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Some remarks about the conformation of ring polymers in the bulk and their potential study by small-angle neutron scattering

Summary — Molten ring polymers are always less viscous than linear polymers identical in nature and molecular weight. The conformation of ring polymers in the bulk is thus believed to be more contracted than that deduced from a Gaussian chain. A model of compaction is suggested, which could be verified by neutron scattering experiments made on an unlabeled block copolymer prepared of identical amounts of ordinary and deuterated monomers, rather than on a deuterium-labeled mixture. Calculation based on this model show the scattering intensity to be affected by compaction quite appreciably and the scattering curve only slightly. A conformation study carried out with a specimen that has been elongated (sheared) could reveal whether compaction is caused by this constraint and to establish the kinetics of compaction.

Key words: ring *vs.* linear polymers, compaction, viscosity, neutron scattering by polymers

It is possible to synthesize ring polymers, *i.e.*, polymers having no ends like a necklace. During the last decade the physical chemists have been interested not

only in the preparation of such polymers, but also in their physicochemical properties [1].

Although ring polymers behave classically in the so-

lution, their viscosimetric properties in the bulk are rather surprising. Today, the viscoelastic properties of polymers are explained in terms of the reptation theory proposed by de Gennes [2] and Edwards [3]. By this theory, a chain polymer can move in the bulk only by a snake-like sliding motion between its extremities. This model, and all its implications, fits very well the experimental results obtained on linear polymers. While trying to extrapolate the model to comprise ring polymers, we are facing the following problem: the chain can not move forward because all it can is to rotate around an obstacle, therefore, its viscosity should be very large.

However, this conclusion is in conflict with experimental results. Various investigators have studied the viscosity as a function of molecular weight in the bulk and found that, at the identical molecular weight, the viscosity is lower for the ring polymer than for the linear polymer. The only explanation proposed so far is to assume the chain not to be extended like a usual Gaussian chain but to be folded on itself so as to form something like a double strand which behaves as a shorter (but a little thicker) linear macromolecule. This hypothesis has never been proved experimentally and it would be useful to verify it and to establish more precisely the conformation of the chain in the bulk. The small-angle neutron scattering technique, which has been used to verify the Gaussian model for linear chains [4], can be helpful again. To provide contrast, one could mix deuterated with hydrogenated molecules of identical molecular weights and try to extract from the signal the information on the conformation of the ring. Some preliminary experiments have been made by using this technique but their results are inconclusive.

Practically, the quantity $I(q)$ (where $q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$), is the scattered intensity evaluated by Casassa [5] as a function of the observation angle P for a ring, is only slightly different from the classical result for linear chains: the radius of gyration is half the radius for the linear chain of identical dimensions and, at large angles, the behavior is identical.

While contemplating the possibilities of improving the sensitivity of this experiment, it has been suggested to use, rather than a mixture of deuterated and ordinary polymers, a two block copolymer made one-half of deuterated and the other half of ordinary monomers, and to look at scattering caused by this system, *i.e.*, by a block copolymer involving two blocks differing only by deuteration (Fig. 1a). Figure 1b shows a very simplified model that could explain the experimental result. If the actual folding of the chain corresponds to what has been drawn, the system would not scatter at all. Fortunately, if there is folding there are no reasons to permit only contacts between the H and the D monomers to occur: the contacts will be formed at random. In this case, some scattering will occur and this paper sets out to evaluate the amount of scattering which, compared to

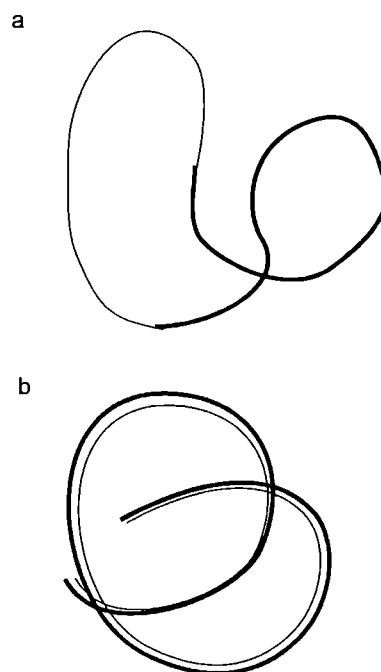


Fig. 1. The ring polymer deuterated (heavy line) and ordinary (light line): (a) assuming Gaussian behavior, (b) folded

experimental results, would speak in favor of such a conformation.

The main problem to make experiments with neutrons is to prepare samples. Fortunately, preparation of this type of block copolymer is not difficult. Starting with a di-functional living initiator in anionic polymerization the reaction is begun with ordinary styrene and completed with an identical quantity of deuterated styrene. This yields a polymer having two living ends. They are joined together by the addition of a di-functional agent. Low concentrations should be used in order to minimize a polycondensation reaction, which is always present and leads to high- M linear polymers. To obtain rings as clean as possible, tedious fractionation must be carried out, involving successive precipitation controlled by Size Exclusion Chromatography (SEC). A narrow peak is assumed to indicate that the polymer is clean. This is not sufficient, however; recent experiments made with another type of chromatography have shown that, even with a narrow peak produced by SEC, some linear polymers continue to persist.

THE MODEL

The objective of this study is to evaluate, in terms of a simple model, the amount of scattering produced by a molecule compacted as required by the reptation theory. Many types of compaction can be imagined, the simplest type is represented in Fig. 1b. Should the molecules obey this model, there would be no scattering because all the scattering objects have the same scattering

length per unit volume, $\frac{a+b}{2}$, where a and b are the scattering lengths of the two monomers. Practically, the situation is as schematized in Fig. 2.

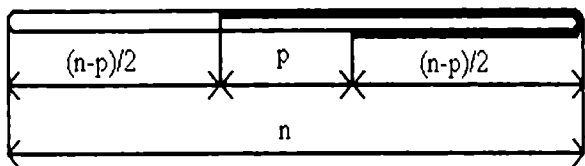


Fig. 2. One possibility of folding a block copolymer chain

The chain is assumed to consist of n D and n H monomers; p is the part of the double chain where H and D monomers follow side by side. With this hypothesis, the ring copolymer may be supposed to be a terpolymer: one block H; one block D; and one block HD. It is evident that the folding point can be anywhere on the chain; if $p = 0$, the chain is reduced to a two-block copolymer: if $p = \frac{n}{2}$, the polymer is no longer a homopolymer, because all the segments are HD monomers and there is no scattering.

THE SCATTERING EQUATION

As evident from Fig. 2, the system may be considered a three-component system, or a three-block copolymer; the central block has a scattering length $(a+b)$ and the two end blocks are $2a$ and $2b$ long, respectively. A general equation has been given in terms of the Random Phase Approximation of de Gennes [3]; it takes into account all the interaction coefficients and, even if an equation exists valid for this problem, it is difficult to handle. In the present model, we assume the interaction parameters χ defined by Flory [5] as interactions between the different entities, *i.e.*, between the H and the D monomers, to be so small as to be negligible.

Fortunately, there is a much simpler way to obtain the result. Even for a copolymer comprising three different blocks one can assume that the middle block, which has the average composition of the sample, behaves like a solvent. This analogy with a solution of the copolymer in a matrix 50/50 of H and D monomers allows to treat the problem as the scattering by a two-block copolymer in a solvent which has the same average scattering length, in this case $(a+b)$, and to take for the scattering object the contrast factor, *i.e.*, the difference between the scattering length of the object and the solvent defined as:

$$\alpha = 2a - (a+b) = a - b, \quad \beta = 2b - (a+b) = b - a = -\alpha$$

This procedure has been introduced by C. E. Williams *et al.* [6]. Moreover, if the system is assumed to be incompressible, there is a general rule proposed by Benoît

and Jannink [7] which makes the calculations simpler provided either one of the constituents is used as a solvent or a fictitious solvent is used, having the average scattering length of the system.

Generally, the scattering equation is:

$$I(q) = \sum \sum \alpha_i \alpha_j \left\langle \exp\left(-i \vec{q} \cdot \vec{r}_{ij}\right) \right\rangle \quad (1)$$

where the summation is extended over all the pairs of scattering objects (excluding the solvent) at the distance r_{ij} . The equation is split into three terms: one for the couples HH for which $\alpha_i \alpha_j = \alpha^2$, another for the pairs DD (contrast α^2), and the third (pair HH-DD) with contrast $-\alpha^2$. The middle part which, by following our method, has a zero scattering contrast, does not scatter and we are left with the expressions corresponding to the HH, DD and HD of the labeled blocks.

$$i(q) = \frac{1}{N} I(q) = \alpha^2 (nu)^2 [S_{HH}(q) + S_{DD}(q) - 2S_{HD}(q)] \quad (2)$$

where N is the number of molecules in the sample, S_{HH} , S_{DD} and S_{HD} are the structure factors of the sequences HH, DD, and HD, respectively. It is the sum of the phase factors over all monomers and all molecules that is divided by $nu = \frac{1}{2}(n-p)$ in order to normalize the structure factors S . The symmetry of the system gives $S_{HH} = S_{DD}$.

Hence $i(q)$ becomes:

$$Ni(q) = 2(\alpha nu)^2 [S_{HH}(q) - S_{HD}(q)] \quad (3)$$

$$\text{where: } u = \frac{n-p}{2n}$$

CALCULATION OF S_{HH}

Evaluation of this double sum proceeds by first supposing that a pair of points is taken on one molecule, and then the average value of the terms corresponding to it is evaluated. Averaging over all the orientations gives the quantity $P(q)$, normalized to 1 for $q = 0$:

$$P_{HH}(q) = \frac{1}{(nu)^2} \sum_{i=1}^{nu} \sum_{j=1}^{nu} \left\langle \frac{\sin(qr_{ij})}{qr_{ij}} \right\rangle \quad (4)$$

There is a second term corresponding to the case where i and j are on two different units; we define it by the factor $Q(q)$ which is:

$$Q_{HH}(q) = \frac{1}{(nu)^2} \sum_{i=1}^{nu} \sum_{j=1}^{nu} \left\langle \frac{\sin(qr_{ij})}{qr_{ij}} \right\rangle \quad (5)$$

The combination of the above equations gives:

$$S_{HH} = (nu)^2 [P_{HH}(q) + NQ_{HH}] \quad (6)$$

P_{HH} is called the form factor of the polymer; in this case this is the form factor of a linear polymer of nu monomers having α as the contrast factor.

S_{HD} is a little more complex. The monomers H and D belonging to the same molecule produce a special form

factor which is called P_{HD} . If the monomers H and D are on different molecules, another term is obtained which is called Q_{HD} . The symmetry of the figure provides that

$$Q_{HH} = Q_{DD} = Q_{HD} \quad (7)$$

With equation (4) the Q -terms disappear and the final result is:

$$i(q) = 2(aun)^2 [P_{HH} - P_{HD}] \quad (8)$$

Now the form factors P_{HH} and P_{HD} have to be evaluated. Debye's classical result allows to write

$$P_{HH} = \frac{2}{(xu)^2} (xu - 1 + \exp(-xu)) \quad (9)$$

where: $x = \frac{q^2 b^2 n}{6}$; b is the length of the statistical element of the chain.

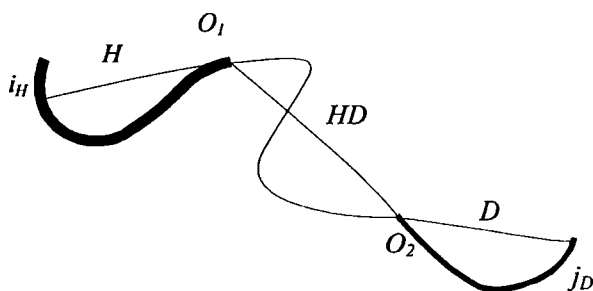


Fig. 3. Illustration for evaluation of term P_{HD}

To evaluate the P_{HD} term, use is made of Fig. 3.

P_{HD} is the sum over all pairs of points i_H and j_D of the average value of the quantity $\langle \exp(-\vec{i}_q \cdot \vec{r}_{ij}) \rangle$ where the vector \vec{r}_{ij} can be written as the sum of three vectors

$$\vec{r}_{i_H j_D} = \vec{i}_H \vec{O}_1 + \vec{O}_1 \vec{O}_2 + \vec{O}_2 \vec{j}_D \quad (10)$$

These three vectors are independent; the average $\langle \exp(-\vec{i}_q \cdot \vec{r}_{ij}) \rangle$ over all the configurations is the product of the averages on each vector:

$$\begin{aligned} \langle \exp(-\vec{i}_q \cdot \vec{r}_{ij}) \rangle &= \exp \left(- \left(\frac{q^2 \langle \vec{i}_H \vec{O}_1 \rangle^2}{6} \right) \right) \\ &\cdot \exp \left(- \left(\frac{q^2 \langle \vec{O}_1 \vec{O}_2 \rangle^2}{6} \right) \right) \exp \left(- \left(\frac{q^2 \langle \vec{O}_2 \vec{j}_D \rangle^2}{6} \right) \right) \end{aligned} \quad (11)$$

The value of the central term is evident:

$$\langle \vec{O}_1 \vec{O}_2 \rangle^2 = \exp \left(\frac{q^2 b^2 p}{6} \right) = \exp \left(- \frac{p}{n} x \right)$$

The others are obtained by simple integration of i or j going from zero to u .

Altogether these calculations give:

$$P_{HD} = \exp \left(- \frac{px}{n} \right) \left[\frac{1 - \exp(-xu)}{xu} \right]^2 \quad (12)$$

The combination of eqs. (8), (9) and (12) leads to

$$\begin{aligned} i(q) &= 2(a-b)^2 \left\{ \frac{1}{x^2} [2(xu - 1 + \exp(-xu))] + \right. \\ &\quad \left. - \exp \left(- \frac{px}{n} \right) [1 - \exp(-xu)]^2 \right\} \end{aligned} \quad (13)$$

This result was obtained by a simple method in which the interaction parameters χ_{HH} , χ_{DD} , and χ_{HD} are ignored. These parameters can be taken into account if a more complete formula proposed by Benoit *et al.* [8] is used. However, since we know nothing about the values of these parameters we may, to a first approximation, neglect their effects. If all the interactions are assumed to be expressed by only one parameter χ , a very simple argument shows that:

$$\frac{(a-b)^2}{i(q)} = \frac{1}{2u^2 (P_{HH} - P_{HD})} - 2\chi \quad (14)$$

As expected, eq. (13) shows that, at small q the scattering is zero and that:

$$i(q) = 2u^2 \left[\frac{2}{3} u + \frac{p}{n} \right] x \quad (15)$$

This equation allows to obtain the apparent radius of gyration. As evident from Fig. 2, this radius increases as p is increased. At a given value of p (or u since $u = \frac{1}{2} - \frac{p}{2n}$), the scattering function can be now evaluated. It is evident that all the u -values between 0 and 1/2 are equally possible and that the only result to be expected is its average value over all conformations. This average value is simply obtained by integrating eq. (13) over u between 0 and 1/2, and dividing by 1/2.

$$\begin{aligned} \langle i(q) \rangle &= \frac{2(a-b)^2}{x^2} \int_0^{1/2} \left[2(xu - 1 + \exp(-xu)) + \right. \\ &\quad \left. - \exp \left(- \frac{px}{n} \right) [1 - \exp(-xu)]^2 \right] du \end{aligned} \quad (16)$$

To integrate this quantity, $\frac{p}{n}$ must be replaced by the quantity $(1-2u)$. This leads to:

$$\langle i(q) \rangle = (a-b)^2 \frac{x^2 - x \left(1 + \frac{1}{2} e^{-x} \right) + \frac{3}{2} (1 - e^{-x})}{x^3} \quad (17)$$

Expansion around $x = 0$ gives:

$$\langle i(q) \rangle = (a-b)^2 \left\{ \frac{x}{48} - \frac{x^2}{120} + \frac{x^3}{480} + O(x^5) \right\} \quad (18)$$

At $q = 0$, the result is $\langle i(q) \rangle = 0$, as expected.

DISCUSSION OF RESULTS

Figure 4 shows the curve representing eq. (17), i.e., $\langle i(q) \rangle$ as a function of the scattering vector q . As usual, the

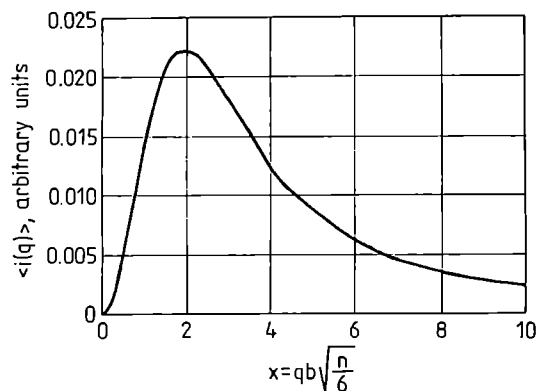


Fig. 4. The average scattering $i(q)$, in arbitrary units, obtained for the model

maximum occurs in the vicinity of $\sqrt{2}$. It is interesting now to compare the results obtained with the present model with the simple result one would get if the chain were purely Gaussian. The behavior of this kind of ring has been evaluated by using the formula:

$$i(q) = P_{HD} - P_T$$

The P_T form factor of the ring has been evaluated by Casassa (9) and P_{HD} by Kosmas *et al.* [10]

$$\langle i(q) \rangle = \frac{2}{x^2} - \frac{2}{x} \exp\left(-\frac{x}{2}\right) - \frac{2}{\sqrt{x}} \exp\left(-\frac{x}{4}\right) \int_0^{\sqrt{x}} e^{-x^2} dx \quad (19)$$

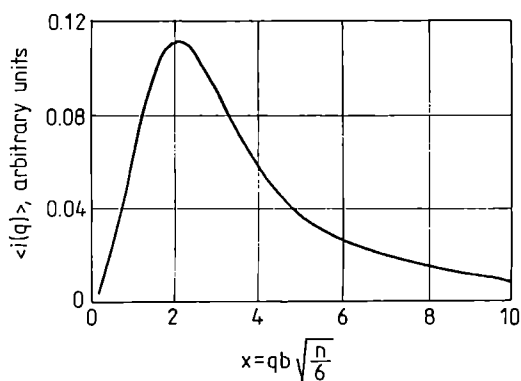


Fig. 5. Scattering by a two-block ring copolymer

and the resulting graph is shown in Fig. 5.

At first sight, the two figures look very similar, but in absolute values, if they can be measured, the associate block copolymer is seen to scatter much less intensely than the Gaussian copolymer. This result is expected because it has less contrast than the Gaussian one and can be easily generalized to any type of association.

This is merely a model but, even if very crude, it shows scattering experiments carried out with copolymers, rather than with completely deuterated rings, to bring information difficult to obtain otherwise.

The last remark concerns the kinetics of compaction. It seems that, if the bulk sample is prepared with no external constraint, there is no reason to expect the behavior to be different from that of the regular chains, which means that the Gaussian statistics should be obeyed and scattering should follow eq. (19).

If the sample is then exposed to a shear gradient, its conformation must change to assume a more condensed state. If an experiment of this type could be performed to study neutron scattering while the sample is being elongated, a drastic change in the scattering intensity should occur which could give information not only on the nature of the transformation but also on its kinetics.

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