

SCATTERING BY A TWO BLOCKS COPOLYMER

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Abstract - A theoretical equation describing the intensity scattered by a two blocks copolymer at any concentration is described. One discusses in the first part its application in three cases a) the bulk taking into account the interaction between the sequences, b) the infinitely dilute solutions and c) at any concentration.

The general feature is the existence of a peak which depends on the second virial coefficient and disappears at a concentration depending on the contrast.

This peak can go to infinity : this means that the system undergoes a phase transition from an isotropic phase to a mesomorphic phase. Some neutron scattering results illustrating these theories are also presented.

INTRODUCTION AND THEORETICAL PART

In this paper I would like to discuss recent results which have been obtained on block copolymers in dilute solution, in more concentrated solution and in bulk. We shall assume that we are in the isotropic phase and we will not consider the case of mesomorphic phase or micellar solutions. During this study, we shall show what is the domain of isotropic phases and where the boundary between isotropic and anisotropic phase can be located.

The problem on which we shall focus our interest is the following. It is now well known that in bulk as soon as there is sufficient contrast between the two blocks, one observes a peak when one plots the scattered intensity as function of the scattering vector $q = (4 \pi \sin \theta/2)/\lambda$ [λ wavelength of the incident radiation, θ scattering angle] (1) More precisely at $q = 0$ $I(0) = 0$, I goes through a maximum for $qR \sim 1$ (R radius of gyration) and decreases going back to zero at large q . In dilute solution, the result depends on the coherent scattering length for neutrons, the refractive index for light or the density of the solvent. If the solvent is chosen in order to match the scattering from one sequence, one obtains a classical diagram with a continuous decrease of the intensity.

One must have therefore a drastic change in the scattering envelope as function of the concentration. This question can be answered in the general case even if one takes into account the polydispersity of the system and the presence of homopolymer. This general solution will be published later (2). In this paper I would like to limit the discussion to the case of the simplest copolymer : a two blocks copolymer A-B made of two chains of equal length but differing in nature. Each chain is made of n units having the same length b . For simplification we shall assume that they are Gaussians and that $R_A^2 = R_B^2 = nb^2$, calling R_A , R_B the radii of gyration of the blocks A and B. We shall not take into account the changes of R_A and R_B as function of concentration in this first approach.

We assume also that these units have the same volume v_s as a solvent molecule and that we have N chains per unit volume. The volume fraction occupied by the polymer $\psi_p = 2nNv_s = 2nN/N_T$ calling N_T the total number of sites ($N_T v_s = 1$).

With these notations, it is possible to write a general equation for $I(q)$, either using the random phase approximation method introduced by de Gennes (3) or a direct method which is a generalization of a procedure introduced by H. Benoît and M. Benmouna (2) (2')

$$I(q) = K N n^2 \frac{(a-b)^2 P + 4(a-s)(b-s)P_T + 4Nn^2 P_T (P-P_T) [(a-b)^2 v - 2(a-s)(b-s)w]}{1 + Nn^2 [4v P_T + 2w(2P_T - P)] - 4N^2 n^4 P_T (P-P_T) w(2v+w)} \quad (1)$$

In this expression K is a constant depending on the type of radiation used (light, neutrons, X rays), a , b and s are respectively the coherent scattering length of the monomeric unit A and B and the solvent s for light scattering, they are the refractive indices or more precisely $a - s = \frac{dn}{dc_A}$ $b - c = \frac{dn}{dc_B}$ calling $\frac{dn}{dc}$ the refractive index increment.

For X rays, a , b and s are respectively the electronic densities.

P is the structure factor of one block i.e. the quantity

$$P(q) = \frac{1}{n^2} \sum_i \sum_j \frac{\sin q r_{ij}}{r_{ij}}$$

where r_{ij} is the distance between two arbitrary segments on a block. $P(q)$ is normalized to unity for $q = 0$ and for a Gaussian chain is given by the Debye expression⁽⁴⁾

$$P(q) = \frac{2}{x} (x - 1 + \exp(-x)) \text{ with } x = q^2 R_a^2$$

$P_T(q)$ is the same expression but for the total chain : the summation is performed on the $2n$ scattering points.

The last things which have to be defined are the thermodynamical quantities v and w . We have assumed to reduce the number of parameters to two that both sequences have the same thermodynamical behavior relatively to the solvent. This means that they have the same theta point. In dilute solution v is the classical excluded volume parameter and is related to the second virial coefficient A_2 by the relation

$$v = 2A_2 m^2/N$$

where m is the molecular weight of the monomer and N Avogadro's number.

In concentrated solution, we can use the Flory Huggins theory of polymer solution and, as we have shown already, v is a function of concentration which can be written as^(2')

$$v = v_s \left(\frac{1}{\psi_s} - 2 \chi_{PS} \right)$$

where ψ_s is the volume fraction of the solvent and χ_{PS} , the Flory's interaction parameter⁽⁵⁾ between polymer and solvent. w is defined as

$$w = v_s \chi$$

where χ is the Flory's interaction parameter between an A and a B unit.

With these hypothesis, we need only the parameter χ_{PS} and χ in order to define the thermodynamics of the system.

If for $q = 0$ the denominator goes to zero this means that we are on the spinodal⁽³⁾. This equation therefore allows also to discuss the boundary between isotropic phases and ordered phase.

THE BULK

In order to study $I(q)$ in the bulk we have to let ψ_s go to zero and to look at the limit of $I(q)$. This is easily done by replacing v and w by their values. Multiplying both the numerator and the denominator by ψ_s and writing $\psi_s = 0$, one obtains after simplification and remembering that in the bulk $2n \psi_s \equiv N_T$

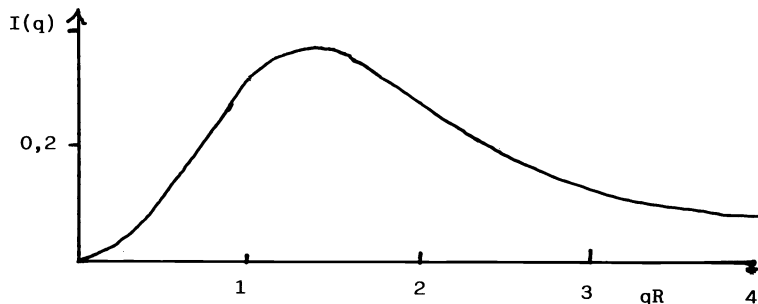
$$I(q) = K \frac{2n(a-b)^2(P - P_T)}{1 - n\chi(P - P_T)}$$

This formula is simpler in the reciprocal form

$$\frac{2nK(a-b)^2}{I} = \frac{1}{P - P_T} - \chi n$$

It has been obtained already by Leibler and Benoît⁽⁶⁾ for $\chi = 0$ and by Leibler⁽⁷⁾ in the general case. It is very similar to the formula written by de Gennes⁽³⁾ for mixtures. As was expected all the terms involving the solvent have disappeared.

The simplest case to which this formula can be applied is the case of the copolymer A-B where one block is hydrogenated and the other deuterated. In these circumstances one can assume that $\chi = 0$ and the scattered intensity is proportional to $P - P_T$. If the chain is Gaussian, this function has the following shape



having a maximum of 0,19 for $qR = 1,38$.

Similar curves have been observed by Duplessix et al. (1) but the maximum was less pronounced probably because of the polydispersity of the sample.

Now it is interesting to explore what happens when the incompatibility i.e. χ increases. The simplest way is to draw the family of curves $I(q)$ for increasing values of χ . One sees that the intensity of the peak increases very fast and that for χ of the order of 5,25 $I(q)$ becomes infinite for $qR = 1,38$. This is very peculiar. As we have already said if $I = \infty$ for $q = 0$, one is on the spinodal but here we have $I = \infty$ for a given value of q, q^* . This means that we go from an isotropic phase to a system where there are enormous fluctuations at a distance $d = 1/q^*$. This is probably the beginning of lamellar structures and a peculiar type of phase transition.

In order to see if it is possible to observe this effect we have made small angle neutron scattering experiments on the reactor of the National Bureau of Standards (Washington D.C.) in collaboration with W.L. Wu, B. Moser and B. Bauer. We had at our disposal a copolymer deuterated polystyrene polymethylmethacrylate made in Strasbourg of two blocks having approximately the same length. A film of 2mm thickness was cast and was looking isotropic under the polarizing microscope. We made experiments at 110-140° and 180°C. As we expected we did have a very large peak but unfortunately it did not change with temperature, probably because of a very small variation of χ with temperature. From this peak a very small value of χ , of the order of 10^{-3} , is to be expected. If one increases the molecular weight one should reach the lamellar structure. The interpretation of this peak is difficult. Frequently, when by X rays one maximum is observed, people claim that they have a poorly organized lamellar structure. We are proposing another interpretation which seems to be coherent with the fact that no other lines could be detected.

As a conclusion of this paragraph, we would like to make two remarks. The first is that the theory we are using for the interpretation of the result is only approximate. It is a mean field theory. The order of magnitude of χ for which the lamellar structure appears must be correct but the result giving $qd^* = 1,9$ should not be taken too seriously because it is known that the periodicity is proportional to something like $M^{1/3}$ and not $M^{1/2}$ as we obtain. The second remark concerns polydispersity: It has been shown by Leibler and Benoit (6) that the polydispersity displaces the peak toward small angle and even suppresses it. This has certainly an effect on the result we have discussed. If there is no peak $P - P_T$ will be a decreasing function of (q) and $I^{-1}(q)$ will be zero at $q = 0$ when χ increases. This means also a phase transition but probably between two isotropic phases.

INFINITELY DILUTE SOLUTIONS

Letting N go to zero, equation (1) gives for the intensity extrapolated at zero concentration $I(q) = K N n^2 [(a-b)^2 P + 4(a-s)(b-s)P_T]$ where P is the structure factor of one block and P_T the structure factor of the whole chain. From this expression one sees that the result depends on the solvent.

In order to see what clearly happens let us put on a χ axis the value of a and b abscissae of the points A and B. The solvent is represented by the point S ($OS = s$) and depending on the relative positions of A, B and S, one can have values of $(a-s)(b-s)$ with different sign and different relative values compared to $(a-b)^2$. Two cases are important:

1) $s = b$. The sequence b has the same scattering power as the solvent, it is not seen; one sees only the sequence a and the preceding equation becomes:

$$I(q) = K N n^2 (a-s)^2 P(a)$$

giving the structure factor of the sequence A.

2) One adjusts the solvent in order for s to be in the middle of the segment A B. One obtains

$$a - s = -s - b \quad a + b - 2s = 0 \text{ and}$$

$$I(q) = K 4 N n^2 (a-s)^2 [P(q) - P_T(q)]$$

This is exactly the same expression as for the bulk. The scattered intensity is zero for $q = 0$, has a maximum and goes back to zero at large q . Since there is no difference in this case between the scattered intensity from the bulk and the dilute solution, one could expect the shape of $I(q)$ to be independent of the concentration. Inspection of equation (1) shows that it is only the case if $w = 0$ i.e. if there are no interactions between the blocks A and B. In order to see the progressive changes when one changes s continuously it is more convenient to introduce the contrast factor $y = a-s/a+b-2s$, and the average coherent scattering length $v_0 = a+b-2s$.

$$I(q) = K N n^2 (v_0^2)^2 [(2y-1)^2 P + 4y(1-y) P_T]$$

It does not change when y is transform in $y' = \frac{1}{2} - y$.

The curves $I^{-1}(q)$ as function of q^2 for different values of y have been plotted by Ionescu et al. (10,11) in a recent publication. When y increases continuously the initial slope of $I(q)$ versus q^2 decreases, and becomes negative for $y > \frac{1}{2} + \sqrt{2}/2$. It means that we have a peak for

$$\frac{1 + \sqrt{2}}{2} < y < \infty \quad \text{or} \quad -\infty < y < \frac{1 - \sqrt{2}}{2}$$

and that the interapt decreases and goes to zero for $y \rightarrow \infty$

I shall not discuss here the effect of polydispersity or the method developed by Ionescu et al. (11) to determine if a chain obey or not to the Gaussian assumption.

CONCENTRATED SOLUTION

The discussion is more difficult since instead of having only one parameter to characterize the thermodynamical interactions we have now two parameters v and w . This is due to our initial assumption, in fact we should in the general case use three parameters v_a , v_b and w .

Let us first try to answer the initial question. We were interested in the value of the concentration for which the scattering diagram was changing its shape from a decreasing quantity as function of q to a function presenting a maximum. We have already seen that for $(y - \frac{1}{2})^2 > 2$ we have a peak in the dilute solution limit.

The simplest method to detect the existence of a peak is to determine the initial slope of the curve $I(q^2)$. If it is positive we have a peak, if it is not, we have a continuously decreasing function.

Let us therefore write equation (1) in the form

$$I = I_0 (1 - m q^2 \frac{R^2}{3})$$

A straightforward calculation gives the following result

$$I = \frac{(a+b)^2}{A} \left[1 - \frac{q^2 R^2}{3} \left(\frac{2}{A} - (2y-1)^2 A \right) \right]$$

with $A = 1 + 2Nn^2(2v+w) = 2A_2Mc$ calling A_2 the second virial coefficient, the c concentration and M the molecular weight of the total polymer. This formula gives some already known results, $A_2c = 0$ gives the dilute solution and $a+b=0$ the bulk case.

Let us take the case where $y=0$ or 1 which corresponds to no contrast between the solvent and one sequence, the condition for having no maximum is

$$A < \sqrt{2}$$

$$1 + 2A_2Mc < \sqrt{2}$$

$$\text{or } 2A_2Mc < \sqrt{2} - 1$$

This result is different from the result of Benmouna and Benoît⁽¹²⁾ which using only the second term in concentration did find $2A_2 < 1$ and shows that the apparition of the peak is still faster than predicted. In a good solvent this condition $2A_2Mc < 0,2$ is reached at already very low concentration. Let us assume for instance $M \sim 10^5$ $A_2 \sim 10^{-4}$ this gives $c = 0,02 = 2\%$.

If one draw a Zimm plot one has on such a system a drastic change of the radius of gyration with concentration which has been observed experimentally, since the coefficient m varies rapidly with the concentration^(13,14,15)

If $y = \frac{1}{2}$ the two quantities $a = b$ are identical and, as can be expected from simple physical argument, one has never a maximum.

The second point which I would like to discuss here is the shape of the scattering curve when one decreases the quality of the solvent approaches a phase transition. This, as we have said, is obtained when the denominator of equation 1 goes to zero and this can be done by two different ways : a) D goes to zero for $q=0$ and we have a classical phase transition between two amorphous phases ; b) D goes to zero at finite q and from what we have seen discussing bulk properties, we have a transition between isotropic and mesomorphic phase.

Both possibilities can happen in this two component system. A detailed study of the phase diagram of such a system is needed. This work has been done already by L. Leibler⁽¹⁶⁾ for a copolymer A-B in the homopolymer A but has never been undertaken for a copolymer + solvent.

Since we had at our disposal a copolymer deuterated PS-PMMA and since it is known that cyclohexanol is approximately a theta solvent⁽¹⁷⁾ for both sequences around 80°C, it was interesting to go down in temperature starting above 80°C to see if before the phase separation, we had a monotonous curve always increasing when q decreases or if we had a peak with increasing height when we reach the phase transition.

The concentration at which we did work was of the order of 20 % and, as it can be expected from the theory, there is a peak which does increase when the temperature decreases suggesting that it goes to infinity on the spinodal and that the new low temperature phase is mesomorphic.

This shows, if it is confirmed that, if two polymers have a too small incompatibility or molecular weight to make mesomorphic phases in the bulk, these phases can be obtained in the presence of a bad solvent.

CONCLUSION

In this lecture we have presented the analysis of the intensity scattered by copolymers using a theory which has been recently developed and which is not yet published. This theory could be called an order zero approximation. It assumed as known the structure factor of each polymer and does not give any method to evaluate them. It does not give either a method for evaluating the thermodynamical interactions. The only things it says is that, if you know the thermodynamics of the system and the structure factor of the molecules, you can in a meanfield approximation evaluate the complete scattering function, or if one prefers the density fluctuations.

In this paper we did present the results for a two component system copolymer + solvent but without major difficulty, this formalism can be extended to any situation and take into account polydispersity. I hope it will be useful for a better understanding of polymer properties.

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