

On the scattering of neutrons by polymers at high scattering angles

Henri Benoît

Centre de Recherches sur les Macromolécules (C.N.R.S. - U.L.P.)
6 rue Boussingault 67083 Strasbourg Cedex (France)

Abstract

In the case of Gaussian chains, in solution or in bulk the expansion of the form factor at large q gives a term in q^{-2} which allows the determination of the statistical element and a term in q^{-4} which depends only on the structure of the chain (presence of cross-links, branches, loops etc. One can evaluate this term for all the branched structures being able to take into consideration the polydispersity. One gives the result for simple rings and a general formula for simple networks. The same methods can be used for block copolymers. An example shows that this formulation allows to measure the kinetics of transesterification.

Introduction

During the last twenty years Neutron Scattering has been a very important method for the characterisation of polymeric materials⁽¹⁾. It did allow not only to obtain experimental results not accessible by any other technique but also to verify and to suggest new theoretical approaches. This technique has been partially responsible of the vigorous increase in our comprehension of the properties of polymeric systems^(2,3).

If one looks in details the experimental results and their interpretation one realises that the majority of the experiments have been devoted to what has been called the small angle domain where qR is small. In this expression R is the radius of gyration of the molecules and q the modulus of the scattering vector i.e. the quantity $(4\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength of the neutrons and θ the observation angle. The behaviour at large values of q has been much more rarely utilised in the field of polymers and this for two reasons ; first, in the domain practically accessible to the small angle scattering technique, the intensity follows, at large q , the law $I(q) \approx q^{-D}$, calling D the fractal dimension of the scattering object. For polymers $D = 2$ if the chain follows the Gaussian statistics. In the general case one writes $D = 1/\nu$, calling ν the exponent of the relation $R = kN^\nu$ between radius of gyration and molecular weight ; as it is well-known ν is equal to .6 in the frame of the Flory⁽⁴⁾ theory.

Moreover the experiments are difficult in this range of q since the signal is of the order of magnitude of the noise and requires long exposures.

In the first part of this paper we would like to show qualitatively why a careful investigation of the intensity in the high q region provides information about the detailed configuration of the chains ; in the second part we shall discuss the effect of polydispersity, branching, cross-links and even the existence of networks on the scattering of homopolymers and copolymers in solution or in bulk. These considerations will essentially be of theoretical nature therefore, in order to show that these theories can be used by experimentalists, we shall give a brief description of the phenomenon called the transesterification and show why neutron scattering is probably the best method to study this reaction in a polymer melt.

1) The general method

a) A qualitative analysis

It is evident that, since the scattering intensity considered as a function of the scattering vector q is the Fourier transform of the pair distribution of the scattering centres, q space and r space are conjugated. In other words one can go from the scattering object (in the space r) to its diffusion pattern (in the space q) by a Fourier transformation. This means that to small q values correspond large r values and vice versa. Looking at a scattering diagram as function of q is just like looking at the scattering object with a magnifying glass of changing power and making afterwards a Fourier transform. When the power increases the field decreases and is of the order of q^{-1} . In this discussion we shall assume that we are studying a dilute solution or a system in which the scattering diagram is completely described by the form structure factor ; we shall generalize these results to any system later.

Working at low q is equivalent to using a low power magnifying glass. In this situation each molecule is practically a point and the only thing one can do is to count the number of points which is equivalent to a measure of the molecular weight. If the solution is more concentrated one can show that neutron scattering gives $\overline{\Delta N^2}$ which, for an ideal solution, is equal to N . To summarize the situation : at $q = 0$ one measures only thermodynamic aspects of the solution and one does not obtain any information about its structure.

If we increase q in order to have q^{-1} of the order of the radius of gyration the molecules are no more point like and what one sees is approximately represented in diagram II. One does not see the details of the shape and the structure of the molecules but only their dimensions. It was shown by Guinier that, in this domain, one measures the radius of gyration.

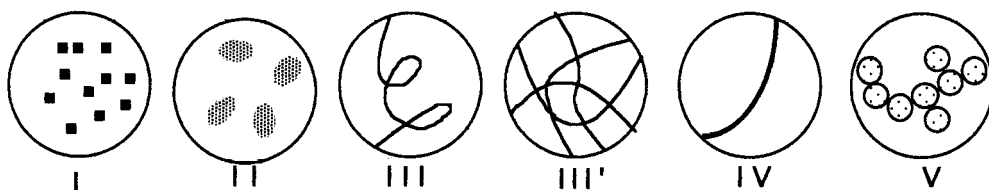


Figure 1 : Schematic representation of the different q domains

If we increases q still further we reach either domain III or III' depending on the concentration : diagram III corresponds to dilute solution, diagram III' to moderately concentrated solution called semi-dilute by de Gennes (1979)). From diagram III it is clear that one sees only a part of a molecule : the scattering does not depend on molecular weight and one obtains information about the statistics of the chain and its persistence length. If the solution is concentrated (diagram III') one sees parts belonging to different chains and one obtains information about the length of the chain which separate two contact points (called the correlation length). Increasing q will leave only one part of one chain in the field. (diagram IV) and if the chain has lateral dimensions small compared to the longitudinal ones it will look like the chain of statistical mechanics.. If the persistence length is large compared to q^{-1} and if the diameter of the cylinder containing the side groups is small enough one will observe a behaviour typical of a rigid rod.

For still larger values of q (diagram V), q^{-1} becomes of the order of the length of the chemical bonds, the local structure of the chain begins to play a role. One is no more in the small angle scattering range and one of difficult problems

which will not be discussed here is to know the exact range of q 's to which the theories summarized in the next part of this paper can be applied.

From this analysis a few conclusion can be deduced :

At large q (diagram III or III' and IV) the scattering intensity does not depend on the molecular weight. The length of the chain is detected only by the effects of chain ends. The probability of observing one of them in the field of observation decreases when q increases. For large q it is a rare event (specially for large molecular weights) which does not affect the results. Neutron scattering gives, in this range, information which is independent of the chain length, polydispersity and even concentration as long as the average distance between two chains is large compared to q^{-1} . In this range, one does not need to extrapolate at zero concentration and the scattering depends only on the nature of the chains.

For many reasons the limits between the different domains which are discussed here and have been arbitrarily fixed at R , the radius of gyration and λ the statistical element of the chains are not precise. One should, to be correct, speak about "cross over" regions where the dominant factor influencing the scattering changes continuously.

To summarize this discussion one can say that for a single linear chain there are three distinct domains 1) the zero angle and the Guinier domain where one can measure the molecular weight and the radius of gyration (R_g), at least for dilute solutions. 2) The intermediate domain $1/R_g < q < 1/\lambda$ where the scattering depends only on the chain statistics and sometimes a third domain $1/\lambda < q$ where, if the monomer is thin enough, the chain behaves like a rigid rod. .

b) The general equation

We have, until now, considered chains with fractal dimensions D saying only that scaling arguments show that, for these chains, in the q range characterised by diagram IV, $I = Cq^{-D}$. The value of the constant C , which depends on the concentration and the scattering length of the monomers, is a classical result for rods, Gaussian chains, and chains with excluded volume and will not be discussed here.

If we consider an asymptotic expansion of $I(q)$ at the high q limit it is evident that, in order to go from diagram IV to diagram III one has to add a new term in the expression of $I(q)$. This problem is difficult in the case of chain with excluded volume since it seems that the simple expression used by Loucheux, Weill and Benoît is not valid. It has been solved for rods but in this lecture we shall limit our attention to the case of Gaussian chains. Introducing the quantity $S(q) = I(q) / a^2 c$ one can write, following Debye⁽⁵⁾

$$S(q) = NP(q) = \frac{2}{\mu^2 N} [\mu N - 1 + \exp(-\mu N)] \quad (1)$$

calling a the contrast factor of the monomer, N the number of monomers in the scattering volume and μ the quantity $q^2 b^2 / 6$ where b is the statistical length or the Kuhn segment.

At high q this reduces to :

$$S(q) = \frac{2}{\mu} - \frac{2}{N\mu^2} \quad (2)$$

The first term gives the asymptotic behaviour and depends only of the statistical element . The second term gives N the molecular weight. One can

explain qualitatively why the second term, which is a correction due to the finite value of N since it disappears for $N = \infty$ decreases the scattered intensity. This is due to the end effects. Each time the magnifier of figure 2 meets an end (Fig. 2b) the scattering diminishes. This term is therefore proportional to the number of chain ends and allows in a polydisperse system the measurement of this number which is equivalent to the number average degree of polymerization N_n . If we compare this result with the result of a f arms star made of identical branches of n segments, we obtain at large q :

$$S(q) = \frac{2}{\mu} + \frac{f-3}{n\mu^2} \quad (3)$$

One sees that for $f=2$ one recovers Eq. 2. The second term which will be called z' writing equation 3 on the general form :

$$S(q) = \frac{2}{\mu} + \frac{z'}{n\mu^2} \quad (4)$$

has a sign which changes for $f=3$. If f is larger than 3 the presence of the cross-link points increases the scattering intensity and suppresses the negative contribution of the chain ends.

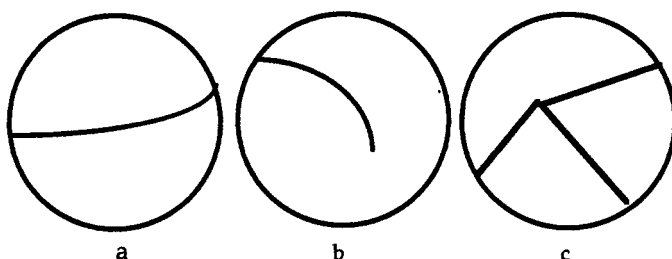


figure 2

a) Infinite chain, b) Influence of a chain end, c) Influence of a cross-link

More generally the problem we want to discuss is the calculation of the parameter z' as a function of the structure of the chain, i. e. the existence of branches, rings and the case of networks. Before doing so it is interesting to discuss the experimental methods one can use to evaluate experimentally the value of the parameter z' .

c) The experimental determination of the parameter z' .

The first method can be the use of what is called the Kratky plot where one plots $q^2 S(q)$ or $q^2 I(q)$ as a function of q^2 . This gives to Eq.4 the form :

$$q^2 S(q) = \frac{12}{b^2} + \frac{36z'}{nb^4 q^2} \quad (5)$$

If one uses this type of diagram one obtains the curves represented on figure 3 (1). If z' is negative one obtains e diagram (a) if it is positive diagram (b). One other way of representing the data uses the Zimm-plot, where, this time $S^{-1}(q)$ is plotted as a function of q^2 as in figure 3(2). The corresponding equation is :

$$S^{-1}(q) = \frac{q^2 b^2}{12} - z \quad (6)$$

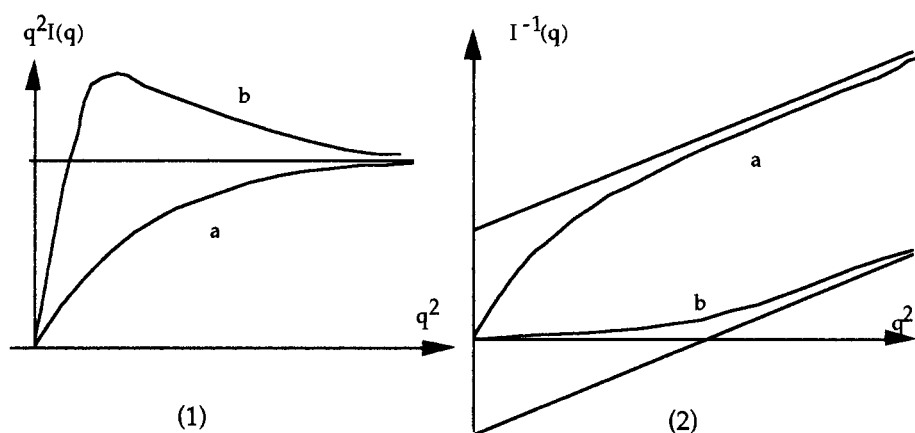


figure 3 : 1) Kratky plot and 2) Zimm -plot

$$\text{with } z = \frac{z'}{4N}$$

All the curves corresponding to the same type of chains have the same asymptotic slope ; the asymptotes are parallel. c is the intercept of these asymptotes with the y axis. The diagram a of figure 3;2 corresponds to c negative and the diagram b to c positive. Since this experimental determination is easy it is worth to examine in more details the theoretical interpretation.

II) The case of branched polymers

Let us consider a chain molecules made of s branches of the same length n ($N = sn$), defining a branch as a linear chain going from one cross-link to another one or from one cross-link to a free end. This chain has c cross-links of functionality f . This means that f branches start from each cross-link point. It is also assumed that no ring structures is present : the structure of the chain is thus that of a Coyle tree. As it has already been shown the calculation of the asymptotic value of $S(q)$ is not difficult . Calling $s_i(q)$ the term corresponding to the branch i and $s_{ij}(q)$ the cross-term corresponding to the interferences between branches i and j one can write :

$$NS(q) = \sum_i n_i s_i(q) + \sum_i \sum_j s_{ij}(q). \quad (7)$$

The contribution of $s_i(q)$ is the contribution of a linear chain. The term $s_{ij}(q)$ vanishes at large q if the chains i and j are not connected. One has just to evaluate the number of connected pairs ($cf[f-1]$), each one contributing for $1/\mu^2$. This leads to⁽⁶⁾ :

$$S(q) = \frac{2}{\mu} + \frac{cf(f-1)}{sn\mu^2} - \frac{2}{n\mu^2} \quad (8)$$

and in the Zimm representation :

$$\frac{1}{S(q)} = \frac{\mu}{2} - \frac{1}{4n} \left[\frac{cf(f-1)}{s} - 2 \right] \quad (9)$$

since the numbers s , c , f are related by the equation $s-1 = c(f-1)$ one obtains the final result:

$$S(q) = \frac{2}{\mu} + \frac{1}{n\mu^2} \left[f-2 - \frac{f}{s} \right] \quad (10)$$

or, using the inverse :

$$S^{-1}(q) = \frac{\mu}{2} - \frac{1}{4n} \left[f-2 - \frac{f}{s} \right] \quad (11)$$

If the number of branches is large, as in the case of low density polyethylene, f/s can be neglected and Eq. 11 becomes :

$$S^{-1}(q) = \frac{\mu}{2} - \frac{1}{4n} [f-2] \quad (12)$$

Before being able to use these equation for the characterisation, of polymers one has to study the effect of polydispersity.

It is difficult to take into account the simultaneous polydispersity of the length of the branches, the functionality and the number of branching points which means that each case requires a special discussion. One could give a general formula but it is more interesting to look at the simple case of low density polyethylene. In this case one can say that $f = 3$ since $f = 2$ corresponds to no branch; Assuming the main chain to be long one obtains :

$$S(q) = \frac{2}{\mu} + \frac{1}{\bar{n}\mu^2} \quad (13)$$

calling \bar{n} the number average length of the branches.

This result is extremely simple and it would be interesting to check it experimentally since this method is the only one able to give a direct estimation of the length of the branches.

The domains of application.

We are now able to discuss the form factor of branched molecules and the question is to know the cases where one can use the formulae we have established. Since, if one uses the Random Phase Approximation of de Gennes⁽²⁾, which is the most used interpretation method, the q dependence appears only by the use of the form factor of the different constituents, it is legitimate to use the approximation which has been proposed in all the cases where R.P.A. is valid.

III) The case of block copolymers.

One assumes that the copolymer is made of two types of units, A and B and that they have the same statistical element (this requires just to change adequately the definition of the degree of polymerisation N_a or N_b). The form factor of such a copolymer changes with the contrast factor of the parts A and B and depends of three terms : the form factor of the part A which will be called $P_{aa}(q)$ the form factor of the part B called $P_{bb}(q)$ and a cross-term :

$$P_{ab}(q) = \frac{1}{N_a N_b} \sum_{i a} \sum_{j b} \exp\{i\mathbf{q} \cdot (\mathbf{r}_{i a} - \mathbf{r}_{j b})\} \quad (14)$$

corresponding to interferences between scattering points A and B.

The calculation of $P_{aa}(q)$ is identical to what has been done in the case of homopolymers and gives, in the frame of our hypothesis, the result of Eq. 8 :

$$N_a P_{aa}(q) = \frac{2}{\mu} + \frac{c_a f_a (f_a - 1)}{s_a n_a \mu^2} - \frac{2}{n_a \mu^2} \quad (15)$$

calling this time s_a the number of branches A of length n_a , f_a the functionality corresponding to the A branches and c_a the number of cross-link points. The result has the same form for the part B and the only problem is the evaluation of the cross-term $P_{ab}(q)$.

Since two interfering points are never on the same branch one sees that the first term $2\mu^{-1}$ in Eq.15 is absent. The only term which has to be evaluate is the μ^{-2} term . It is the sum of the $f_a f_b$ contributions of the junctions where f_a branches A meet f_b branches B. This can be written formally as :

$$(N_a N_b)^2 P_{ab}(q) = \sum \frac{2c_i f_{ai} f_{bi}}{\mu^2 n_a n_b} \quad (16)$$

Sometimes one can use the following method : if one considers the copolymer as an homopolymer one can express the total form factor as the following sum :

$$(N_a + N_b)^2 P(q) = N_a^2 P_a(q) + N_b^2 P_b(q) + 2N_a N_b P_{ab}(q) \quad (17)$$

The calculation of the scattering in the general case is to complicate to be presented here and we shall give only one example : the linear multiblock copolymer in bulk⁽⁷⁾



figure 4

The copolymer is made of $2s$ blocks ($s_a = s_b$), each of them comprising n_a monomers a and n_b monomers b. Following the notations of Benoît and Hadzioannou we introduce $n = n_a + n_b$ and the quantities u and v such as $n_a = un$ and $n_b = vn$ ($u+v = 1$).

Using Eq. 15 one obtains for $P_{aa}(q)$ or $S_{aa}(q)$:

$$S_a(q) = \left[\frac{2}{\mu} - \frac{2}{n\mu^2} \right] = \frac{2}{\mu} \left(1 - \frac{1}{n\mu} \right) \quad (18)$$

$S_b(q)$ is obtained replacing a by b and u by v.

The direct calculation of $S_{ab}(q)$ is tedious and we use Eq. 17 which takes the form :

$$P(q) = u^2 P_a(q) + v^2 P_b(q) + 2uv P_{ab}(q) \quad (19)$$

The use of Leibler⁽⁸⁾ expression for the scattered intensity of a two types of blocks copolymer in bulk leads, when there are no interactions, to :

$$S(q) = \frac{2uv}{\mu} \left\{ 1 - \frac{1}{\mu n} \left[\frac{1}{u} + \frac{1}{v} - \frac{1}{s} \right] \right\} \quad (20)$$

This formula can be obtained starting from the value evaluated for the whole copolymer.

If the system is polydisperse the only polydispersity which has to be taken into account is the polydispersity of the length of the segments and one can show that one obtains, using this time the inverse form :

$$\frac{1}{\bar{S}(q)} = \frac{\mu}{2uv} + \frac{1}{4(uv)^2} \left[\frac{1}{\bar{n}_a} + \frac{1}{\bar{n}_b} - \frac{1}{\bar{N}} \right] \quad (21)$$

calling \bar{N} , \bar{n}_a and \bar{n}_b the number average molecular weight of the polymer and of the blocks A and B. If the number of blocks is large \bar{n}_a and \bar{n}_b are smaller than \bar{N} and the last term can be neglected making the measurement of \bar{n} possible. It is interesting to note that when the distribution of the blocks A and B is the most probable distribution $n_w/n_n = 2$ the straight line of Eq. 21 in the $S^{-1}(q)$ representation gives the scattering curve for any value of q . This is the generalisation of a classical result on homopolymers, obtained by Zimm who showed that, if $M_w/M_n = 2$, $S^{-1}(q)$ is a linear function of q^2 .

IV) Chains with loops

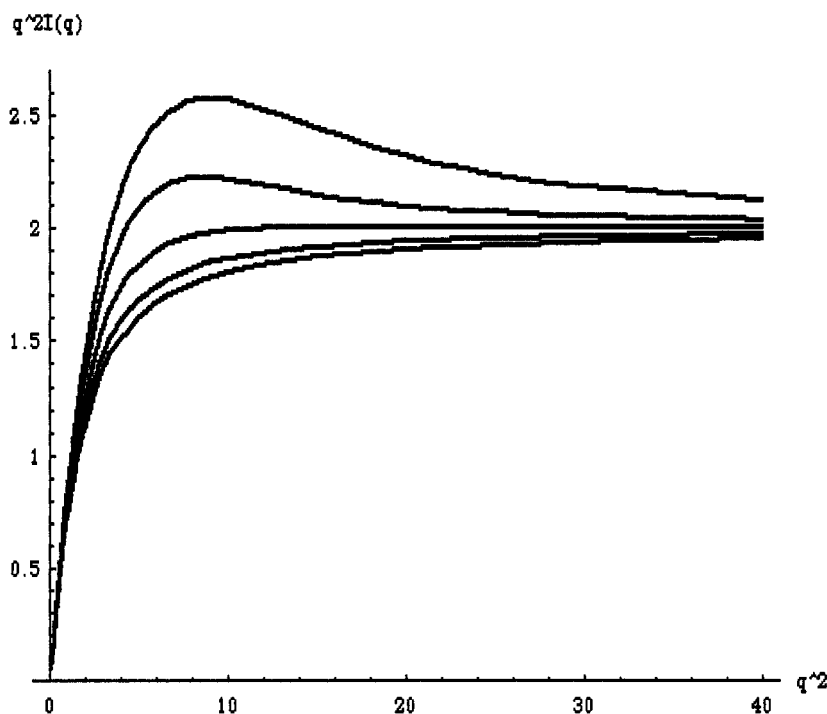


Figure 5 The quantity $\mu P(\mu x)$ in arbitrary units for different values of the parameter z . Going from top to bottom one has successively $z = 1, 0.8, 0.5, 0.2, 0$.

Until now we have only consider chains where there is only one way to go from one point to another. If one wants to generalize the preceding paragraphs to chains presenting loops one has first to evaluate the large angle scattering by a Gaussian chain forming a ring. This has been done by Casassa⁽⁹⁾ obtaining :

$$S(q) = \frac{2}{\mu} + \frac{4}{\mu^2 N} \quad (22)$$

One recovers the Gaussian μ^{-1} term but the second term which, following our qualitative discussion should be zero is positive and identical to what has been evaluated for a four arms star. Instead of evaluating the total ring

one can calculate the scattering by a segment of n statistical units in a ring of N segments. This calculation has been done by Kosmas and al.⁽¹⁰⁾ which obtain:

$$S(q) = \frac{2}{\mu} + \frac{2}{\mu^2 n} \left(2 \frac{n}{N} - 1 \right) \quad (23)$$

When N is infinity one recovers the linear chain and when $z = n/N = 1$ the complete ring. Figure 5 illustrates this result showing, in the Kratky representation, the quantity $\mu S(q)$, for all values of q , as a function of μ for different values of $z = n/N$. One sees that the maximum which is clearly visible for $z = 1$ disappears as soon as z becomes smaller than $1/2$.

These formula should allow, in principle to evaluate the scattering by one segment of a cycle if one knew the quantity $N-n$ i. e. the length of the chain equivalent to the network.

Another quantity which is needed to make calculation for networks is the cross-term $P_{ab}(q)$ characterizing the interferences between a segment and a contiguous ring, as in figure 6 :

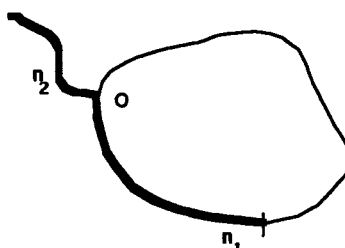


figure 6 a linear chain grafted on a cycle

As expected, there is no term in μ^{-1} and one obtains :

$$P_{12}(q) = \frac{1}{n_1 n_2 \mu^2} \quad (24)$$

which is identical to the result obtained in the absence of cycles. This suggests that, regardless of the structure of the network the contribution of the cross-terms is limited to the interaction between contiguous segments and has for value $1/n_1 n_2 \mu^2$.

V) Networks

These results show that the theory exposed in this paper in the case of polymers which can be described as a Cayley tree can be generalized to network but, without at the present time being able to give explicit formulae except in very simple cases. Fortunately a very simple argument based on the comparison of a Gaussian network with an electrical network of resistors by Kirkpatrick⁽¹¹⁾ allows, using simple hypothesis about the symmetries of the network, to derive the following formula⁽¹²⁾:

$$S(q) = \frac{2}{\mu} + \frac{2}{\mu^2 n} \left[2f - 1 - \frac{4}{f} \right] \quad (25)$$

calling f the functionality of the network, n the number average degree of polymerization of the elastic chains. The quantity μ is, as before, $q^2 b^2 / 6$. This formula assumes that all the junctions have f as functionality and that there are no pending chains or loops where both extremities of the same elastic chain are

bounded to the same cross link. This formula gives always a positive value to the second term which is normal by comparison with ring structures. Experimentally one observes often in Kratky plots this type of behaviour but, until now, no experimental verification has been tried.

In this review we have limited our discussion to the case of Gaussian chains in an isotropic medium forgetting the existence of interactions characterized by the parameter χ . One could introduce the term χ in all the equations which have been written but this is only possible if χ is small and does not perturb the Gaussian statistics of the chains. The extension of these results to chains under an anisotropic stress is possible⁽⁶⁾ as well as the extension to rodlike chains⁽¹³⁾ but it remains to show that this kind of result can be extended to chains with excluded volume⁽¹⁴⁾.

VI) Application to the problem of transesterification

In order to show that these theories can be used by experimentalist, I would like to discuss its application to the problem of transesterification discussed by Benoit, Fischer and Zachmann⁽¹⁵⁾

Let us assume that we have a mixture of two identical polyesters (for instance poly(ethylene terephthalate) one usual the other completely deuterated. The large angles neutron scattering signal is easily measured and be evaluate using Eq. 6 and the de Gennes theory giving :

$$\frac{uv}{i(q)b^2} = \frac{\mu}{2} + z \quad (26)$$

where u is the fraction of deuterated material and n_D , n_H and n_T the number average degree of polymerization of the deuterated polymer, the normal polymer and the mixture of both polymers. $i(q)$ is the intensity scattered per statistical element ; b is the contrast factor between deuterated and normal polymer and z the quantity :

$$z = \frac{1}{2} \left[\frac{1}{n_D} + \frac{1}{n_H} - \frac{1}{n_T} \right] \quad (27)$$

expression very similar to the result obtained on block copolymers in Eq.21.

Now if one heats this system in bulk the signal disappear after a time which depends on temperature. The mixture of the two polymers A and B is transformed in a polydisperse mixture of copolymers containing A and B blocks.

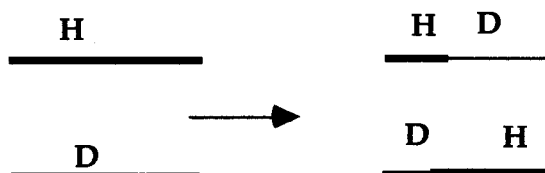


Figure 7 The first step of the transesterification reaction

The figure represents the first step of the reaction where the scission of one ordinary and one deuterated molecule forms two ,two blocks, copolymers. As soon as this process has begun on has to replace equation 27 by equation 21 obtaining for z :

$$z = \frac{1}{2} \left[\frac{1}{\bar{n}_D(t)} + \frac{1}{\bar{n}_H(t)} - \frac{1}{\bar{n}_T} \right] \quad (28)$$

where, this time, $\bar{n}_D(t)$ and $\bar{n}_H(t)$ are respectively the number average degree of polymerization of the blocks D and H. Since, after each scission, these averages diminish one obtains Zimm-plots similar to the diagram of figure 8 : the curves stay parallel but the intercept (z) increases as a function of time

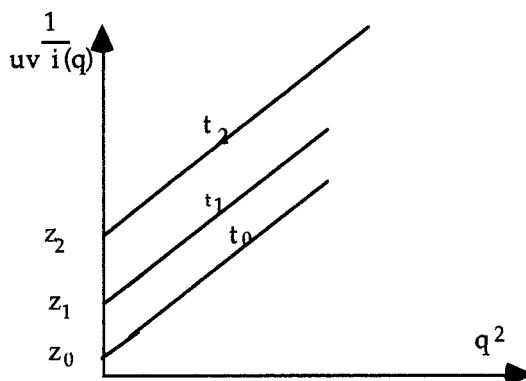


Figure 8. Evolution of the intensity scattered by a mixture of H and D homopolymers as a function of time $t_0 < t_1 < t_2$

Each time a scission of the type represented on figure 7 is produced, the number of chains of H and of D increases from one unit and after S scission one has :

$$\frac{1}{\bar{n}_D(t)} = \frac{1}{\bar{n}_D(0)} + \frac{S(t)}{N_D} \quad \text{and} \quad \frac{1}{\bar{n}_H(t)} = \frac{1}{\bar{n}_H(0)} + \frac{S(t)}{N_H} \quad (29)$$

calling N the total number of monomers and N_D , N_H the monomers D and H. The only parameter of the problem is therefore the number of scission as a function of time $S(t)$. This number is determined by application of the classical laws of chemical physics and one obtains :

$$S(t) = Nuv[1 - \exp(-\frac{1}{2}kNt)] \quad (30)$$

where k is the kinetic constant of the reaction which should depend exponentially of the temperature.

One can plot the intercept z as function of time and one obtains :

$$z(t) - z(0) = \frac{1}{2} [1 - \exp(-\frac{t}{\tau})] \quad \text{calling } \tau \text{ the quantity } \tau = 2/kN.$$

This method has already been applied to P.E.T. and other mesoionic copolymers. It has the advantage of being mostly sensible to the beginning of the reaction. If the number of scissions is equal to the number of molecules the quantity z is divided by 2 and easy to measure contrarily to other technique, which, in the case of large molecular weights, give only a weak signal.

Conclusion

I hope that these simple considerations can convince the specialists of neutron scattering that it is important and useful to study the large angle scattering. This is more difficult than the zero angle scattering but, if the

experiments are made correctly the interpretation is easier, since one has not to take into account the problem of aggregates and interactions, and can bring new information on the structure of polymers.

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