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Scattering by cyclic polymers and copolymers at large scattering vectors*)

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*) *Dedicated to Prof. Fischer on the occasion of his 65th birthday*

Abstract: General formulae allowing the evaluation of the form factors of cyclic block copolymers are established and graphs for cyclic copolymers of the form $(A–B)_N$ are shown. When N is large, the linear and the cyclic copolymer have the same behaviour. It is possible to extend at large angle an analytical expression given for linear polymers. This allows to show that, in the study of transesterification by small-angle neutron scattering, one can neglect the effect of cycles.

Keywords: Neutron scattering – cyclic polymer ring copolymers – transesterification

Introduction

In a recent paper [1] the intensity scattered by multiblock linear copolymers, in bulk or in solution, was evaluated and the results applied to the problem of transesterification [2]. In this calculation, the formation of rings during transesterification was neglected; this approximation was justified by a qualitative and not very rigorous argument. Since this theory has already been used experimentally with success [3, 4], it is perhaps worthwhile to study more rigorously the effect of ring structures on the values of the form factor for copolymers. The main difficulty in this kind of calculation is that the integrals which describe the results are not reducible to classical functions and must be evaluated numerically. The problem of diblock circular copolymers has already been studied by Huber [5] and Benmouna [6], but they did not extract from their results rules which can be extrapolated to more complex cases. For instance, the scattering at large angles is interesting since, as in the case of linear copolymers, it depends only on the topology of the sample and not on the details of the structure [7]. Our intention in this paper is to revisit the problem of cyclic polymers and copolymers, to extend the results recently obtained [5, 6] and to establish methods for the evaluation of the scattering due to complex ring copolymers. These results will be applied to multiblock cyclic copolymers in order to generalize the formulae used in studying transesterification.

General formulae

In the context of the Random Phase Approximation description of the scattering of polymers or copolymers [7, 8] one knows that the scattered intensity depends only on combinations of the form factors and thermodynamic quantities. The form factor of a ring section is defined as:

$$n^2 P(q) = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \exp(-iq \cdot r_{ij}) \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \left\langle \exp\left(\frac{-q^2 \bar{r}_{ij}^2}{6}\right)\right\rangle , \quad (1)$$

where q is the modulus of the scattering vector, i.e., the quantity $(4\pi/\lambda)\sin(\theta/2)$, λ being the wavelength of the incident beam and θ the observation angle. The quantity $\bar{r}_{ij}^2$ is the mean square distance between two points on the scattering block and is defined, in the case of rings, by the classical relation:

$$\bar{r}_{ij}^2 = b^2(|i-j|)\left\{1 - \frac{|i-j|}{N}\right\}, \tag{2}$$

where b is the length of the statistical element.

Introducing the quantities: $\mu = q^2 b^2/6$, $z = n/N$, $u = \frac{|i-j|}{n} = \frac{p}{n}$ and transforming the double sum into a simple sum allows the evaluation of the form factor $P(q)$, normalized to unity for $q = 0$:

$$n^2 P(q) = 2\int_0^n dp(n-p)\exp\left\{-\mu p\left(1 - \frac{p}{N}\right)\right\}$$

$$= 2n^2 \int_0^1 du(1-u)\exp\{-\mu n u(1-uz)\} \tag{3}$$

Completing the square in the exponential and writing $\mu n = x$ leads after simple calculation to an expression depending on what is called the Dawson integral. Calling $\varepsilon(t)$ the function:

$$\varepsilon(t) = \int_0^t \exp[u^2]\, du ,$$

one obtains for $P(q)$ the expression

$$P(q) = \exp\left[-\frac{x}{4z}\right]\left\{\frac{2z-1}{z^{3/2}\sqrt{x}}\left[\varepsilon\left(\sqrt{\frac{x}{4z}}\right) - \varepsilon\left(\sqrt{\frac{x}{4z}}(1-2z)\right)\right] + \frac{1}{xz}(1 - \exp[-x(1-z)])\right\}. \tag{4}$$

$P(q)$ depends on two parameters: the quantity $x = \frac{q^2 b^2}{6} n$, which is the classical variable for scattering by Gaussian chains, and the ratio $z = n/N$ of the length of the scattering chain to the total length of the cycle. It will be shown that all the characteristics of the scattering of rings can be expressed as a function of $P(q)$ which will be called $P(x, z)$. In Fig 1a, we have plotted (using the *Mathematica* program) the quantity $q^2 P(x, z)$ which, in dilute solution, is proportional to the product $I(q)q^2$ of the scattered intensity by the square of the modulus of the scattering vector as a function of x for different values of z. For $z = 0$ ($N = \infty$) one recovers the classical linear Gaussian chain and, for $z = 1$ ($n = N$), the Casassa [9] formula for the complete cycle.

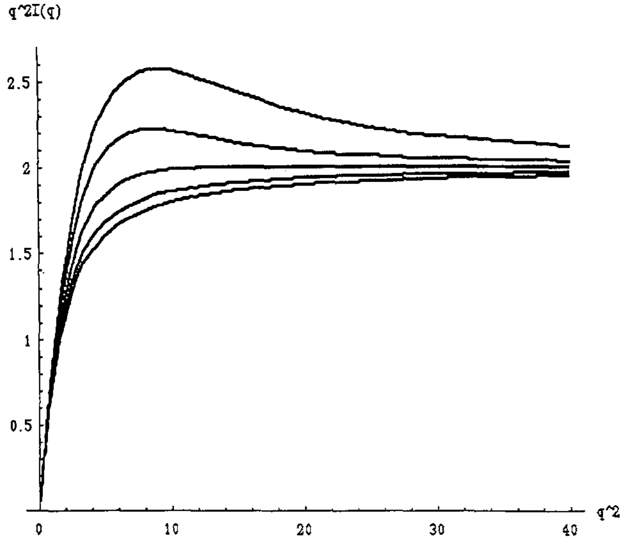

Fig. 1a. The quantity $q^2 I(q)$ in arbitrary units as a function of $q^2 R^2$ corresponding to different values of the parameter z. Going from top to bottom one has successively $z = 1, 0.8, 0.5, 0.2, 0$

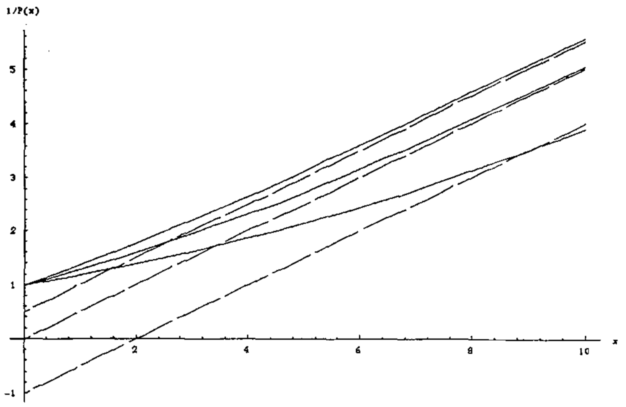

Fig. 1b. Zimmplots and asymptotes for three characteristic cases. Going from top to bottom: 1) the linear polymer, 2) the polymer making half a ring, and 3) the complete ring. (In this last case the asymptote cuts the curve around $qR = 9$)

One could also use the classical Zimm representation $P^{-1}(x, z)$ as a function of x (Fig. 1b). In both representations the shape of the diagram changes completely for $z = 1/2$. For z less than $1/2$ the curves are similar to those obtained for linear polymers. When q increases the curves reach, in Fig. 1a, the asymptotic value from below. When $z > 1/2$, one has a maximum in the Kratky plot for $qb\sqrt{n/6} = 2, 3$.

The case $z = 1/2$, where the scattering segment is exactly half of the ring, is interesting since it is the only case where Eq. (4) can be integrated in closed form, leading to [8]:

$$P(x, 1/2) = \frac{1-\exp(-x/2)}{x/2} . \tag{5}$$

It is a simple exponential function and gives $b^2 n/8$ for the square of the radius of gyration. In the classical Zimm plot ($P^{-1}(q)$ as a function of x) all the curves have the same final slope, but the intercept is a decreasing function of z: it is one-half for $z = 0$, 0 for $z = 1/2$ and -2 for the complete ring.

In this diagram, one sees that the radius of gyration depends on z and a simple calculation shows that:

$$\overline{R^2} = \frac{b^2 n}{6}\left(1 - \frac{z}{2}\right) . \tag{6}$$

It is a linear function of $z/2$ when one goes from the linear chain to the complete ring.

In order to study the behavior at large q values we shall, as explained in the appendix I, develop Eq. (4) as a function of the variable $\mu = q^2 b^2/6$ obtaining for $z \neq 1$:

$$nP(q) = \frac{2}{\mu} + \frac{2}{\mu^2 n}(2z-1) . \tag{7}$$

This formula gives the classical first term valid for Gaussian chains of any structure. The second term is a linear function of the parameter $z = n/N$. This term is positive for $z > 1/2$ and becomes negative for $z < 1/2$. In the case of stars it was possible to explain why this second term changes sign when the number of arms increases. Unfortunately, such an explanation is no longer possible for rings. The only thing one can say is that, when the portion of the ring which scatters increases, its structure becomes more compact and the scattering decreases quickly with increasing q (it is difficult to show even qualitatively why the term in $1/q^4$ is the same for a four branch star and a complete ring).

For $z \ll 1$, one recovers the classical Gaussian chain, but there is an anomaly around $z = 1$. For this value of z, Eq. (7) corresponds to the complete ring and gives $2/\mu^2 N$ for the second term; this is inexact. Going back to Eq. (4) and making $z = 1$, one recovers the exact Casassa [8] result:

$$S(q) = \frac{2}{\mu} + \frac{4}{\mu^2 N} . \tag{8}$$

This comes from the fact that for $n = N$ both ends of the chain, which were more or less independent, become suddenly joined and this evidently modifies the form factor in the large q (small distances) limit. This abrupt change would be difficult or even impossible to detect experimentally.

The cross form factor

Since we want to apply these calculations to the case of ring copolymers with many blocks, it is also necessary to evaluate the cross term or, more precisely, the interference between two subchains of the same ring.

Two cases are possible depending on whether these subchains are contiguous or not, or in other words, whether $n_3 = 0$ or not (n_3 is the length of the chain O_1O_2 separating both subchains (see Fig. 2)).

The method which is the most convenient is to reduce the problem of the calculation of these cross terms to the preceding problem since it has the advantage of transforming a double integral into a single integral.

Let us consider first the case of connected segments:

a) Interference between two contiguous segments: ($n_3 = 0$ in Fig. 2). Using O as common origin for the numeration of segments 1 and 2, we write:

$$\overline{r_{ij}^2} = b^2(i+j)\left(1 - \frac{i+j}{N}\right) , \tag{9}$$

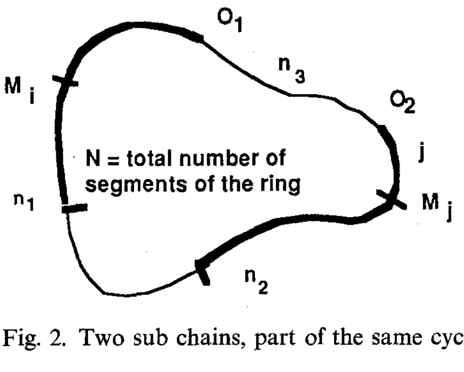

Fig. 2. Two sub chains, part of the same cycle interfering

and:

$$n_1 n_2 P_{12}(q) = \sum_{i=0}^{n_1} \sum_{j=0}^{n_2} \exp[-\mu(i+j)\left(1-\frac{i+j}{N}\right). \tag{10}$$

The double integral by which one replaces this summation is not easy to evaluate and it is more convenient to use the following indirect way:

One considers the segment 1–2 as the sum of segments 1 and 2, writing for its form factor P_T:

$$(n_1 + n_2)^2 P_T(q) = n_1^2 P_1(q) + n_2^2 P_2(q) + 2 n_1 n_2 P_{12}(q) . \tag{11}$$

Introducing the variables x and z this equation becomes:

$$2 n_1 n_2 P_{12}(q) = (n_1 + n_2)^2 P(x_1 + x_2, z_1 + z_2) - n_1^2 P(x_1, z_1) - n_2^2 P(x_2, z_2) , \tag{12}$$

which makes the evaluation of $P_{12}(q)$ straightforward since the function $P(x, z)$ is known.

b) the two segments are not contiguous:

One has to write three equations similar to Eqs. (11) and (12)

$$2 n_1 n_3 P_{13}(q) = (n_1 + n_3)^2 P(x_1 + x_3, z_1 + z_3) - n_1^2 P(x_1, z_1) - n_3^2 P(x_3, z_3) , \tag{13}$$

$$2 n_2 n_3 P_{23}(q) = (n_2 + n_3)^2 P(x_2 + x_3, z_2 + z_3) - n_2^2 P(x_2, z_2) - n_3^2 P(x_3, z_3) , \tag{14}$$

$$\begin{aligned}(n_1 + n_2 + n_3)^2 P(x_1 + x_2 + x_3, z_1 + z_2 + z_3) &= n_1^2 P(x_1, z_1) + n_2^2 P(x_2, z_2) + n_3^2 P(x_3, z_3) \\ &+ 2 n_1 n_2 P_{12}(q) + 2 n_2 n_3 P_{23}(q) \\ &+ 2 n_1 n_3 P_{13}(q)\end{aligned} \tag{15}$$

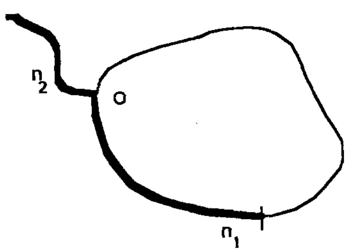

Fig. 3. A linear chain grafted on a cycle

Since we have three equations and three unknowns P_{12}, P_{23}, P_{13}, the problem is formally solved.

c) Interferences between a grafted chain and a cycle

This case corresponds to Fig. 3. It is assumed that there are no correlations between the elements of the chain and of the ring. This allows one to write directly:

$$\begin{aligned} n_1 n_2 P_{12}(q) &= \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} \langle \exp(-iq \cdot r_{ij}) \rangle \\ &= \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} \left\langle \exp\left(-\frac{q^2 \bar{r}_{ij}^2}{6}\right)\right\rangle , \end{aligned} \tag{16}$$

with $\bar{r}_{ij}^2 = b^2 [i + j(1 - j/N)]$.

The summations on i and j are independent and transforming them into integrals gives:

$$\begin{aligned} P_{12}(q) = &\int_0^{n_2} \exp\left(-\frac{q^2 b^2 i}{6}\right) \frac{di}{n_2} \\ &\times \int_0^{n_1} \exp\left[\left(-\frac{q^2 b^2}{6}\right)\left(j\left(1 - \frac{j}{N}\right)\right]\frac{dj}{n_1} . \end{aligned} \tag{17}$$

Making the classical changes of variable and integrating yields:

$$\begin{aligned} P_{12}(q) = &\frac{1 - \exp(-x_2)}{x_2} \frac{\exp\left(-\frac{x_1}{4z}\right)}{\sqrt{\frac{x_1}{z}}} \\ &\times \left\{\varepsilon\left(\sqrt{\frac{x_1}{4z}}\right) - \varepsilon\left(\sqrt{\frac{x_1}{4z}}\right)(1 - 2z)\right)\right\} . \end{aligned} \tag{18}$$

$P_{12}(q)$ *for large values of* q

Since we now have analytical expressions for $P_{12}(q)$ as a function of what we have called $P(x, z)$, it is easy, using Eq. (12), to obtain the asymptotic expressions for $P_{12}(q)$. If the two subchains are contiguous and if $(n_1 + n_2) < N$, one obtains:

$$P_{12}(q) = \frac{1}{n_1 n_2 \mu^2} . \tag{19}$$

As one could have guessed, there is no term in μ^{-1} (or q^{-2}) since there are no interferences between scattering centers situated on the same chain. There is only one term in μ^{-2} (q^{-4}), which is independent of the length of the segments 1 and 2 and it is insensitive to the existence of a cycle since it is identical to the result obtained for linear chains [7].

If $n_1 + n_2 = N$, one has to replace $P(n_1 + n_2, z_1 + z_2)$ by the expression valid for the complete ring and one obtains:

$$P_{12}(q) \approx \frac{1}{n_1 n_2 \mu^2} . \tag{20}$$

If the two subchains are separated there are no terms of the order of μ^{-1} or μ^{-2} in the expansion of $P_{12}(q)$. This was to be expected since, at large angles, the interference between non contiguous subchains disappears.

The third case is that of a linear chain attached to a ring: Using the expansion of the function $\varepsilon(x)$ given in the appendix, one obtains

a) if $n_1 < N$ (or $z_1 < 1$): $P_{12}(q) \approx \frac{1}{n_1 n_2 \mu^2}$

b) if $z_1 = 1$: the lateral chain is attached to a complete ring and:

$$P_{12}(q) \approx \frac{2}{n_1 n_2 \mu^2} \tag{21}$$

The case where the grafted chain and the ring have no common point has not been discussed but, from what we know already, it is evident, that in this case also there is no term in q^{-2} or q^{-4}.

Some applications to cyclic multiblock copolymers

a) General formula

We have now all the tools necessary to evaluate, at least at large angle, the scattering by complex cyclic structures. It is known that multiblock copolymers can be made by transesterification of mixtures of H and D polymers. In order to interpret the results, one usually assumes that all the chains are linear. But one could as easily obtain cycles. It is therefore interesting to see if the existence of cycles has a substantial effect on the scattering of these copolymers.

The classical Leibler [12] formula allows one to write the scattering intensity of a copolymer in bulk as:

$$i(q) = \frac{I(q)}{vN} = \kappa^2 N u^2 v^2 \frac{P_1(q)P_2(q) - P_{12}^2(q)}{P_T(q)} , \tag{22}$$

calling $i(q)$ the scattered intensity per monomer, k the contrast factor (difference in scattering length between the two types of monomeric units), v the number of chains having N monomeric units and u the ratio $u = \frac{n_1}{n_1 + n_2}$ ($v = 1 - u$).

We consider the simple case where $n_1 = n_2$ ($u = v = 1/2$) and $P_1(q) = P_2(q)$. In this case:

$$\begin{aligned} 4P_T(q) &= P_1(q) + P_2(q) + 2P_{12}(q) \\ &= 2P_1(q) + 2P_{12}(q) , \end{aligned} \tag{23}$$

and Eq. (22) can be replaced by:

$$i(q) = \kappa^2 \frac{N}{4} (P_1(q) - P_T(q)) . \tag{24}$$

Since the form factor $P_T(q)$ of the complete cycle is given by $P(x, 1)$ the only term which needs evaluation is $P_1(q)$, the form factor of the part 1 of the copolymer This is done using the method defined by Eq. (14) which allows the determination of all the cross terms as a function of the

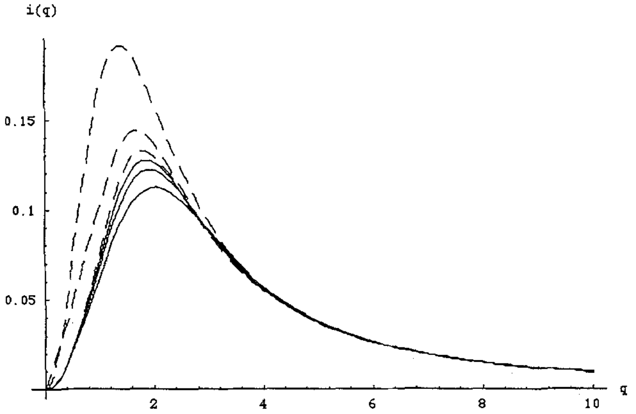

Fig. 4. Scattering by cyclic and linear copolymers of the type $(\text{A-B})_z$; the blocks A and B are identical. $i(q)$ is the scattered intensity in reduced units as a function of $q\sqrt{b2n/6}$ in arbitrary units. Going from bottom to top, it corresponds to the full curves with $z = 1, 2, 4$. The first dotted line corresponds to a copolymer with an infinite number of blocks of linear as well as a cyclic structure. The two other dotted lines correspond to linear block copolymer with $z = 4$ and $z = 1$

quadratic terms. The calculation is easy for the first terms and one obtains:

for $p = 1$:

$$P_1(q) - P_T(q) = P(x, 1/2) - P(2x, 1) \qquad (25)$$

for $p = 2$:

$$P_1(q) - P_T(q) = \frac{3}{4}(P(x, 1/4) + \frac{9}{4}P(3x, 3/4) - 2P(2x, 1/2) - P(4x, 1) \qquad (26)$$

for $p = 3$

$$P_1(q) - P_T(q) = \frac{2}{3}(P(x, 1/6) - \frac{8}{3}P(2x, 1/3) + 3P(3x, 1/2) - P(6x, 1) \qquad (27)$$

and for $p = 4$

$$P_1(q) - P_T(q) = \frac{1}{2}(P(x, 1/8) - 2P(2x, 1/4) + \frac{27}{8}P(3x, 3/8) - 4P(4x, 1/2) + \frac{25}{8}P(5x, 5/8) - P(8x, 1) \qquad (28)$$

Figure 4 shows the scattered intensity as function of $x = q\sqrt{b^2 n/6}$ in arbitrary units. Going from bottom to top, the curves correspond successively to $p = 1, 2, 4$.

On the same graph we have plotted the curve corresponding to $p = \infty$ in the case of linear multiblocks copolymers (it is the lower dashed lines curve. Finally the two last curves correspond to linear copolymers with $p = 1$ and 4. This graph shows a continuity between the cyclic block copolymer and the linear one.

All these curves have the same shape, especially in the high q range, where the differences are much less pronounced. When p is large there is no difference between a linear and a cyclic copolymer; this justifies the fact that the presence of cyclic copolymers can be neglected in transesterification. One sees also that cyclic copolymers scatter much less than the linear one. When the number of blocks increases the scattering increases in the case of cyclic copolymers and decreases in the case of linear copolymers. This means that the compatibility of cyclic copolymers is larger than the compatibility of linear copolymers; this compatibility decreases with the number of blocks for the cyclic copolymer and increases for the linear one.

b) Behavior at large angles

In this section, we intend to give expressions valid in the large q range for cyclic block copolymers made of z identical blocks of n_1 statistical elements and z block of n_2 statistical elements. Evidently, $N = z(n_1 + n_2)$. Since we limit our expansion to the terms in q^{-4}, we do not need the term in $P_{12}^2(q)$ which it is of higher order. Thus, Eq. 18 becomes:

$$i(q) = \frac{I(q)}{vN} = \kappa^2 N u^2 v^2 \frac{P_1(q) P_2(q)}{P_T}. \qquad (28)$$

The only contribution to the term $P_1(q)$ is given by the scattering of the blocks (none of the blocks 1 are contiguous) and one finds (remembering the normalization to unity of $P_1(q)$:

$$P_1(q) = \frac{2}{\mu z n_1} - \frac{2}{z n_1^2 \mu^2} + \frac{4}{z N n_1 \mu^2} \qquad (29)$$

since none of the blocks covers the complete cycle but the copolymer is a complete cycle, $P_T(q)$ is given by Eq. (8):

$$P_T(q) = \frac{S(q)}{N} = \frac{2}{\mu N} + \frac{4}{\mu^2 N^2} \qquad (30)$$

Using Eq. (28), one obtains for the scattered intensity at large angle:

$$i(q) = \kappa^2 u v \left[\frac{2}{\mu} - \frac{2}{\mu^2}\left(\frac{1}{n_1} + \frac{1}{n_2} - \frac{2}{N}\right)\right] \qquad (31)$$

Sometimes, one prefers to write $i^{-1}(q)$, obtaining:

$$\frac{i^{-1}(q)}{\kappa^2} = \frac{1}{2uv}\left[\mu + \frac{1}{n_1} + \frac{1}{n_2} - \frac{2}{N}\right]. \qquad (32)$$

This result is similar to the result obtained for linear polymers: only the last term in $1/N$ (which can be neglected when the number of blocks is large) has a different coefficient (2 instead of 1). This confirms what has been seen already in discussing the figures, i.e., that the formation of cycles in the transesterification reaction can be neglected as soon as the quantity z ($z = N/n_1 + n_2$)) is sufficiently large.

Conclusion

In this paper we have confined the discussion to the case where the blocks on a cycle are all identical (or monodisperse). The introduction of polydispersity is unnecessary since its effect will be identical to that observed with linear copolymers. [1]. The only thing which needs to be repeated is taht, in polydisperse media, the quantities n_1 and n_2 which appear in Eq. (31, 32) must be replaced by their number average values.

We could also have used our method in order to discuss the problem of grafted cycles. One can easily consider the case of a cycle with many branches and evaluate the form factor of such an object. This could perhaps be better than the classical model of stars with many arms starting all from the same point. But, since the calculation is simple, it is better to begin with experimental examples in order to compare experiment and theory.

It is also possible to use these results in the case of dynamics scattering as has been done by Borsali and Benmouna [13].

We could also have discussed the case of polymers or copolymers with many cycles or, in other words, of networks and gels. This extension will be presented shortly.

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References

1. Benoît H, Hadziioannou G (1988) Macromolecules 21:1449
2. Benoît H, Fischer E, Zachmann HG (1989) Polymer 30:379
3. Macdonald WA, McLenaghan ADW, McLean JG, Richards RW (1991) Macromolecules 24:6164
4. Li MH, Brûlet A, Keller P, Strazielle C, Cotton JP (1993) Macromolecules 26:119
5. Huber K (1988) Macromolecules 21:1305–1309
6. Benmouna M, Borsali R, Benoît H (1993) J Phys II France 3:1041
7. Benoît H, Joanny J-F, Hadzioannou G, Hammouda B (1993) Macromolecules 26:5790
8. Casassa EF (1965) J Polym Science Part A 3:605
9. de Gennes Scaling concept in Polymer Physics Cornell University Press (1979)
10. Vilgis TA, Benmouna M, Benoît H (1993) Macromolecules 24:4482
11. Borsali R, Benmouna M, Benoît H (1993) Physica A 201:129
12. Leibler L (1980) Macromolecules 13:1902
13. Borsali R, Benmouna M (1993) Eutrophysics Letters 23:263

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Appendix I

Series expansion of the function $\varepsilon(x)$ *at large* x

For this calculation, we need the expansion of the integral:

$$\varepsilon(x) = \int_0^x \exp(u^2)\,du \,.$$

Using the identity:

$$\exp(u^2) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp(-t^2 + 2ut)\,du \,,$$

one writes the expression of $\varepsilon(x)$ and performing first the integration on u one obtains:

$$\varepsilon(x) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{\exp(-t^2)}{2t}[\exp(2t) - 1]\,dt \,.$$

This function behaves normally and the point $t = 0$ is not a singularity. Making the substitution $t - x = w$, $\varepsilon(x)$ becomes:

$$\varepsilon(x) = \frac{\exp(x^2)}{2\sqrt{\pi} x_{\infty}} \int_{-\infty}^{\infty} \frac{\exp(-w^2)}{1 + \frac{w}{x}} \times [1 - \exp\{-2x^2 - 2xw\}]\,dw$$

$\exp(-w^2)$ has a shape maximum around $w = 0$, so we can expand the rest of the integral around this point and calculate the series of the terms. The second part $\exp(-2x^2 - 2xw)$ does not contribute, in the $w \to \infty$ limit one can therefore write:

$$\varepsilon(x)=\frac{\exp(x^2)}{2\sqrt{\pi}\,\mathbf{x}_{\infty}}\int_{-\infty}^{\infty} dw\exp(-w^2)\left\{1-\frac{w}{x}+\left(\frac{w}{x}\right)^2-\left(\frac{w}{x}\right)^3+\left(\frac{w}{x}\right)^4-\cdots\right\}.$$

The odd powers vanish and one obtains as final result:

$$\varepsilon(x)=\frac{\exp(x^2)}{2x}\left\{1+\frac{1}{(2x^2)^2}+\frac{1.3}{(2x^2)^3}+\frac{1.3.5}{(2x^2)^3}+\cdots\right\},$$

which has been used in this paper.

Appendix II

S(q) for the cycle copolymer $(\text{A-B})_3$

If all blocks are identical, the formula is:

$$S(q)=2(P_a-P_{ab})=4(P_a-P_{\mathrm{T}})$$

with evident notations: $P_a(q)$ is the form factor of the species A, $P_b(q)$ of the species B, $P_{\mathrm{T}}(q)$ is the form factor of the cycle and $P_{ab}(q)$ the interferences between A and B momoners. All these functions of q are such as $P(0)=1$. It is assumed that all the blocks are identical, each of them made of n links. This gives for the total number of links $N=6n$.

We divide the copolymers into its six distinct blocks; the double sum $P_{\mathrm{T}}(q)$ is made of the 36 squares: We call pij the terms corresponding to the square i, j

Table 1. How to divide the block copolymers into 3 blocks (1, 3, 5) and evaluate the interferences between all the pairs of blocks

	1	2	3	4	5	6
1	p11	p21	p31	p41	p 51	p61
2	p12	p22	p32	p42	p52	p62
3	p13	p23	p33	p43	1p5 3	p63
4	p14	p24	p34	p44	p54	p64
5	p15	p 25	p135	p45	p55	p65
6	p16	p26	p36	p46	p56	p66

taking the symmetries into account one has: $pij=pji$. Moreover:

$p12=p23=p34=p45=p56$

and $p13=p24=p35=p46=p15$.

The table is therefore made of only four different terms $p11$, $p12$, $p13$ and $p14$ (see Table 2):

Table 2. The different terms in this product and the way to evaluate them

	1	2	3	4	5	6
1	p11	p12	p13	p14	p13	p12
2	p12	p11	p12	p13	p14	p13
3	p13	p12	p11	p12	p13	p14
4	p14	p13	p12	p11	p12	p13
5	p13	p14	p13	p12	p11	p12
6	p12	p13	p14	p13	p12	p11

The form factor of the copolymer A made of the three blocks 1, 3, 5 is given, following the figure, by:

$$9P_a=3p11+6p13\ ,$$

where $p11$ is defined, following Eq. (4), as: $p11=P(x, 1/6)$

more generally, if we consider the tables made of the squares lying on the upper left hand side, one has:

$$P(x, 1/3)=1/4(2p11+2p12)$$

$$P(3x, 1/2)=1/9(3p11+4p12+2p13)$$

These equations allow the evaluation of $p11$, $p12$, $p13$

$$p11=p(x, 1/6);\quad 2p12=4P(2x, 1/3)-P(x, 1/6)$$

$$\text{and } 2p13=9P(3x, 1/2)-8P(2x, 1/3)-P(x, 1/6)$$

From the definition of P_a, one obtains immediately Eq. (27):

$$P_a(q)=\frac{2}{3}P(x, 1/6)-\frac{8}{3}P(2x, 1/3)+3P(3x, 1/2)$$

The generalization to higher orders is evident.