Macromolecules **1993,** *26,* 5790–5795

Scattering by Linear, Branched, and Copolymer Chain Molecules for Large Scattering Vectors

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Received April 15, 1993; Revised Manuscript Received July 14, 1993®

ABSTRACT: If one expands the expression of the intensity scattered by polymers or copolymers in the large q range, one observes that, for Gaussian chains, this intensity follows a law of the type $i(q) = Aq^{-2} + Bq^{-4}$. The coefficient A characterizes the length of the statistical element, and the coefficient B is easily measured using the Zimm representation. For a linear chain B gives the number-average degree of polymerization. In the case of branched polymers without loops, it depends mainly on the number of statistical elements between two cross-links or one cross-link and an end. If the polymer is sufficiently long, it gives the number-average degree of polymerization of these branches. A general formula is given and applied to classical examples: star, alternating, a comblike copolymer. The effect of polydispersity and the case of block copolymers with blocks of different chemical nature are discussed. These results are also extended to stretched polymers. This method could give new information in the interpretation of neutron scattering data.

I. Introduction

It is well known[1] that, regardless of the architecture of the molecule, at large angles the scattering of polymer chains obeys a law of the form

$$I(q) = kq^{-1/\nu}$$

where $I(q)$ is the intensity scattered as a function of the modulus of the scattering vector $q = (4\pi/\lambda_0)\sin(\theta/2)$, where λ_0 is the wavelength of the neutron beam and ν is the swelling exponent defined from the relation $R \sim N^\nu$ between the size R of the chain and the number N of units; k is a prefactor to be evaluated later.

This type of behavior is well illustrated by the linear Gaussian chain. The scattered intensity is directly proportional to the structure factor $I(q) = \bar{b}^2\phi S(q)$, where ϕ is the volume fraction occupied by the polymer and $\bar{b}^2$ is the contrast factor. The structure factor of a Gaussian chain has been calculated by Debye:[2]

$$S(q) = NP(q) = \frac{2}{\lambda^2 N}(\lambda N - 1 + \exp(-\lambda N)) \qquad (1)$$

where the parameter λ is defined as $q^2b^2/6$. b^2 is the mean square value of the statistical element, and $P(q)$ is the form factor normalized to unity when $q = 0$. At large wave vectors the structure factor decays as $S(q) = 2/\lambda$.

The scattered intensity is usually represented either as a Kratky[3] plot, i.e., $q^2I(q)$ or $\lambda I(q)$ as a function of q^2 or λ, or as a Zimm[4] plot where $1/I(q)$ is plotted as a function of the same variable (Figure 1). In these representations, the large wave vector behavior allows the verification of the value of the exponent and gives the length b of the statistical element, either from the intercept of the horizontal asymptote (Kratky plot) or from the slope of the asymptote (Zimm plot). The low wave vector behavior (the Guinier[5] range) gives access to the molecular weight and the radius of gyration.

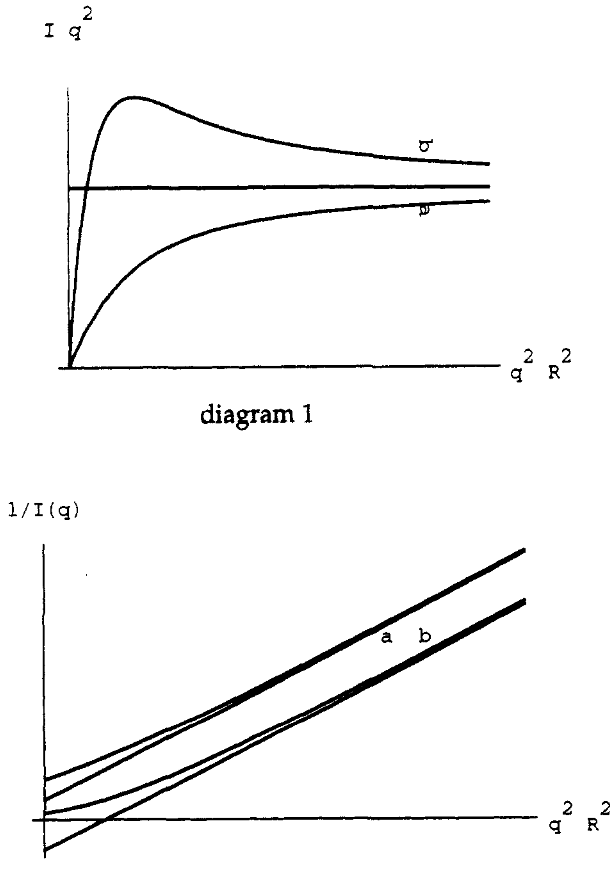

diagram 1

diagram 2

Figure 1. Representation of scattering results on Gaussian polymers: diagram 1, Kratky plot, $q^2I(q)$ versus q^2; diagram 2, Zimm plot, $1/I(q)$ versus q^2. Curve a corresponds to a linear polymer, and curve b to a highly branched one. The straight lines are the corresponding asymptotes.

When the size of the polymer is small, the experimental window of the q values in classical neutron scattering

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® Abstract published in *Advance ACS Abstracts,* September 1, 1993.

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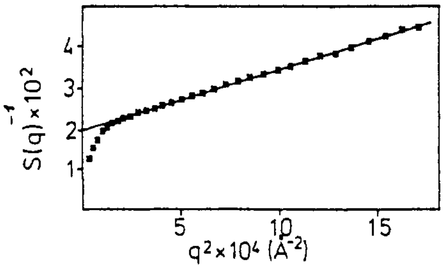

Figure 2. Zimm plot of a mixture of usual and deuterated PET during transesterification. The straight line defines the asymptote.

experiments gives access to both the initial and asymptotic parts of the curve. If the polymer is too large (having a radius of gyration of more than 500 Å), the low q range is inaccessible (due to experimental constraints) and the experiments are limited to the high q range, i.e., to the tail of the curve.

In many experimental situations, for example when one is studying gelation or networks, one is confronted with large objects, posing difficulties for the interpretation of the small q range. It is therefore interesting to study in detail the information contained in the tail of the curve. For a Gaussian chain an expansion of eq 1 to next order gives

$$S(q) = \frac{2}{\lambda} - \frac{2}{N\lambda^2} \qquad (2)$$

The molecular weight of the chain can thus be obtained in the Zimm plot from the intercept of the asymptote with the horizontal axis. It is clear that if the polymer is polydisperse, it is the number-average molecular weight which is measured this way[6] and not the weight-average as in the Guinier range.

As an example we show in Figure 2 small-angle neutron scattering results obtained by Kugler et al.[7] on a mixture of deuterated and hydrogenated poly(ethylene terephthalate) (PET) of molecular weight of the order of 90 000 heated at 280 °C for 10 s and quenched at room temperature. Transesterification occurs and Figure 2 shows $I^{-1}(q)$ as a function of q^2. One sees clearly that the only quantities which can be measured accurately are the final slope (which corresponds to the nature of the polymers and copolymers) and the intercept, which is the quantity we are interested in.

In this paper, we wish to generalize this idea to more complex situations. We consider the case of branched chains, chains with excluded volume, polydisperse systems, chains submitted to a unidirectional force as in an extended rubber sample, and block copolymers in a molten phase.

II. Branched Polymers

In this section, we discuss the scattering by branched polymers. For the sake of simplicity we use Gaussian statistics. We first derive a general equation, then consider the effect of polydispersity and some specific cases.

(a) General Equation. The polymer is made of s branches having the same length n and has $N = sn$ monomers. We define a branch as a linear chain going from one cross-link to another one or from one cross-link to a free end. The chain has c cross-links of functionality f (meaning that f branches start from each cross-link). Finally, the chains are Gaussian and no ring structures are present; the structure of the chain is thus that of a Cayleigh tree or a Bethe lattice. In other words, there is only one way to go along the chain from one point to another one. We call $S_i(q)$ the form factor of one branch made of n_i monomers; it is given by the Debye function (eq 1) where we have replaced N by n_i. $S_{ij}(q)$ is the interference factor between points k and l belonging to the blocks i and j:

$$S_{ij}(q) = \sum_k \sum_l \exp\{i\mathbf{q}\cdot(\mathbf{r}_{ik} - \mathbf{r}_{jl})\} \qquad (3)$$

where the summation is extended to all pairs of points k and l belonging to segments i and j, respectively. A simple calculation shows that[8]

$$S_{ij}(q) = \frac{1}{\lambda^2}(1 - \exp(-\lambda n_i))(1 - \exp(-\lambda_{n_j}))\exp(-\lambda m_{ij}) \qquad (4)$$

calling m_{ij} the number of units separating the blocks i and j. The total structure factor of the molecule can then be decomposed in the following manner:

$$NS_T(q) = \sum_i n_i S_i(q) + \sum_i \sum_j S_{ij}(q) \qquad (5)$$

Since all branches are identical ($n_i = n$ and $S_i = S$), the summation over i just gives a factor s equal to the total number of branches. The large wave vector expansion of the first term is then obtained from eq 2. On the other hand, the interference term decays exponentially with q, unless $m_{ij} = 0$; therefore, in the large q limit, only interferences between blocks coming to the same junction point are important.

The number of pairs of branches present in the molecule for an f-functional cross-link is evidently $f(f-1)$, and since there are c cross-links, we obtain $cf(f-1)$ pairs of branches. This leads to the following structure factor:

$$S(q) = \frac{2}{\lambda} + \frac{cf(f-1)}{sn\lambda^2} - \frac{2}{n\lambda^2} \qquad (6)$$

If we take the inverse in order to use the Zimm representation, we obtain

$$\frac{1}{S(q)} = \frac{\lambda}{2} - \frac{1}{4n}\left[\frac{cf(f-1)}{s} - 2\right] \qquad (7)$$

In the case of chains with no loops there is a simple relation between the number of branches and the number of junctions of functionality f. If there is only one cross-link of functionality f, there are f branches in the molecule. Each time a new cross-link is added, $f - 1$ branches are added to the molecule. A molecule with c cross-links has therefore $f + (c - 1)(f - 1) = c(f - 1) + 1$ branches and

$$s - 1 = c(f - 1) \qquad (8)$$

Inserting this value in eqs 6 and 7 leads to

$$S(q) = \frac{2}{\lambda} + \frac{1}{n\lambda^2}\left[f - 2 - \frac{f}{s}\right] \qquad (9)$$

$$S^{-1}(q) = \frac{\lambda}{2} - \frac{1}{4n}\left[f - 2 - \frac{f}{s}\right] \qquad (10)$$

These formulas are extremely simple and can be checked in all known limiting cases.

For instance, if one considers a linear chain as made of s blocks with junctions of functionality 2, the Debye formula is recovered. One can also find the results obtained by Burchard[9] and Hammouda[10] on dendrimers. It is interesting to note that as soon as there is branching, the second term in (10) is negative (except for the three-arm star for which it vanishes); this means that in the Zimm plot the asymptote has a negative intercept and in the Kratky plot the curve reaches its asymptote from above, as has been frequently observed on multiarm stars and networks.

If the number s of branches becomes large, f/s can be neglected with respect to $f-2$ and the structure factor can be approximated by

$$S^{-1}(q) = \frac{\lambda}{2} - \frac{1}{4n}[f-2] \tag{11}$$

The tail of the scattering curve no longer depends on the size of the polymer, and if n is known, one determines f or, reciprocally, if f is known, one can measure n. An example is given in a paper of Khorramian and Stivala[11] where the authors studied stars and evaluated the terms of eq 11, which are in good agreement with what is known about the samples.

(b) Effect of Polydispersity. Up to now we have only considered monodisperse systems. Most real systems are polydisperse and it is important to take into account the effect of polydispersity. This effect is difficult to introduce in a general formula since the four variables which characterize a branched polymer—n, s, f, and c—can vary independently. We shall simplify the problem by taking into account the method of preparation. For instance, it seems that, regardless of the method, the length and the polydispersity of the branches are independent of the architecture of the polymer. This allows n to be averaged separately. Using the procedure developed for homopolymers,[6] it is seen that the average to be used is the number average $\bar{n}$, defined as $\bar{n} = \sum \nu_i n_i / \sum \nu_i$, where ν_i is the number of branches made of n_i statistical elements.

(c) The Case of Stars. A star has only one branching point with $s = f$ arms. When one takes into account the polydispersity of the length of the arms, eq 9 becomes

$$S(q) = \frac{2}{\lambda} + \frac{f-3}{\bar{n}\lambda^2} \tag{12}$$

In this case the only polydispersity left is the polydispersity in the functionality f. The average of f which must be introduced is the weight average f_w defined as $\sum \nu_i f_i^2 / \sum \nu_i f_i$. The final result is

$$S^{-1}(q) = \frac{\lambda}{2} - \frac{1}{4\bar{n}}[f_w - 3] \tag{13}$$

This gives a method to determine f and n for an unknown star. The large-angle scattering provides $f_w/\bar{n}$, and the low-angle neutron scattering (or the light scattering at zero angle if the star is too large) provides $n_w f_w$. If one knows the molecular weight of the arms (which is possible for the "arm first" method[12]), both f_w and the polydispersity of the arms $n_w/\bar{n}$ can be determined. This is useful for the precise determination of the structure of stars, especially when they are used as model polymers made to check theoretical predictions. It also extends the analysis proposed by Kosmas et al.,[13] who discussed the interpretation of the zero-angle scattering knowing the polydispersity of the arms.

(d) The Case of Random Branching. Branched polymers are obtained in radical polymerization as, for example, in the polymerization of low-density polyethylene. In this case f cannot be larger than 3 and there is no polydispersity in functionality (when $f = 2$, the chain is linear). Substituting $s - 1 = 2c$, one can rewrite eq 9 as

$$zS(q) = \frac{2}{\lambda} + \frac{s-3}{s\bar{n}\lambda^2} \tag{14}$$

To take into account polydispersity, one must average $1/s$; this introduces the number-average value $\bar{s}$. Assuming $\bar{s}$ large compared to 3, the structure factor reduces to the simple form

$$S(q) = \frac{2}{\lambda} + \frac{1}{\bar{n}\lambda^2} \tag{15}$$

The length of the segments can be easily measured. Note that the second term is positive, contrary to the case of the homopolymer.

(e) The General Case. In the general case, the structure factor is given by eq 6 with n replaced by the number average $\bar{n}$:

$$S(q) = \frac{2}{\lambda} + \frac{cf(f-1)}{\bar{n}s\lambda^2} - \frac{2}{\bar{n}\lambda^2} \tag{16}$$

The polydispersity requires the averaging of $f(f-1)$. The average is written as a function of the average functionality $\bar{f}$ and its variance $\bar{\Delta}f^2$ as $[\bar{f}(\bar{f}-1) + \bar{\Delta}f^2]$. For each molecule, introducing $s - 1 = c(\bar{f} - 1)$ and averaging over s, we obtain

$$S(q) = \frac{2}{\lambda} + \frac{1}{\bar{n}\lambda^2}\left\{\bar{f} - 2 + \frac{\bar{\Delta}f^2}{\bar{f}-1} - \frac{1}{\bar{s}}\left[\bar{f} + \frac{\bar{\Delta}f^2}{f-1}\right]\right\} \tag{17}$$

The result is similar to the monodisperse case but there is an extra contribution, due to the variance $\bar{\Delta}f^2$, which should not be forgotten.

III. Chains in a Good Solvent

Up to now we have assumed that the chains obey Gaussian statistics but it is well known that, in a good solvent, the excluded volume modifies the form of the structure factor. In an athermal solvent and in dilute solution the root mean square distance between two segments is given by

$$\bar{r}^2 = b^2 N^{2\nu} \tag{18}$$

where ν is a critical exponent which has a value close to the Flory[13] value 0.6. One first approximation can be to assume that the probability distribution remains Gaussian.[15] The large q expansion of the structure factor is then obtained as

$$S(q) = 2\epsilon\Gamma(\epsilon)\frac{1}{\lambda\epsilon} - 2\epsilon\Gamma(2\epsilon)\frac{1}{N\lambda^{2\epsilon}} \tag{19}$$

where $\lambda = (q^2b^2)/6$ and $\epsilon = 1/(2\nu) = D/2$, calling D the fractal dimension of the polymer; $\Gamma(\epsilon)$ is the classical Gamma function. If the system is polydisperse, one replaces N by its number average $\bar{N}$:

$$S^{-1}(q) = \frac{1}{2\bar{N}}\frac{\Gamma(2\epsilon)}{\epsilon\Gamma(\epsilon)^2} + \lambda^{\epsilon}\frac{1}{2\epsilon\Gamma(\epsilon)} \tag{20}$$

Equation 20 leads us to believe that all what we have said on Gaussian chains can be generalized to chains in a good solvent, replacing eq 2 by eq 19, replacing λ by λ^{ϵ}, and introducing new constants. This seems to be consistent with the fact that when one writes $\epsilon = {}^1/_2$ the chains behave like rods and eq 20 takes the form (except for the numerical coefficients) obtained rigorously for rods.[16] It seems, even if this procedure has been utilized successfully by experimentalists, that one has to be very cautious since a direct expansion of the formulas given by Duplantier[17] at first order in $4 - d$ (where d is the dimension of space) does not seem consistent with this result.[18]

IV. Stretched Chains

The structure factor of a chain under a finite tension τ is directly obtained from the structure factor of a

Gaussian chain (eq 1) by replacing the wave vector q^2 with an effective wave vector $q'^2 = q^2 - 2i\tau\cdot\mathbf{q}/kT$ and taking the real part of the Debye function.[19]

The expansion at large wave vectors leads to

$$S(q) = \frac{2}{\lambda}\left[1 - 4\cos^2\theta\left(\frac{\tau}{qkT}\right)^2\right] - \frac{2}{N\lambda^2} \qquad (21)$$

where θ is the angle between the scattering vector and the force. Upon averaging over the orientation of the force, we obtain

$$S(q) = \frac{2}{\lambda} - \frac{2}{\lambda^2}\left(\frac{1}{N} + \frac{2}{3g}\right) \qquad (22)$$

where we have introduced the number of monomers of the so-called Pincus[20] blob $g = 6(kT)^2/(\tau^2b^2)$; g is such that the chains with a number of monomers smaller than g remain Gaussian and the chains with a number of monomers larger than g are stretched. The intercept of the Zimm plot gives in this case a measure of the tension of the chain or of the size of the blobs; this could be useful for example in stretched gels.

V. Block Copolymers

We now study block copolymers of various architecture in solution or in the melt (for a review article, see ref 21). We consider for the sake of simplicity only block copolymers made of two types of units called a and b. Within a mean field approach such as the RPA the structure factors characterizing the copolymer require three quantities: P_i the form factor of the blocks made of the species a or b and the cross-term P_{ab} corresponding to interferences between the blocks. The copolymer is made up of s_a segments of length n_a and if we ignore the b units (and consider only the a units), it has c_a cross-links of functionality f_a. The structure factor $S_a(q)$ is given by eq 6:

$$S_a(q) = \frac{2}{\lambda} + \frac{\sum c_{ai}f_{ai}(f_{ai} - 1) - 2s_a}{s_a n_a \lambda^2} \qquad (23)$$

Here we have allowed for a polydispersity in the functionality; c_{ai} is the number of cross-links of functionality f_{ai}.

When the copolymer is composed of disconnected a segments or groups of segments (having no connections with other a segments) the structure factor is the sum of the structure factor of the individual segments.

The interference term $P_{ab}(q)$ has no term proportional to λ^{-1}, and the coefficient of λ^{-2} is the sum of the $f_a f_b$ contributions of the junctions where f_a segments a meet with f_b segments b:

$$(s_a n_a s_b n_b)^2 P_{ab}(q) = \sum \frac{2c_i f_{ai} f_{bi}}{\lambda^2 n_{ai} n_{bi}} \qquad (24)$$

The scattering behavior at large q of systems containing copolymers can then be evaluated from eqs 23 and 24. As in the case of homopolymers, for a polydisperse system in which the length of the branches is independent of the structure of the copolymer, the number-average lengths of the segments, $\bar{n}_a$ and $\bar{n}_b$, must be used.

To avoid cumbersome equations we now apply these formulas to simple examples: the star with arms of different nature, the alternating block copolymer, and the comb like copolymer.

One interesting case corresponds to copolymers in the bulk. The scattered intensity is calculated using the Leibler[22] formula. The copolymer is made of $N = s_a n_a + s_b n_b$ monomeric units. We define its composition by

$$u = \frac{n_a s_a}{n_a s_a + n_b s_b} \quad \text{and} \quad v = \frac{n_b s_a}{n_a s_a + n_b s_b} = 1 - u \qquad (25)$$

and obtain for the scattering per monomeric unit

$$i(q) = \bar{b}^2 uv \frac{S_a S_b - S_{ab}{}^2}{S_T} \qquad (26)$$

where $(n_a + n_b)S_T = n_a S_a + n_b S_b + 2S_{ab}$.

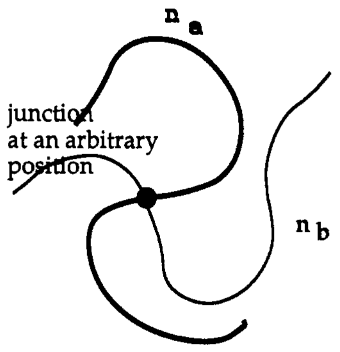

Figure 3. Model for a four-arm star with a random cross-link point.

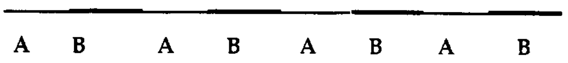

Figure 4. Model for an alternating copolymer.

(a) The Four-Arm Star. The first example is a four-arm polymer (see Figure 3) made of two chains having respectively n_a and n_b monomers and cross-linked at an arbitrary position along the chains (all the positions of the junction point have the same probability). Since we assume polydispersity in the position of the branch point, we cannot follow the preceding procedure. We divide the polymer into two units, one made of a segments and the other of b segments. Each subunit has a form factor given by the Debye function, S_a or S_b, corresponding to n_a or n_b monomers. The form factor of the total copolymer reads

$$S_T = \frac{1}{n_a + n_b}[n_a{}^2 P_a + n_b{}^2 P_b + 2n_a n_b P_{ab}] \qquad (27)$$

When we average over all positions of the junction, the only term to be averaged is the cross term $P_{ab}(q)$. Zimm[23] has shown that its average value is given by

$$\overline{P_{ab}} = P_a P_b \qquad (28)$$

Using this result, we obtain the total structure factor:

$$S_T(q) = \frac{2}{\lambda} + \frac{4}{\lambda^2(n_a + n_b)} \qquad (29)$$

When $n_a + n_b = 4\bar{n}$, one recovers the result for a four-arm star, $f = 4$ in eq 11. This illustrates the fact that the λ^{-2} term is only sensitive to the topology of the chain and not to the details of its architecture.

For a melt of random stars with two branches of different nature, eqs 26–29 give the scattered intensity as

$$i(q) = \bar{b}^2 \frac{2uv}{\lambda}\left\{1 - \frac{1}{\lambda n}\left[\frac{1}{u} + \frac{1}{v} + 2\right]\right\} \qquad (30)$$

(b) The Alternating Copolymer of the Type $(A–B)_s$ (Figure 4). This polymer is made of s blocks, each of them comprising n_a monomers a and n_b monomers b. The total number of monomers in the copolymer is $n = n_a + n_b$ so that $n_a = nu$ and $n_b = n(1 - u) = nv$; the total number of monomers in the copolymer is $N = sn$. Equation 2

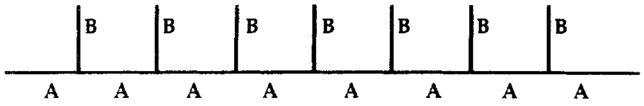

Figure 5. The comblike copolymer.

applied to the a part of the copolymer gives

$$S_a(q) = \frac{2}{\lambda} - \frac{2}{nu\lambda^2} = \frac{2}{\lambda}\left(1 - \frac{1}{\lambda nu}\right) \tag{31}$$

A similar result is obtained for the b part by replacing a by b and u by $1 - u = v$. The evaluation of $i(q)$ using eq 26 requires the value of S_{ab}. A careful examination shows that if one limits the expansion of $i(q)$ to the second term in λ^{-1}, the contribution of S_{ab}^2 to $i(q)$ can be neglected. One has therefore the choice of evaluating S_T either directly or using the formula (see eq 4)

$$s(n_a + n_b)S_T(q) = sn_aS_a(q) + sn_bS_b(q) + S_{ab}(q) \tag{32}$$

The determination of S_T is straightforward:

$$S_T = \frac{2}{\lambda}\left(1 - \frac{1}{\lambda sn}\right) \tag{33}$$

Replacing S_a, S_b, and S_T by their values leads to

$$\frac{i(q)}{\bar{b}^2} = \frac{2uv}{\lambda}\left\{1 - \frac{1}{\lambda n}\left[\frac{1}{u} + \frac{1}{v} - \frac{1}{s}\right]\right\} \tag{34}$$

For systems with polydisperse blocks nu, nv, and ns are replaced by their number averages:

$$\frac{\bar{b}^2}{i(q)} = \frac{\lambda}{2uv} + \frac{1}{4(uv)^2}\left[\frac{1}{\bar{n}_a} + \frac{1}{\bar{n}_b} - \frac{1}{N}\right] \tag{35}$$

This formula has already been obtained[8] and used to study the transesterification reaction.[24]

(c) The Comblike Copolymer (Figure 5). A third example is the case of a comblike polymer made of a skeleton a of s_a segments on which are grafted s_b chains of nature b. This copolymer has $c = s$ cross-links of functionality 3 (2 for the blocks a and 1 for the blocks b), $s_a = s + 1$ and $s_b = s$. The general formula gives

$$S_a(q) = \frac{2}{\lambda}\left[1 - \frac{1}{n_a(s+1)\lambda}\right] \tag{36}$$

since the a blocks form a classical Gaussian chain of $(s + 1)n_a$ statistical elements.

For S_b we obtain

$$S_b(q) = \frac{2}{\lambda}\left[1 - \frac{1}{n_b\lambda}\right] \tag{37}$$

The evaluation of P_{ab} is made from eq 24 in which we set $c = s$, $f_a = 2$, and $f_b = 1$:

$$S_{ab} = 2N(N+1)n_an_bP_{ab}(q) = 2s/\lambda^2 \tag{38}$$

As before, we define $N = n_a(s + 1) + n_bs$ and the composition of the copolymer $u = n_a(s + 1)/(n_a(s + 1) + n_bs)$; this gives

$$S_T(q) = \frac{2}{\lambda}\left[1 + \frac{1}{\lambda}\frac{s-1}{N}\right] \tag{39}$$

and, using eq 34, the scattering intensity

$$\frac{i(q)}{\bar{b}^2} = \frac{2uv}{\lambda}\left[1 - \frac{1}{\lambda}\left[\frac{1}{Nu} + \frac{1}{n_b} - \frac{s-1}{N}\right]\right] \tag{40}$$

If the system is polydisperse, with the same structure, one has to replace n_a, n_b, and N by their number averages.

The main difference between the linear and the comblike copolymers is that the final result, instead of depending on the total number of monomers and on the values of $\bar{n}_a$ and $\bar{n}_b$, depends on $\bar{n}_b$ and on the total length of the chain a. This is not surprising since the division of this chain into subunits is a computational procedure without any physical basis. If the chain is very long, $1/Nu$ can be neglected and $(s - 1)/N$ can be approximated by $1/(n_a + n_b)$. The scattered intensity depends then on the total length of the a part, on the length of the branches, and on the structure of the copolymer.

This list of examples could be very easily extended but it is sufficient to prove that the second term in the expansion of the intensity at large wave vectors depends only on the length of the different kinds of segments from which the chain has been built. In all the examples, we have calculated the scattering in the bulk using eq 26 which leads to a combination of P_a, P_b, and P_{ab} or P_T. For a copolymer solution, the three functions can be measured independently by contrast matching of one of the species a or b. More detailed information on the copolymer can be obtained.

VI. Conclusions

The aim of this paper was to show that the first correction to the asymptotic behavior of the structure factor of polymers at large wave vectors gives important information. This has been illustrated by many examples, and in most cases this correction to the asymptotic behavior depends only on the local architecture of the chain. In particular, it does not depend on the overall size of the molecules when the small-scale structure is kept constant. This can be shown in the general case by taking the limit of large s in eq 17:

$$S(q) = \frac{2}{\lambda} + \frac{1}{\bar{n}\lambda^2}\left\{\bar{f} - 2 + \frac{\bar{\Delta}\bar{f}^2}{\bar{f} - 1}\right\} \tag{41}$$

None of the parameters used in this formula depends on the size of the molecule. In practice, this means that, if the size of a branched polymer increases in a polymerization reaction, after a certain size (which depends on the window of the experimentally accessible q values), the scattering function no longer changes and depends only on the size of the branches. This result is even more obvious for monodisperse block copolymers[8] of any structure for which the total scattering function is independent of the size of the molecule. Experimentally, this has been verified by comparing the scattering by copolymer stars and by a network prepared using these stars as building blocks; no explanation was then proposed to explain this phenomenon.[25]

One of the experimental problems which must be solved in each case is to recognize the range of q for which our approximations are valid. The only rule is that the length of all the chains which we have called segments should be large enough in order to neglect the factor $\exp(-\lambda n)$. This requires, to give an order of magnitude, that n must be at least larger than the persistence length of the copolymer. As an example one can say that this kind of experiment does not allow the measurement of short chain branching in polyethylene.

One last remark concerns the existence of loops in the structure. We have supposed throughout that there is only one path to go from one scattering point to another one and we therefore have ignored any loops. The application of our results to networks and gels is then hazardous. Experimentally, however, it is observed that the scattering function of an elastic chain in a network is the same as the scattering function in the same environment but without any coupling of the precursor;[26] this suggests that one can neglect the existence of the loops. A qualitative argument in the same direction has been developed by Krause et al.,[27] and more quantitative treatment shows that the results obtained here are only slightly modified when one takes into account the existence of loops.[28]

References and Notes

(1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(2) Debye, P. *J. Appl. Phys.* **1944**, *15*, 338.
(3) Kratky, O.; Porod, G. *Rec. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.
(4) Zimm, B. *J. Chem. Phys.* **1948**, *16*, 1099.
(5) Guinier, A.; Fournet, G. *Small Angle Scattering of X Rays*; John Wiley and Sons, Inc.: New York, 1955.
(6) Benoît, H. *J. Polym. Sci.* **1953**, *11*, 507.
(7) Kugler, J.; Gilmer, J. W.; Wiswe, D.; Zachmann, H. G.; Hahn, K.; Fischer, E. W. *Macromolecules* **1987**, *20*, 1116.
(8) Benoît, H.; Hadziioannou, G. *Macromolecules* **1988**, *21*, 1449.
(9) Burchard, W.; Kajiwara, K.; Nerger, D. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 157.
(10) Hammouda, B. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *30*, 1387.
(11) Khorramian, B. A.; Stivala, S. S. *Polym. Commun.* **1986**, *27*, 40.
(12) Rempp, P.; Lutz, P. *Makromol. Chem., Macromol. Symp.* **1992**, *62*, 213.
(13) Kosmas, M.; Vlahos, C.; Hadjichristidis, N. *Macromolecules* **1991**, *24*, 5727.
(14) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(15) Loucheux, C.; Weill, G.; Benoît, H. *J. Chim. Phys.* **1958**, *55*, 540.
(16) Luzzati, V.; Benoît, H. *Acta Crystallogr.* **1961**, *14*, 297.
(17) Duplantier, B. *J. Phys. (Paris)* **1986**, *47*, 1633.
(18) Joanny, J. F.; Johner, A., unpublished results.
(19) Picot, C.; Duplessix, R.; Decker, C.; Benoît, H.; Boué, F.; Cotton, J. P.; Daoud, M.; Farnoux, B.; Jannink, G.; Nierlich, M.; de Vries, A. J.; Pincus, P. *Macromolecules* **1977**, *10*, 436.
(20) Pincus, P. *Macromolecules* **1976**, *9*, 386.
(21) Hammouda, B. *Adv. Polym. Sci.* **1993**, *106*, 87.
(22) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(23) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1093.
(24) Benoît, H.; Fischer, E. W.; Zachman, H. G. *Polymer* **1989**, *30*, 420.
(25) Duplessix, R. Thesis, 1975. See also: Benoît, H.; Picot, C.; Krause, S. In *New Trends in Physics and Physical Chemistry of Polymers*; Lee, L. H., Ed.; Plenum Press: New York, 1988; p 471.
(26) Beltzung, M.; Picot, C.; Rempp, P.; Herz, J. *Macromolecules* **1982**, *15*, 1594.
(27) Krause, S.; Benoît, H.; Picot, C. In *New Trends in Physics and Physical Chemistry of Polymers*; Lee, L. H., Ed.; Plenum Press: New York, 1988; p 483.
(28) Hammouda, B., to be published.