameter "d" of a worm-like model. "d" should be taken into consideration in order to describe correctly the hydrodynamic properties of the chain.

When we plot the left part of Eqn. (7) or (8) as a function of $\mathrm{M}^{1/2}$, the slope of the curve gives M/LA, i.e. the rigidity of the chain. The intercept on the ordinate enables us to determine A/d and, hence, the chain diameter d.

Equations (7) and (8) give a well known result that in the region of very high molecular weights, when the first term of the right part (depending on M) is much higher than the second one, the dependence of diffusion and viscosity on the molecular weight corresponds to the M–K Eqns. (1)–(3) with $\alpha = \beta = 0{\cdot}5$. However, one should bear in mind that in nonideal solvents the relative importance of excluded-volume effects increases with M and hence α and β values become higher than $0{\cdot}5$. Evidently, this effect is observed in solutions of high molecular weight deoxyribonucleic acid.(12, 13)

If M is not too high and the chain is rather rigid, the second term in the right part of Eqns. (7) and (8) becomes relatively more important and this corresponds to an increase in α in Eqn. (1) up to values close to unity (cellulose derivatives, DNA).

Finally, for very rigid chain molecules in the region of low molecular weights, when the chain length L is much greater than d (a slightly bending thin rod), theory(11) gives the expression:

$$[\eta] = 2\pi N_AL^2[45(\mathrm{M}/L)(\ln(A/d) - 1{\cdot}03)]^{-1}[1 - f(L/A)]. \tag{9}$$

It follows from this that the α exponent in Eqn. (1) lies in the region between 1 and 2. This case actually occurs, for example for polypeptide molecules in helical conformation.(14)

Thus, for the above-mentioned well-known rigid-chain polymers high values of α in Eqn. (1) were obtained.

Nevertheless, this fact should by no means be regarded as a general rule, since for Gaussian chains the values of α and β are determined by intramolecular hydrodynamic interaction which depends not only on the degree of coiling (L/A) of the chain but also on its diameter d.

Thus, it follows from Eqns. (7) and (8) that if the molecular chain's diameter d is comparable with the segment length A (e.g., $A = 4d$, $\ln(A/d) = 1{\cdot}43$), the values of

α and β in Eqns. (1)–(3) will be close to 0·5, independent of the rigidity of the chain. This situation occurs, for example, for oligomers with flexible chain molecules.(15–18) As will be shown below, this can also occur for some rigid-chain polymers having very long A segment.

It follows from the above that both the viscosity and the translational friction values and their dependence on the molecular weight can be very different depending upon the main parameters of the chain, viz. it diameter, contour length and segment length as well as upon its thermodynamic interaction with the solvent.

Hence, in some cases it is not sufficient to use only hydrodynamic properties in order to determine the rigidity, conformation and internal structure of macromolecules. The information obtained is much more complete if the investigation of hydrodynamic properties of solutions is supplemented by the investigation of their dynamo-optical and electro-optical properties.

(*b*) *Dynamo-optical properties of chain molecules*(19)

The segment length A or the persistence length a being a measure of the equilibrium rigidity of the main chain also reflects to a certain degree another important property: the orientational order within the molecule.

Nevertheless, optical anisotropy is a more direct and much more sensitive measure of the orientational order of the molecular structure.

The optical anisotropy of the chain molecule is measured by the difference $\gamma_1 - \gamma_2$ of its two principal polarizabilities γ_1 and γ_2 in the directions parallel to the vector h (connecting the two ends of the chain) and normal to it, respectively.

For the simplest model of the Gaussian chain,(3, 10) the optical anisotropy of the molecule $\gamma_1 - \gamma_2$ in equilibrium conformation does not depend on its contour length L, i.e. on its molecular weight, and is near to the anisotropy of the segment $\alpha_1 - \alpha_2$:

$$\gamma_1 - \gamma_2 = \tfrac{3}{5}(\alpha_1 - \alpha_2). \tag{10}$$

The difference in the polarizabilities of the segment $\alpha_1 - \alpha_2$ depends on the anisotropy of the monomer unit $\mathrm{a}_{\parallel} - \mathrm{a}_{\perp}$ and on the number of the monomer units S making up the segment

$$\alpha_1 - \alpha_2 = S(\mathrm{a}_{\parallel} - \mathrm{a}_{\perp}). \tag{11}$$

Hence, molecules with a high rigidity (i.e. having high S) are characterized by a high optical anisotropy.

On the other hand, it was shown that the expansion of the molecules in good solvents greatly changing their size and hydrodynamic properties practically does not influence their optical anisotropy.(33) Hence, the anisotropy may serve as a measure of the true skeletal rigidity of the molecular chain independent of the effects of the excluded volume, i.e. of the thermodynamic interaction of the molecule with the solvent.

It is very important that the anisotropy of the monomer unit $\mathrm{a}_{\parallel} - \mathrm{a}_{\perp}$ and, hence, the anisotropy of the molecule, may be either positive or negative depending on the degree and the character of the ordering of the valence bonds of the monomer unit with respect to the direction of the main chain.

Consequently, the optical anisotropy is a measure of the axial orientational order of the structural elements of the main chain and of its side groups.

The anisotropy of the molecule described by the Gaussian chain may be determined by measuring flow birefringence Δn in the solution of the polymer investigated and by calculation from the formula:

$$\Delta n/\Delta\tau \equiv \Delta n/g(\eta - \eta_0) = [n]/[\eta] = [4\pi(n^2 + 2)^2/45kTn](\alpha_1 - \alpha_2) \tag{12}$$

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

If the refractive index increment dn/dc in the polymer–solvent system is not equal to zero, an additional anisotropy of the molecule appears due to the optical interaction of the fragments of the chain; it is the "form effect".$^{(19)}$

The molecule with a high skeletal rigidity is characterized by the anisotropy connected with the interaction of the nearest neighbours in the chain or the anisotropy of "microform". Its value is proportional to the molecular weight of the segment $M_s = A(M/L)$ and to the square of the refractive index increment $(dn/dc)^2$

$$(\gamma_1 - \gamma_2)_{fs} = 3(M/L)(10\pi N_A\bar{v})^{-1}A\left(\frac{dn}{dc}\right)^2. \tag{13}$$

Consequently, for rigid-chain molecules the experimental measurement of the micro form effect is an independent method of determining the skeletal rigidity of the molecular chain.

If the contour length L of the chain molecule is not very great in comparison with the segment length A (i.e. the condition $h \ll L$ is not fulfilled), it cannot be regarded as a Gaussian chain and the Kuhn formula$^{(10)}$ cannot be applied to it.

In this case the difference between the main polarizabilities of the molecule having length L is calculated from the theory of persistent anisotropy$^{(20)}$ which leads to the relationship

$$(\gamma_1 - \gamma_2)_L = \tfrac{3}{5}(\alpha_1 - \alpha_2)(1 - e^{-5x/6}) \tag{14}$$

where $x = L/a = 2L/A$.

In contrast to the Gaussian chains, the anisotropy of the persistent chain grows with an increase in its length L (and, hence, its molecular weight) and tends (as $x \to \infty$) to the limiting value $\tfrac{3}{5}$ $(\alpha_1 - \alpha_2)$ corresponding to the anisotropy of the Gaussian chain (curve 1, Fig. 1).

In accordance with it, in contrast to the Gaussian coils [Eqn. (12)], the reduced

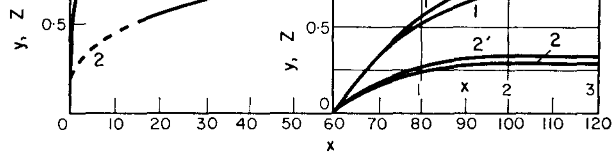


FIG. 1. Anisotropy of persistent chain and flow birefringence as functions of the parameter $x = L/a$. Curve 1—anisotropy of the persistent chain $Z(x) \equiv (\gamma_1 - \gamma_2)_L/(\gamma_1 - \gamma_2)_\infty$ 1′—the same according to theory,$^{(20)}$ curve 2—y (x) orientational birefringence of kinetically rigid chains; 2′—the same according to theory,$^{(20)}$ 3—orientational–deformational birefringence of kinetically flexible chains.

flow birefringence $[n]/[\eta]$ of the persistent chains solution should increase with their molecular weight curve 2 and 3, Fig. 1).

One should bear in mind that according to theory [Eqn. (14)] a decrease in the molecular anisotropy with a decrease in the chain length in contrast to hydrodynamic properties is determined only by the parameter $x = L/a$ and not by the absolute value of the segment length A. Hence, this phenomenon should occur not only for rigid chain molecules but also for flexible ones in the region of comparatively low molecular weights (oligomers). Actually, a decrease of anisotropy in flow with molecular weight was experimentally found in oligomers with flexible chain molecules(18) though their hydrodynamic behaviour had no peculiarities.

This phenomenon is of particular importance for rigid-chain molecules (high A) since in this case it should be observed in the region of comparatively high molecular weights and can serve as direct evidence of high skeletal rigidity of the chain. Reduced flow birefringence for rigid worm-like chains ($A \gg d$) in the region $x < 3$ is governed by the equation:

$$[n]/[\eta] = (4\pi/45nkT)(n^2 + 2)^2 \cdot (\gamma_1 - \gamma_2)_L \cdot F(x). \tag{15}$$

Here $F(x)$ is the tabulated(20) function reflecting a change in the geometric asymmetry of the molecule with an increase in its length.

A comparison of the experimental dependence of birefringence on molecular weight with the theoretical one (15) enables us to determine the persistence length $a = A/2$ of the molecular chain.

These peculiarities of the optical properties of rigid-chain molecules predicted by theory are independent both of the effects of the excluded volume and of the hydrodynamic interaction in the molecular chain. Hence, the use of these properties for characterizing the rigidity and the ordering of the structure of the molecule is not complicated by the necessity to take into account the thermodynamic quality of the solvent and the draining effect.

(*c*) *Electro-optical properties*

In studying the order of the macromolecular structure, one should distinguish between the orientational axial order and the orientational dipole one. Many chain molecules contain polar groups or bonds, and if the mutual orientations of these groups has a coaxial order, the macromolecule should have a high total dipole moment. Nevertheless, it usually does not occur for flexible-chain molecules. One of the reasons for this may be mutual compensation of the local group moments under their vector addition. But the main reason is the softness of the molecular structure. Because of this, the local polar groups of the molecule in the external electrical field are oriented practically independently of each other. In this case the dipolar polarization of the molecule in the electrical field is simply equal to the sum of polarizations of its polar units and practically does not differ from that of a liquid monomer of equal mass.

In the case of rigid-chain molecules, the situation may be very different. Owing to the hardness of the molecular structure, the orientations of the polar groups of the molecule in the electrical field are not independent of each other but are to a larger or smaller extent mutually correlated along the molecular chain or its segments. Consequently, if the vector sum of the local group moments is not zero, (i.e. if inside the molecule they have a polar orientational order), then the molecule may have a considerable dipole moment and may rotate as a rigid particle under the influence of the electrical field.

In solutions of such polar rigid-chain molecules in the electrical field E, a high birefringence (Kerr effect) appears. The value Δn and the sign of birefringence depend on the value and the sign of the optical anisotropy of the molecule $\gamma_1 - \gamma_2$, as well as on the value of its dipole moment μ and the angle ϑ formed by the axis of the dipole and the optical axis of the molecule.(21)

$$(\Delta n/cE^2) \underset{\substack{c\to 0\\ E\to 0}}{=} \frac{\pi N_A}{15n}\left(\frac{n^2+2}{3}\right)^2\left(\frac{\epsilon+2}{3}\right)^2\frac{\gamma_1-\gamma_2}{\mathrm{M}}\left(\frac{\mu}{kT}\right)^2(3\cos^2\vartheta - 1) \tag{16}$$

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

Experimental investigation of this effect and the comparison of results with data on flow birefringence enabled one to obtain information on the value and direction of the molecular dipole and to draw supplementary conclusions on the conformation, rigidity and ordering of the structure of the molecule.

Modelling the semi-rigid molecule by a persistent chain, one can connect(4, 22) the value of its dipole moment μ with the contour length $L = ax$ of the chain by the theoretical relationship

$$\overline{\mu^2} = (\mu_0 S)^2(x - 1 + e^{-x})/2 \tag{17}$$

or

$$\overline{\mu^2}/L = (\mu_s^2/A)[1 - (1 - e^{-x})/x] \tag{18}$$

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

Experimental investigation of the dependence of the dipole moment on the molecular weight M and comparison of this dependence with the theoretical one [Eqns. (17) and (18)] permits determination of the persistence length of the chain a and thus to evaluate the rigidity of the molecule on the basis of electro-optical data.

Solutions of rigid-chain polar molecules in the alternating electrical field reveal the frequency dependence of the Kerr effect which indicates that the relaxation phenomena take place in the process of the dipole orientation. The investigation of the frequency dependence permits us to determine the rotational mobility of the molecules and to obtain additional data on their conformation and rigidity.

3. SOME EXPERIMENTAL RESULTS

(*a*) *Molecules with secondary structure*

(*i*) *Deoxyribonucleic acid* (*DNA*). DNA may be regarded as a classical example of a polymer with semi-rigid chain molecules. The generally accepted model of the molecule is the rigid double helical structure of Krick and Watson(23) supported by hydrogen bonds which bind purine and pyrimidine bases of the DNA chains.

The application of the hydrodynamic theory of worm-like chain to experimental data on sedimentation [Eqn. (8)] gives the value of the segment length A = 700–900 Å.(11–13) This is 3–4 times higher than the value obtained for cellulose derivatives.(1)

The optical anisotropy of the DNA molecules found from flow birefringence is very high and negative in sign. This corresponds to a high degree of orientational order of the bases whose planes are perpendicular to the axis of the molecule.

Optical anisotropy increases with the molecular weight of DNA(24) in agreement with the persistent chains theory(20) (Fig. 2). A comparison of the experimental and the theoretical curve [Eqn. (15)] gives $A = 600$ Å.(24)

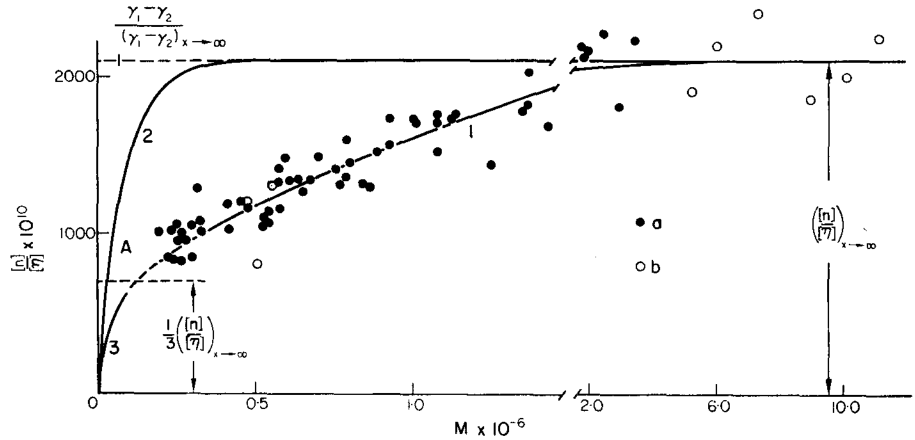
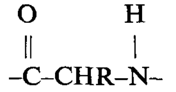


FIG. 2. Flow birefringence $[n]/[\eta]$ and optical anisotropy of the DNA molecules as a function of molecular weight M 1—curve $[n]/[\eta] = f(M)$ plotted from experimental points: (*a*)—DNA fragments are obtained by treating the solutions with DNA'ase. (*b*)—fragments are obtained by ultrasonic destruction, 2—curve of relative anisotropy of the molecule as a function of $x = L/a$; 3—initial portion of the theoretical curve.(20)

(*ii*) *Polypeptides*



$$-\overset{\overset{\displaystyle O}{\|}}{C}-CHR-\overset{\overset{\displaystyle H}{|}}{N}-$$

Polypeptides in helical conformation(25) are good examples of rigid-chain molecules with very high rigidity. The most complete information about hydrodynamic, optical and electrical properties of the molecules was obtained for poly-γ-benzyl-L-glutamate (PBLG).

A high value of exponents α and β in the Mark–Kuhn Eqn. (1–3) is the first indication of high rigidity of helical molecules.(14, 22, 26)

Experimental data on diffusion and sedimentation were used for a quantitative rigidity determination.

Figure 3 shows the value DM/RT, or the sedimentation coefficient $[S]$ as a function of the square root of the molecular weight $M^{\frac{1}{2}}$. The slope of the straight line with the use of (8) gives $A = 2200$ Å(14, 22) Flow birefringence in soutions of α-helical polypeptides is very high and increases with the molecular weight (Fig. 4). This dependence and the theory of persistent anisotropy [Eqn. (14) and (15)](20) give the values of anisotropy and the segment length $\alpha_1 - \alpha_2 = 20{,}000.10^{-25}$ cm^3 and $A = 2400$ Å respectively. These values agree with hydrodynamic data and show that the molecule possesses a high degree of orientational order.

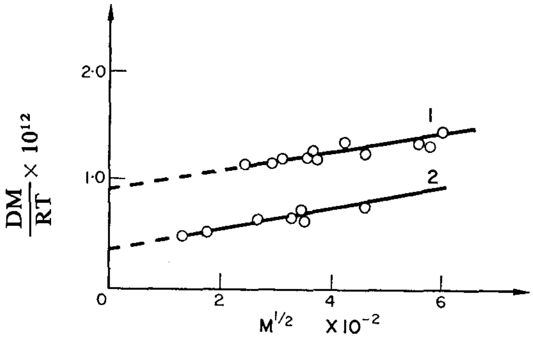


FIG. 3. DM/RT as a function of $M^{\frac{1}{2}}$ for poly-γ-benzyl-L-glutamate (curve 1) and polybutylisocyanate (curve 2).

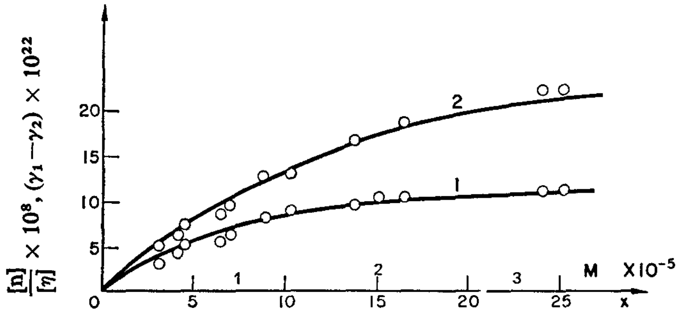


FIG. 4. Reduced anisotropy of solution $\Delta n/g(\eta - \eta_0) = [n]/[\eta]$ (curve 1) and $\gamma_1 - \gamma_2$ (curve 2) as a function of molecules weight for fractions of poly-γ-benzyl-L-glutamate in dichloroethane.

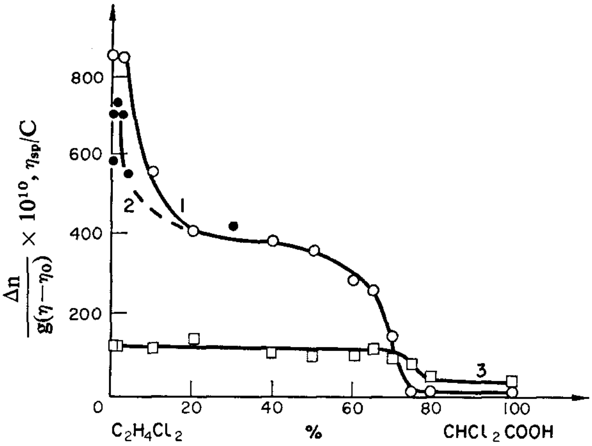


FIG. 5. Variation in optical anisotropy (curves 1 and 2) and of viscosity (curve 3) of the solution of poly-γ-benzyl-L-glutamate during destruction of the helical structure of the molecule. Curve 1—solvent dichloroethane—dimethylformamide (2 per cent) with addition of dichloroacetic acid. Curve 2—solvent—dichloroethane with addition of dichloroacetic acid.

In an electrical field, the PBLG solutions exhibit high birefringence, which indicates that the molecule has a high degree of dipole orientational order. The positive sign of the Kerr effect means that the total dipole moment of the molecule is directed along its axis and is a sum of the local moments of the $C = O \cdots H\text{–}N$ groups bonded by hydrogen bonds. Comparison of the dynamo-optical and electro-optical data allows us to determine the segment length of *A*. The value of *A* obtained by this method is 1400 Å. This value is lower than those found from diffusion, sedimentation and flow birefringence.

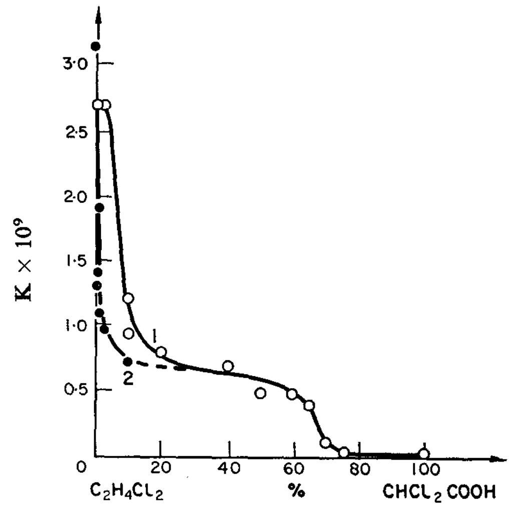


FIG. 6. Variation in Kerr's constant (*K*) of the solution of poly-benzyl-L-glutamate during destruction of the helical structure of the molecule. Curve 1—solvent dichloroethane–dimethylformamide with addition of dichloroacetic acid, curve 2—solvent dichloroethane with addition of dichloroacetic acid.

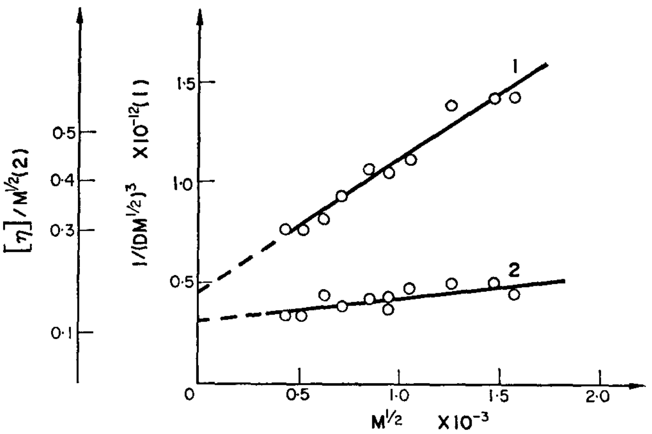


FIG. 7. $(1/DM^{\frac{1}{2}})^3$ (curve 1) and $[\eta]/M^{\frac{1}{2}}$ (curve 2) as functions of $M^{\frac{1}{2}}$ for fractions of poly-N-isobutylmaleinimide in butylacetate.

This fact means that the orientation processes of polar polypeptide molecules in mechanical and in electrical fields cannot be identified. Evidently, a marked difference exists between the degrees of the axial and polar correlation of the units in the helical polypeptide chain.

High values of optical anisotropy and dipole moments are characteristic only for polypeptide molecules in helical conformation supported by hydrogen bonds. When the latter break in strong solvents, the breakdown of the helical structure is accompanied by a practically complete disappearance of the tremendous optical effects observed in mechanical and optical fields. This is illustrated in Figs. 6 and 7 which show a change in the flow and electrical birefringence and in the viscosity of the PBLG solution during intramolecular conformational helix-coil transition.

(*b*) *Polymer molecules with rings in the main chain*

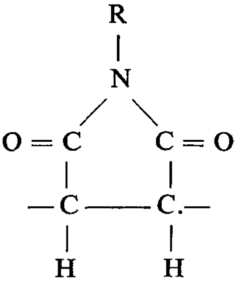
The rigidity of the helical conformation of polynucleotides or polypeptides is supported by hydrogen bonds which form intramolecular cyclic segments of the chain and produce the network structure of the molecule.

One might expect the same result to be attained in chain synthetic polymers due to additional chemical bonds between the atoms of the molecule if these bonds cause the formation of intramolecular rings.

Even though many polymers with heterocycles in the chain have been obtained in recent years,(27–30) quantitative data on the conformation and the rigidity of these molecules in solution are very scarce. Probably, this is partly due to low solubility of these polymers in common solvents.

Detailed quantitative data about solution properties were obtained for polymers of N-substituted maleinimides(31) which are well soluble in organic solvents and have a comparatively wide range of molecular weights.(32)

(*i*) *Poly-N-isobutylmaleinimide*(32)



As the structural formula of this polymer shows, the existence of the imide rings reduces twofold the amount of the single bonds around which the rotation in the main chain is possible. In accordance with this, one may expect high rigidity of the molecular chain. The rigidity was determined from experimental data on sedimentation, diffusion and viscometry. In order to eliminate the influence of excluded volume effects and to establish unperturbed molecular dimensions, hydrodynamic data were extrapolated to low molecular weights in accordance with Eqns. (4) and (6). The plot is given in Fig. 7 for the PIBMI fractions in butylacetate. The intercepts of the straight lines on the ordinate give the Kuhn segment length $A = 35\text{–}40$ Å. This is twice the value usually obtained for flexible chain molecules having no rings in the chain.(1)

At the same time, a twofold increase in the rigidity due to the cyclization of the chain is not great enough to place these molecules into the class of semi-rigid ones according to their behaviour in solution. Thus, for the PIBMI molecules the values of $\alpha = 0{\cdot}65$ and $\beta = 0{\cdot}59$ in the Mark–Kuhn Eqns. (1–3) higher than 0·5 are due to the excluded volume effects but not to the high chain rigidity. In accordance with this, the molecular anisotropy and reduced birefringence $\Delta n/\Delta_T$ for the PIBMI solutions correspond to Kuhn's Eqns. (10) and (12) for Gaussian chains and do not depend on the molecular weight.(32)

Thus, in order to decrease the flexibility of the chain to the value characteristic for semi-rigid chain molecules, the contribution of cyclized units should be much greater than one half.

When all units are completely cyclized, a "ladder" polymer is formed having maximum rigidity.

(*ii*) *Ladder polyphenylsiloxane.*(36) This polymer was obtained by several investigators.(34, 35) The probable structure of its molecule is shown in Fig. 8. Here the cyclization is arrived out by cross linking Si–O bonds which fix the double-chain structure of the molecule.

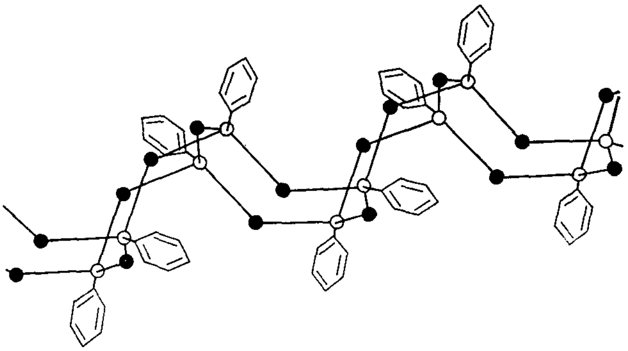


FIG. 8. Structure of the molecule of ladder polyphenylsiloxane: ○—silicon atoms, ●—oxygen atoms.

Investigation of hydrodynamic solution properties of fractions gives the M–K dependencies(1–3) in which the exponents are much greater than 0·5 ($\alpha = 0{\cdot}88$, $\beta = 0{\cdot}63$).(36) This is due to a considerable skeleton rigidity of the chain (draining effect) whereas the part played by the excluded volume effects is very small and may be neglected.

In accordance with this, the rigidity of the chain may be determined quantitatively by plotting $[S]$ and $M/[\eta]$ as a function of $M^{\frac{1}{2}}$ as shown in Fig. 9. The slopes of these straight lines (on the basis of the theory Eqns. 7 and 8) give the value of the segment length $A = 200$ Å. This value is 10 times higher than that for chain molecules of linear polyphenylsiloxane without rings in the chain.(1) A considerable rigidity of the molecules of the ladder polymer proves to be quite sufficient for the appearance of the properties characteristic of semi-rigid chain molecules.

These properties are clearly revealed in the optical behaviour of the solutions. They exhibit high negative flow birefringence and its reduced value increases with molecular

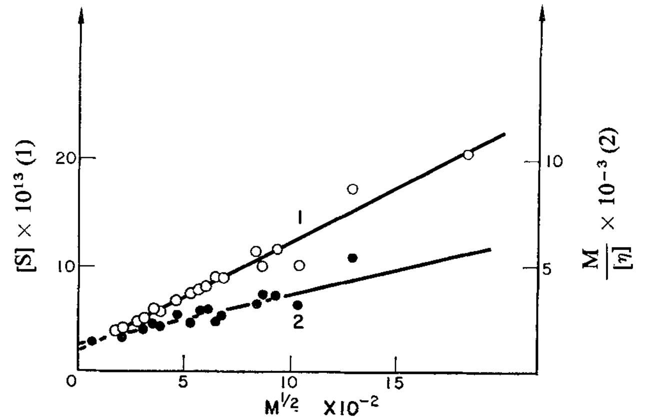


FIG. 9. $[S]$ (curve 1) and $M/[\eta]$ (curve 2) as functions of $M^{\frac{1}{2}}$ for fractions of ladder polyphenylsiloxane.

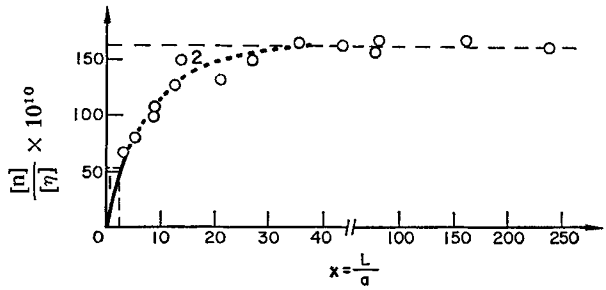


FIG. 10. Reduced birefringence $[n]/[\eta]$ as a function of molecular weight (x parameter) for fractions of ladder polyphenylsiloxane. 1—theoretical curve; 2—experimental curve. Experimental curve corresponds to the value of persistence length $a = 100$ Å.

weight (Fig. 10) in complete agreement with the theory of the anisotropy of persistent chains (Eqns. 14 and 15).

The segment length A estimated from the initial slope and the asymptotic limit of the experimental curve in Fig. 10 agrees with the value obtained from hydrodynamic data.

The segment anisotropy determined from the asymptote of the curve in Fig. 10 is equal to $a_1 - a_2 = -1800.10^{-25}$ cm^3. This is 20 times higher than the anisotropy of linear isotactic methylphenylsiloxane without rings in the chain.(37)

At the same time, the values of the contribution Δa to the molecular anisotropy by one phenyl ring practically coincide for the ladder and the linear single-chain phenylsiloxanes ($\Delta a \approx -11\ 10^{-25}$ cm^3). This means that the oxygen cross links, binding the double-chain molecule of the ladder polymer and sharply increasing its skeletal rigidity, do not have a large effect upon the rotational mobility of the side phenyl groups.

Although the rigidity of the molecules of the ladder polymer is great, it is limited. For instance it is similar to that of the chains of cellulose esters.(1) When the molecular weight is of the order of one hundred thousand, the molecule by its many properties is already a Gaussian coil, i.e. it reveals a considerable flexibility. One should note that the ladder polymer presents an example of the mechanism of chain flexibility very different from that of the linear chain molecules without secondary structure. Here the flexibility is not caused by a hundered rotation around the valency bonds (or the rotational isomerism) but by microdeformations of the macromolecular "lattice" during its thermal vibrations. Nevertheless, it is possible that the local defects within the intramolecular lattice play a certain part in this.

The rigidity of the molecules of the ladder polymer may be sharply decreased by the formation of defects in its lattice, i.e., by introducing single bonds into the molecular chain. Such partial decyclization of the molecule produces partial- "step-ladder" structure.(38, 46) Evidently, the poly-N-isobutylmaleinimide under investigation may serve as an example of a "semi-ladder" polymer.

The conformational properties of the molecules of other possible step-ladder polymers have not been investigated.

(*c*) *Molecules with resonance interaction in the chain*

All the above-mentioned polymers with rigid-chain molecules are characterized by the presence of additional intramolecular bonds (hydrogen or chemical) which "cyclize" the structure and thus ensure its rigidity.

Up to comparatively recently, one might think that these structural properties are a necessary condition for the occurrence of semi-rigid chain molecules.

Nevertheless, the synthesis of polyisocyanates(39, 40) and the investigation of the properties of their solutions(41, 44) have refuted this view. The molecules of several polyalkylisocyanates in solution proved to have an exceptionally high rigidity and ordering of structure.

Poly-N-butylisocyanate (PBIC) has been investigated in greatest detail:

$-\underset{\underset{O}{\|}}{C}-\underset{\underset{R}{|}}{N}-$

The solutions of this polymer in non-polar solvents are characterized by high values of the α and β exponents ($\alpha = 1\cdot 2$, $\beta = 0\cdot 85$) in the Mark–Kuhn Eqns. (1–3).

In order to illustrate high rigidity of the PBIC molecules, the viscometric data obtained may be treated using the basic equations(44) of the theory of the viscosity of solutions of rigid ellipsoids:

$$[\eta] = \bar{v}\nu(p) \qquad H^3 = 6p^2\bar{v}M/\pi N_A. \tag{19}$$

Here $p = H/d$. H and d are, respectively, the major and the minor axes of the ellipsoid modelling the molecule, $\bar{v}$ and M are the partial specific volume and the molecular weight of the polymer, $\nu(p)$ is the viscosity increment, a function tabulated by Simha.(1)

The values of $d = H/p$ and H/z estimated from (19) using the experimental values of $[\eta]$,$\bar{v}$ and M are shown in Fig. 11 as functions of the degree of polymerization Z.

A decrease in H/z and a growth of d with an increase in Z indicate considerable flexibility of the chain and the deviation of its shape (with the growth of Z) from that of the rod. Nevertheless, the limiting values of $(H/Z)_{z\to 0} = 2.10^{-8}$cm and $d_{z\to 0} = 11.10^{-8}$cm reasonably agree with the length and the diameter of the monomer unit of the PBIC molecular chain.

This analysis indicates that in the region of the molecular weight of several tens of thousand (Fig. 11) the shape of the PBIC molecule is similar to that of a straight rod.

The analysis of data on diffusion and sedimentation with the use of the theory of

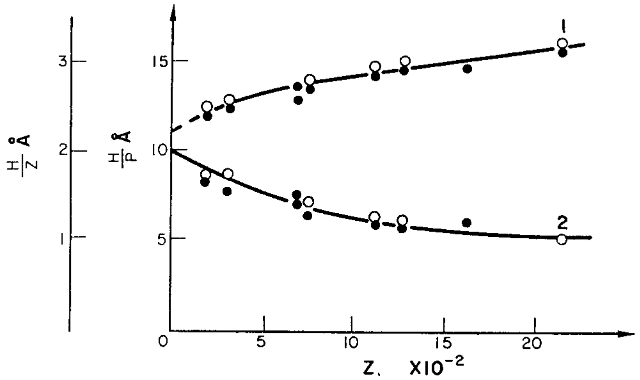


FIG. 11. $H/p = d$ (curve 1) and H/z (curve 2) as functions of degree of polymerization Z for fractions of polybutylisocyanate in various solvents: ○—benzene,(4) ●—tetrahydrofurane,(41), ◑-benzene.(44)

worm-like chains (the slope of the straight line 2, Fig. 3, Eqn. 8) gives(44) a tremendously high value of the segment length $A = 3000$ Å which is higher even than the segment length of the helical polypeptide molecules.

Data on flow birefringence, which is very high and positive in sign in the PBIC solutions, lend to similar conclusions.

The microform effect (Eqn. 13) enables us to evaluate the segment length. The value obtained ($A = 2600$ Å) is close to that found from hydrodynamic data.

The segment anisotropy is very high ($\alpha_1 - \alpha_2 = 9000.10^{25}\text{cm}^3$) and, in its order of magnitude, is close to that of the helical polypeptide molecules.

The PBIC solutions also exhibit very high electrical birefringence which is positive in sign.(44) This indicates that the molecule possesses not only axial orientational order but also the polar one.

A marked frequency dependence of the Kerr effect (Fig. 12) also proves high rigidity and high ordering of structure and may be used for determining of the orientational relaxation time and the geometrical parameters of the molecule.(44)

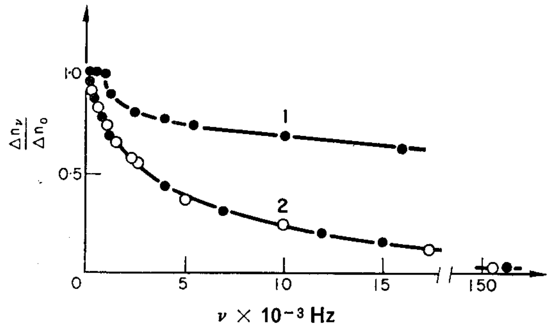


FIG. 12. Relative value of electrical birefringence $\Delta n_\nu/\Delta n_0$ as a function of frequency ν for solutions of polybutylisocyanate in tetrachloromethane. 1—sample M = 1·6 × 10⁵, 2—M = 0·66 × 10⁵.

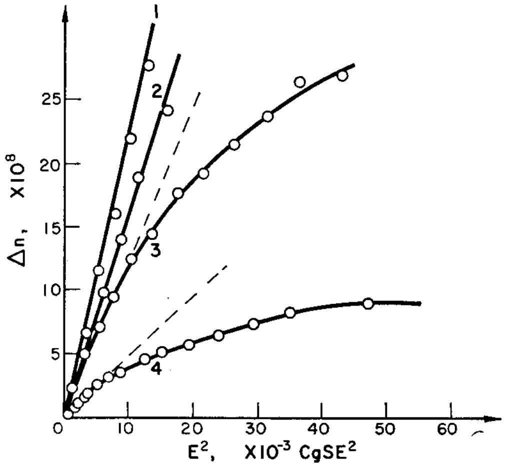


FIG. 13. Electrical birefringence Δn as a function of square of field strength E^2 for solutions of polybutylisocyanate and polytolylisocyanate. 1—bromoform; 2—polytolylisocyanate in bromoform ($C = 1\cdot 77$ g/dcl) 3,4—polybutylisocyanate in tetrachloromethane (3-sample M = $1\cdot 6 \times 10^5$, C = $0\cdot 6 \times 10^{-3}$ g/dcl); (4-sample M = $0\cdot 66 \times 10^5$, $c = 0\cdot 7 \times 10^{-3}$ g/dcl).

The effect of saturation of electrical birefringence found in strong fields (Fig. 13) suggests a high value of the molecular dipole and it may be used for determining the dipole moment of the molecule μ.(44) The values obtained are close to those of the dipole moments of polypeptide molecules in helical conformation. Similar results are obtained from a comparison of dynamo-optical and electro-optical data.(44)

The molecular dipole moments μ obtained from dielectric measurements(43) also may be used for determining of the segment length A. The plot of μ^2/L against the contour length L is shown in Fig. 14. In accordance with the theory (Eqn. 18) the initial slope of the curve gives the square of the dipole moment per unit contour length of the chain $(\mu\text{sec}/A)^2$. The ratio of the asymptotic limit to the initial slope gives the segment length A. The value, $A = 3000$ Å, obtained by this method agrees with the value found from hydrodynamical data.

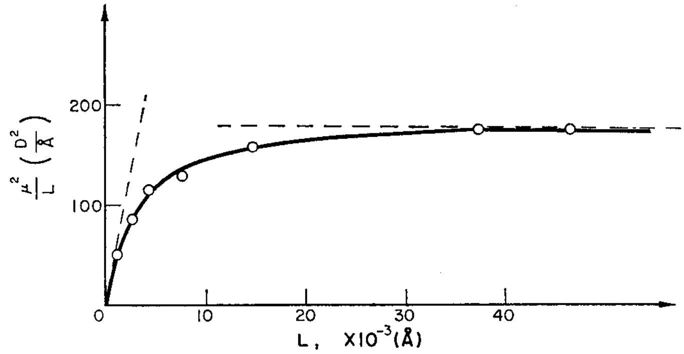


FIG. 14. μ^2/L as a function of L for polybutylisocyanate in benzene.

The list of molecular characteristics of PBIC is given in Table 1.

TABLE 1. THE LENGTH OF STATISTICAL SEGMENT $A = 2a$, SEGMENTAL ANISOTROPY $\alpha_1 - \alpha_2$, ANISOTROPY OF THE MONOMER UNIT $a_{\parallel} - a_{\perp}$ AND DIPOLE MOMENT μ OF SOME SEMI-RIGID CHAIN MOLECULES

Polymer	$A \cdot 10^8$cm	$(\alpha_1 - \alpha_2) \cdot 10^{25}$cm^3	$(a_{\parallel} - a_{\perp}) \cdot 10^{25}$cm^3	$\mu \cdot 10^{18}$ abs. unites
Polystyrene (for comparison)	20	−140	−18	1–2
Trinitrocellulose	230	−300	−15	1–2
Tribenzoatecellulose	200	−900	−45	1–2
Phenylcarbomate cellulose	200	−1200	−60	1–2
Ethylcellulose	200	420	20	1–2
Polyisobutylmaleineimide	40	160	10	1–2
Polyphenylsilsesquioxane (ladder)	200	−1800	−22	—
Deoxyribonucleic acid	800	−40000	−200	—
Poly-γ-benzyl-L-glutamate	2400	200000	17	470
Polybutylisocyanate	2600	9000	7	830
Phenylmethacrylic ester of cetyloxybenzoic acid	65	−2500	−100	30

All the reported experimental data show that the conformation of the PBIC molecules in weakly polar solvents corresponds to the model of a worm-like chain. The rigidity and the order of its structure determined by different methods are very high and are close to those of the synthetic polypeptide molecules having the secondary structure of the α-helix.

Similar properties were revealed in the polymers of other alkylisocyanates, viz. polyhexylisocyanate(42) and polychlorohexylisocyanate.

The chemical structure of the polyisocyanate molecules is close to that of the polypeptide molecules. Nevertheless, it differs from the latter by the presence of a side radical at the nitrogen atom (substituting hydrogen) and by the absence of –CHR– groups in the main chain. The first peculiarity (the absence of the N–H bond) excludes the possibility of the formation of a rigid α-helical conformation due to the effect of intramolecular hydrogen bonds.

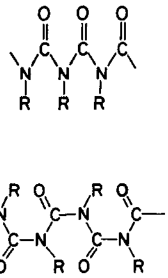


FIG. 15. *Trans-* and *cis*-conformations of polyisocyanate chains.

But the second peculiarity may be of decisive importance in stabilizing the rigidity of the molecular chain. And indeed, since the peptide bonds in the polyisocyanate molecule are not separated by the –CHR– groups, the coplanarity of all bonds inside one peptide group (–CO–NR–) can spread to each neighbouring pair of the peptide groups ensuring rigid conformation of the whole chain. The resonance interaction of every nitrogen atom is spread to both adjacent carbonyl groups imparting to the C–N bonds the rigidity of the conjugated ones.(42)

The *cis*-form is the more probable of the two possible planar chain structures (Fig. 16) since only this form can ensure the molecular dipole moment parallel to the axis of the molecule and, in accordance with this, the coincidence of the signs of electrical and dynamical birefringence.(44)

Thus, polyalkylisocyanates present a unique case where an exceptionally high rigidity of the conformation and a high degree of intramolecular order of the chain molecule are not due to its secondary structure but to the true skeletal rigidity of its single-strand chain.

At the same time, the structure of the side group at the nitrogen atom also plays an important part in the formation of these properties. Thus, the replacement of an aliphatic group by an aromatic group (tolylisocyanate)(44) causes damage of the unique structure of the molecule. The reason for this may be found both in the weakening of the resonance interaction in the nitrogen–carbonyl system due to the effect of the conjugated bonds of the aromatic cycle and in the steric repulsion of the neighbouring tolyl radicals.

(*d*) *Molecules with chain side groups*

The effect of the size and the structure of the side groups on the conformation of the polymer molecules and the rigidity of their main chain has been studied in a number of publications. Although in principle this effect should occur, the effects observed experimentally were always insignificant.(1)

Recently new information was obtained on this problem in connection with the investigation of the conformational and optical properties of chain molecules having comb-like structure. The latter is typical for molecules with comparatively long side groups or else it may be obtained by grafting one chain polymer to the other. In all cases the side groups should be much shorter than the main chain.

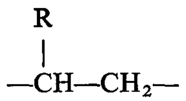
A new approach to the investigation of conformations of these molecules is to apply the theory of persistent anisotropy to the optical properties of the side groups and to calculate their optical anisotropy in the axes of their first element.(20, 47) In this case the contribution Δb_L, introduced by the side radical into the anisotropy of the monomer unit of the molecule is:

$$\Delta b_L = -S^* \Delta a \cdot (1 - \mathrm{e}^{-6n/s^*})/12 \tag{20}$$

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

Thus this method permits us to study the anisotropy and the flexibility of the side groups on the basis of the changes introduced into the anisotropy of the whole molecule by these groups.

(*i*) *Poly-α-olefines.*



$$\begin{array}{c} \mathrm{R} \\ | \\ -\mathrm{CH}-\mathrm{CH_2}- \end{array}$$

Systematic experimental data about the dependence of the anisotropy of the molecule on the number n of the methylene groups in its side groups were obtained for several poly-α-olefines.(48)

It was shown that in the series of poly-α-olefines the elongation of the side group is accompanied by a monotonous increase in the negative anisotropy of the molecule $\alpha_1 - \alpha_2$. This increase may be produced both by an increase in the rigidity of the main chain (an increase in *A* or *S*) and by an increase in the negative contribution introduced into the anisotropy of the nomomer unit of the molecule by its side group with the elongation of the latter.

If we neglect the change in the rigidity of the main chain with an increase in the length of the side group (actually this can be assumed only for lower homologues of the series), the experimentally established dependence can be represented in the form $\Delta b_L = -2{\cdot}73.10^{-25}\text{cm}^3$. On the other hand, if the flexibility of the side hydrocarbon chain of the poly-α-olefine molecule is assumed to be equal to that of the polyethylene chain, assuming $S^* = 16$ we obtain from Eqn. (20) the theoretical dependence $\Delta b_L = -7{\cdot}3.10^{-25}\ (1 - e^{-3n/8})$. Both dependencies are shown in Fig. 16.

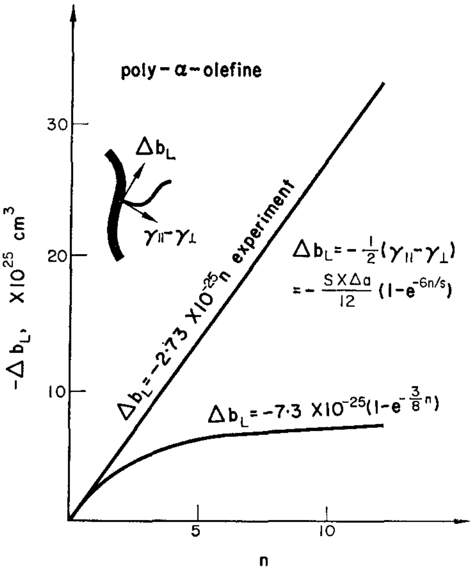
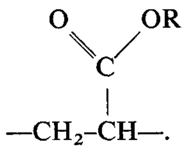


FIG. 16. Contribution Δb_L of the side group to the anisotropy of the monomer unit of poly-α-olefine molecule as a function of number of carbon atoms in the side chain. (1) Theory of non-interacting chains with flexibility equal to that of polymethylene chain. (2) Experimental data.

The theoretical curve shows that, owing to the flexibility of the side chain, the anisotropy Δb_L should attain the asymptotic limit determined by the degree of flexibility of the side group.

Nevertheless, the experimental dependence does not exhibit a tendency to saturation over the investigated range of the *n* values. This means that the rigidity and the orientational order of the side groups of poly-α-olefines greatly exceed the values which can be obtained from the experimental investigation of the conformational and optical properties of single hydrocarbon chains in solution.

(*ii*) *Polyalkylmethacrylates*



An investigation of the conformation and optical anisotropy of the molecule in the polyalkylmethacrylate series leads to similar conclusions.(9)

In contrast to poly-α-olefines not only the optical data but also data on the rigidity of the main chain have been obtained for this series.(9, 49, 50) Hence, the treatment of these data may be more quantitative than in the previous case.

Experimental data on the rigidity of the main chain and the anisotropy of the molecule of polyalkylmethacrylates are given in Table 2. Up to $n = 8$, the length of the side group practically does not affect the rigidity of the main chain (the number of the monomers S in its segment is close to 7 or 8). With a further increase in the length of the side chains, the rigidity of the main chain markedly grows, and even when $n = 16$ it is two times higher than that of the molecules of many polymers with flexible chains. Evidently, this growth should be regarded as a result of the interaction between the long side groups of the molecule.

TABLE 2. NUMBER OF MONOMER UNITS S IN SEGMENT, SEGMENTAL ANISOTROPY $\alpha_1 - \alpha_2$ AND ANISOTROPY OF MONOMER UNIT $a_{\parallel} - a_{\perp}$ OF SOME ESTERS OF POLYMETHACRYLIC ACID. n IS THE NUMBER OF CARBON ATOMS IN THE SIDE ALKYL CHAIN OF THE MOLECULE

Polymer	n	S	$(\alpha_1 - \alpha_2)\cdot 10^{25}\text{cm}^3$	$(a_{\parallel} - a_{\perp})\cdot 10^{25}\text{cm}^3$
Methylmethacrylate	1	7·0	−2	−0·2
Butylmethacrylate	4	6·7	−14	−2·1
Hexylmethacrylate	6	8·6	−40	−4·6
Octylmethacrylate	8	7·9	−47	−5·9
Cetylmethacrylate	16	19	−170	−8·9
Phenylmethacrylic ester of cetyloxybenzoic acid	16	25	−2500	−100

An increase in the negative anisotropy of the molecular segment $\alpha_1 - \alpha_2$ is expressed much sharper with an increase in the length of the side groups. The corresponding experimental values of the anisotropy $a_{\parallel} - a_{\perp}$ of the monomer unit of the chain are given in Fig. 17 as a function of $z = n + 2$. The points fall quite satisfactorily on the theoretical curve (20) (where n is replaced by z) when $S^* = 60$ (full curve). The dashed line shows the theoretical dependence corresponding to $S^* = 16$, i.e. to the flexibility of the side chain equal to that of the polyethylene chain.

Thus, the rigidity of the side chains of polyalkylmethacrylates in the range under investigation (up to $n = 16$) is four times greater than that of the carbo-chain polymers of similar structure. This result means that the side chains of the macromolecules have an orientational order which greatly exceeds that of the usual Gaussian chains. Probably this ordering is due to the interaction of alkyl radicals having the regular structure. This interaction causes the formation of intramolecular structure with

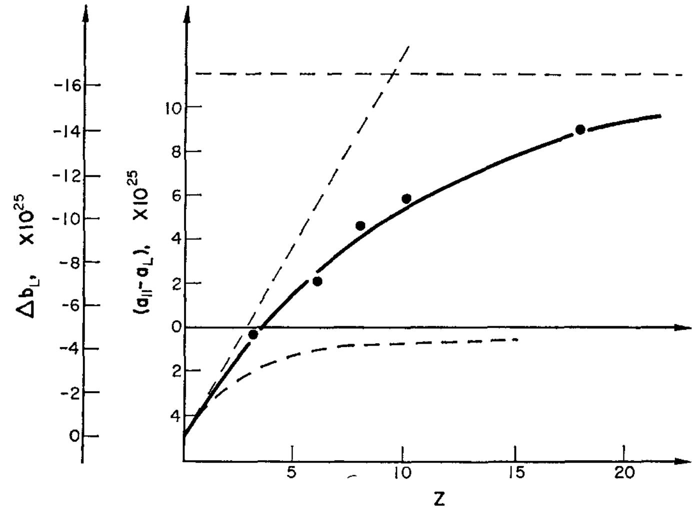


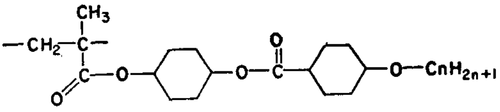
FIG. 17. Anisotropy of the monomer unit of alkylic esters of polymethacrylic acid as a function of the number of valency bonds $z = n + 2$ in the side chain. Full curve—theoretical dependence from Eqn. (20) if $\Delta a = 3{\cdot}3 \times 10^{-25}\text{cm}^3$ and $S^* = 60$. Dashed curve from Eqn. (20) when $\Delta a = 3{\cdot}3 \times 10^{-25}\text{cm}^3$ and $S^* = 16$. Points—experimental data.

orientational short range order in the arrangament of the side chains. The longer the side chains, the more manifest is this effect. It is similar to the facilitation of crystallization of the polyalkylmethacrylates in mass owing to the elongation of the side chains.

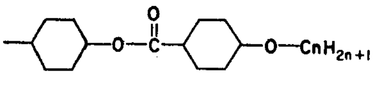
A natural consequence of this effect is also a decrease in the flexibility of the main chain.

(*iii*) *Polyphenylmethacrylic esters of alkyloxy-benzoic acids.* In order to obtain the most convincing confirmation of the fact that this increase in the rigidity and in the orientational order both in the main chain (an increase in S) and in the side chains (an increase in S^*) is due to the interaction of the side groups, one should investigate the conformational properties of the molecules of some polymeric esters of alkyloxybenzoic acids.[51]

These polymers having the structural formula


$$-CH_2-\underset{\underset{O}{\overset{\|}{C}}-O-C_6H_4-O-\overset{O}{\overset{\|}{C}}-C_6H_4-O-C_nH_{2n+1}}{\overset{CH_3}{\overset{|}{C}}}-$$

may be regarded as esters of polymethacrylic acid where the


$$-C_6H_4-O-\overset{O}{\overset{\|}{C}}-C_6H_4-O-C_nH_{2n+1}$$

group replaces hydrogen.

Thus, the main chains of these macromolecules have the structure of polyalkylmethacrylate while the side chains are characterized by the presence of groups contributing to the formation of the liquid crystal phase, i.e. of the state with a strongly expressed orientational order.(52)

The structural characteristics of the macromolecules of one of these polymers: the polyphenylmethacrylic ester of cetoxybenzoic acid (PMECBA, $n = 16$ in the $C_n H_{2n+1}$ group) are also given in Tables 1 and 2. The presence of strongly interacting side groups increases the rigidity of the main chain of the polymer ($S = 25$). But its optical properties are quite unique. Negative segmental anisotropy of the molecule exceeds by more than one order that of polycetylmethacrylate and is comparable only with the anisotropy of "crystal-like" molecules of polyisocyanate or poly-γ-benzyl-L-glutamate (Table 2), while the anisotropy $a_{\parallel} - a_{\perp}$ of the PMECBA monomer unit is even much higher than that of the monomer units of these molecules. The latter fact means that a very high anisotropy of the PMECBA molecules is not so much due to the rigidity of its main chain (which is much lower than that of crystal-like molecules) as to a very perfect orientational order in its side groups.

It is also remarkable that this order is not only an axial one but also a polar one—the PMECBA solutions exhibit high negative birefringence in the electrical field. These experimental data combined with Eqns. (12) and (16) give for the components of the dipole moment along the axis of the molecule the value $\mu = 30.10^{-18}$cgse.

It is characteristic that these unique properties are combined with those characteristic for flexible chain polymer: in contrast to the size of crystal-like molecules, that of the PMECBA molecules is sensitive to the thermodynamic quality of the solvent and can vary greatly with a change in the latter.

All these facts show that the PMECBA molecules exhibit orientational order of the mesomorphic type in which the side chains form a mobile liquid crystal structure.

(*iv*) *Graft copolymers.* Similar though less perfect structures are evidently formed in other macromolecules of comb-like type, viz. in the graft copolymers. They are revealed in very specific optical properties such as those of the styrene-alkylmethacrylates graft copolymers.(47, 53, 54) Thus, optical anisotropy of the molecules of a graft copolymer may be many times greater than that of the separate homopolymers. Moreover, it is positive, i.e. it is opposite in sign to the negative anisotropy of the polystyrene although polystyrene is the main component (90 per cent) of the graft copolymer.

The analysis of these experimental data in comparing with hydrodynamic properties of the molecules enables us to determine the rigidity of both the main chain of the copolymer and the grafted chains. The properties observed may be accounted for not only qualitatively but also quantitatively by intramolecular structure with a high degree of orientational order existing in the polymer.(42)

It is interesting to note that in spite of high rigidity of the main chain of graft polymer ($A = 100$–200 Å) the exponents in the M–K Eqns. (1–3) for this polymer are close to $\alpha = \beta = 0 \cdot 5$. This is due to a high value of the diameters "d" of the worm-like chain modelling the graft polymer molecule, in complete agreement with the theory (Eqns. 7 and 8).

CONCLUSION

It seems obvious that the list of molecular structures which may be included in the group of semi-rigid structures is not limited to the above mentioned examples.

Thus, when ionogen groups in polyelectrolyte chain molecules dissociate, the latter uncoil under the action of intramolecular forces of electrostatic repulsion. In contrast to osmotic swelling,(5, 6) electrostatic increase in the size of the molecular coil is equivalent to an increase in the skeletal rigidity of the molecular chain. This is revealed both by hydrodynamic properties of the chain(57) and by its optical properties.(55, 56) Hence the polyelectrolytic "swelling" of the chain molecules is actually a conformational transition from a flexible chain structure to that of a semi-rigid chain molecule.

Nevertheless, a detailed investigation of these interesting problems would lead us too far from the subject of this symposium.

On the other hand, in choosing the material to be discussed, we dwelt only on examples in which the conformational properties of the molecules had been investigated quantitatively and in sufficient detail so that definite conclusions could be drawn.

At the same time we think that the material investigated is useful in at least two respects. Firstly, it contains various examples of the structural peculiarities of the polymer which may be responsible for those properties of its molecules which are characteristic for semi-rigid chains. Secondly, it shows that hydrodynamic and optical behaviour of chain molecules in solution are reliable criteria for quantitative determination of their rigidity and internal order of structure.

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