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this band in a derivative of this octane would indicate that the atomic group whose motion is responsible for the band has been changed by the added terms, while the persistence of the band would indicate that the added terms are not connected to that group in such a way as to interfere with its motion.

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The Intrinsic Viscosity of Polymer Solutions

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1. INTRODUCTION

RECENTLY some articles have been published dealing with the behavior of polymers of the coiling type suspended in a flowing liquid.[1] One of the issues is to establish a physical reason for Staudinger's rule according to which the intrinsic viscosity of polymer solutions should be proportional to the molecular weight of the polymer. I would like to present here a detailed picture of the motion of the polymer molecule and its parts, which makes it easy to see why the rule should hold for the very simplified model currently substituted for the actual molecule.

2. MOTION OF THE POLYMER MOLECULE

The model is as usual a number of identical atomic groups connected to each other by rigid links, the consecutive ones making a definite angle with each other and able to turn freely around each other. It is also assumed that each of these groups is acted upon by a frictional force fv if in a solvent flowing along with the velocity v and that neither the links suffer friction from the medium nor any interaction between the different groups exists, due to their individual disturbance of the general flow.

The velocity of the liquid in a rectangular x, y, z system of coordinates may be represented by the vector $\mathbf{V}$ with the components

$$\mathbf{V}=\begin{cases}\alpha z=v_x\\ 0=v_y\\ 0=v_z\end{cases} \tag{1}$$

as it would result for instance from the motion of a plate in the x,y-plane moving with a constant velocity in the x-direction at a constant distance above another parallel plate at rest. The velocity gradient in the z-direction is α.

A polymer molecule suspended in this liquid will be set in motion by the frictional forces acting upon each atomic group of the chain. If now we confine our attention to the center of gravity of the molecule, it can easily be seen that this center of gravity (apart from its irregular Brownian motion) will move with the velocity of the liquid as it is at the position where this center is momentarily situated. In this way we have taken care of the condition that the sum of all the forces acting on the whole molecule, averaged over all the configurations the chain can acquire is zero.

Let us now take the center of gravity as the origin of our system of coordinates. Equation (1) will then represent the relative velocity of the liquid with respect to this center and will appear as represented in Fig. 1. It is evident from Fig. 1 that the still remaining frictional forces will now tend to rotate the molecule as a whole around the y-axis. Call the angular velocity of such a

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[1] John G. Kirkwood, J. Chem. Phys. **14**, 180, 347 (1946); H. A. Kramers, J. Chem. Phys. **14**, 415 (1946), a sequence to an article by J. J. Hermans, Physica **10**, 777 (1943).

rotation ω. A group at the position x, y, z will, due to this rotation, have a velocity $\mathbf{v}$ with the component,

$$\mathbf{v}=\begin{cases}\omega z\\ 0\\ -\omega x\end{cases} \tag{2}$$

and the frictional force acting on such a group will be $\mathbf{F}=f(\mathbf{V}-\mathbf{v})$. In the steady state we will have to satisfy the condition that the average moment of this force around the center of gravity is zero. The instantaneous moment $\mathbf{M}$ has the components

$$\mathbf{M}=\begin{cases}f\omega \sum xy\\ f[(\alpha-\omega)\sum z^2-\omega\sum x^2],\\ -f(\alpha-\omega)\sum yz\end{cases} \tag{3}$$

the summation extending over all the groups of the molecule. Since in the average the products xy and yz are zero and

$$\mathrm{Av}\,\langle x^2\rangle=\mathrm{Av}\,\langle z^2\rangle=\mathrm{Av}\left\langle\frac{r^2}{3}\right\rangle,$$

in which r is the distance of the group from the center of gravity, the average moment will only have a component in the y-direction and this will be equal to

$$\mathrm{Av}\,\langle M_y\rangle=f(\alpha-2\omega)\,\mathrm{Av}\left\langle\sum\frac{r^2}{3}\right\rangle. \tag{4}$$

In the steady state this average moment has to be zero and so we conclude that the molecule rotates as a whole with an angular velocity

$$\omega=\alpha/2. \tag{5}$$

But even so the liquid will still have relative velocities with respect to the different groups. For one of them this relative velocity $\mathbf{V}-\mathbf{v}$, will have the components

$$\mathbf{V}-\mathbf{v}=\begin{cases}\dfrac{\alpha}{2}z\\ 0\\ \dfrac{\alpha}{2}x\end{cases} \tag{6}$$

as follows from (1) and (2) with $\omega=\alpha/2$.

The flow lines of this relative flow of the liquid through the skeleton of the molecule are represented in Fig. 2. The frictional energy-losses connected with this flow will appear in the form of an increased viscosity of the solution.

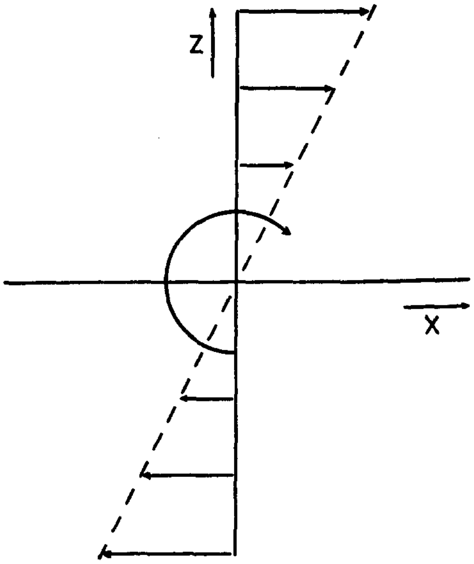

FIG. 1. Relative velocity of the medium with respect to the center of gravity of the molecule before rotation.

The flowlines themselves are hyperbolas with the equation

$$z^2-x^2=\mathrm{const.}$$

and the absolute value of the velocity

$$\frac{\alpha}{2}(z^2+x^2)^{\frac{1}{2}}$$

is constant on circles around the y axis, increasing proportionally with the distance from this axis.

3. ENERGY LOSSES

In the flow represented by Fig. 2 and Eq. (6) the frictional force on one of the groups is

$$f\frac{\alpha}{2}(z^2+x^2)^{\frac{1}{2}}$$

and since this force is in the direction of the velocity, the work in unit time for one group is

$$f\frac{\alpha^2}{4}(z^2+x^2).$$

If n is the number of molecules per cc, the increase in energy losses per sec. and in 1 cc due to the presence of polymer molecules will in the average be equal to

$$w = nf\frac{\alpha^2}{4}\mathrm{Av}\,\langle\sum(z^2+x^2)\rangle = nf\frac{\alpha^2}{6}\,\mathrm{Av}\,\langle\sum r^2\rangle. \quad (7)$$

This increase makes itself felt by an observable increase of the macroscopic viscosity from a value η to a higher value η'. Now in a medium of viscosity η the total energy loss per sec. and per cc for a velocity distribution as represented by Eq. (1) is

$$w = \eta\alpha^2. \quad (8)$$

This is easily checked by realizing that if one of the two parallel plates of surface S at a distance h is moving with the velocity $v = \alpha h$ with respect to the other, which is at rest, the frictional force on the upper plate is $F = \eta\alpha S$ and the displacement of this plate per unit time is $v = \alpha h$. Consequently the total amount of work dissipated in the volume Sh per sec. is $Fv = \eta\alpha^2 Sh$. If due to the presence of the polymer molecules the medium acts as if the viscosity is increased from η to η', the corresponding increase in dissipated energy will be

$$w = (\eta' - \eta)\alpha^2. \quad (9)$$

Equations (7) and (9) represent the same quantity in two different forms, so we conclude that

$$\eta' - \eta = \tfrac{1}{6}nf\sum \mathrm{Av}\,\langle r^2\rangle. \quad (10)$$

It can now already be seen at once that the increase in viscosity will be proportional to the square of the number of links contained in the chain of the molecule. It is well known that the average of the square of the distance from beginning to end of the chain is proportional to N, denoting by N the total number of links. From this it follows immediately that the average of the square of the distance of one of the groups from the center of gravity of the whole molecule will also be proportional to N. On the other hand the number of terms in the sum of Eq. (10) is $N+1$. Neglecting terms of the relative importance $1/N$ against 1, we thus come to the conclusion that the sum is proportional to N^2. In a qualitative way this dependence is caused by the fact that in longer molecules the average distance of each group from the center of gravity is larger. Consequently each group comes into a region in which the relative velocity of the medium with respect to the rotating molecule is also larger. Increasing the length of the molecule therefore means not only increasing the number of centers which contribute to the energy losses but also increasing at the same time the individual energy loss due to each center.

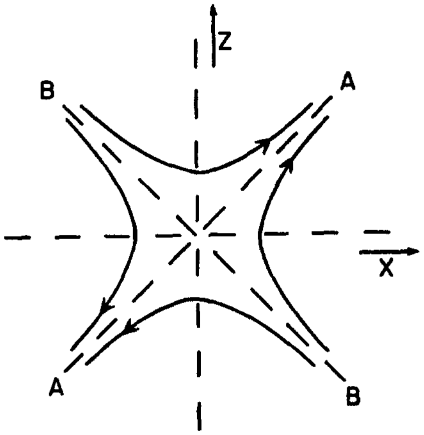

FIG. 2. Relative velocity of the medium with respect to the center of gravity of the rotating molecule.

4. INTRINSIC VISCOSITY

In order to complete the calculation indicated in Eq. (10), we have to know what the average square of the distance is of one of the groups from the center of gravity. Obviously this average will depend on the position of the group in the chain and we expect that for a group in the middle it will be smaller than for a group near the end of the chain. This is confirmed by a calculation not reproduced here, which although somewhat more involved proceeds along the same lines followed in calculating the average square of the distance from beginning to end, which is

$$R^2 = \frac{1+p}{1-p}Na^2. \quad (11)$$

In Eq. (11) a is the length of a link and p is the cosine of the angle between two consecutive links ($\frac{1}{3}$ for C–C bonds).

If we number the $N+1$ groups of the chain from O to N and concentrate our attention on group number ν, it is found that the average square of the distance of this group from the center of gravity is

$$r_\nu^2=\frac{1+p}{1-p}Na^2\left[\frac{1}{3}-\frac{\nu}{N}\left(1-\frac{\nu}{N}\right)\right]. \tag{12}$$

The factor in front of the brackets being equal to R^2, we see that for $\nu=0$ or $\nu=N$ (the ends of the chain) $r^2=\frac{1}{3}R^2$, whereas a minimum value is reached for $\nu/N=\frac{1}{2}$ (the middle of the chain) equal to $r^2=\frac{1}{12}R^2$. Substituting (12) in (10) and performing the summation, which within the limits of accuracy can be represented by an integral, we find

$$\begin{aligned}\eta'-\eta&=\frac{1}{6}nf\frac{1+p}{1-p}Na^2\sum_{\nu=0}^{\nu=N}\left[\frac{1}{3}-\frac{\nu}{N}\left(1-\frac{\nu}{N}\right)\right]\\&=\frac{1}{6}nf\frac{1+p}{1-p}N^2a^2\int_0^1\left[\tfrac{1}{3}-\xi(1-\xi)\right]d\xi \qquad (13)\\&=\frac{1}{36}nf\frac{1+p}{1-p}N^2a^2.\end{aligned}$$

From the increase in viscosity we obtain the relative increase in dividing by η and the intrinsic viscosity $[\eta]$ in dividing by the concentration, which is nNm if m is the mass of one of the groups of the chain. The final result for the intrinsic viscosity is

$$[\eta]=\frac{1}{36}\frac{f/\eta}{m}\frac{1+p}{1-p}Na^2, \tag{14}$$

which represents Staudinger's rule that the intrinsic viscosity is proportional to N and therefore to the molecular weight of the whole molecule. Should we represent each group by a sphere of radius ρ and apply Stokes law, according to which in this case $f=6\pi\eta\rho$, we will find

$$[\eta]=\frac{\pi}{6}\frac{\rho R^2}{m}. \tag{14$'$}$$

As is evident from the definition of $[\eta]$ it has the dimension of a specific volume and this is according to the theory represented here by the quotient of a volume which is $\pi/6$ times the product of the radius of the sphere, representing each group multiplied by the average square of the distance from beginning to end of the chain, divided by the mass of a single group. In order to show by an example that the order of magnitude is correct we take a polymer of molecular weight 500,000, each single group having the molecular weight 50. We now have $N=10{,}000$ and with $a=1.54\text{A}$ (the C−C distance) it follows that $R^2=47{,}400.10^{-16}$ cm². Since $m=82.10^{-24}$ g we find that in order to explain a supposedly observed intrinsic viscosity $[\eta]=100$ cc/g (which in the customary practical units, 1 g and 100 cc, corresponds to the intrinsic viscosity (1) it is necessary to represent each group by a sphere of radius $\rho=0.33\text{A}$.

As to the streaming double refraction, which may be expected from the model, it is immediately evident from Fig. 2 that in a second approximation the molecule will in the average lose its central symmetry, be elongated in the direction AA, and compressed in the direction BB. With bonds having different polarizabilities parallel and perpendicular to their direction this will lead to observable double refraction of the solution in motion with axes under 45° against the direction of flow. At the same time it is also evident with respect to the viscous behavior of the solution that in a second approximation and due to the distortion of the molecule proportionality between the shearing stress and the velocity gradient will cease to exist.