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Theoretical Approach to Enhanced Low-Angle Scattering from Moderately Concentrated Polymer Solutions

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ABSTRACT: Experimental measurements have shown that the elastic light-scattering intensity of moderately concentrated polymer solutions presents a strong rise at small angles and a linear behavior at high angles in the Zimm representation. In a first attempt at analysis, we use the Benoit–Benmouna theory (which is an extension of the Zimm theory) of light-scattering intensity from moderately concentrated solutions. This theory is in good agreement with experimental observations for the high-angle range. To explain the excess of scattered light intensity at small angle, we propose to introduce an attractive potential $-(fv/rd^2)\exp(-r/d)$ in addition to the excluded volume $v\delta(r)$; d is a mean distance between the inhomogeneities and f is a constant that characterizes the amplitude of the potential. The calculated scattering function gives a good account of the downward curvature of the Zimm plot in the range of $qR_G < 1$.

Introduction

The first observation of anomalous excess of intensity at small angles in light-scattering measurements (LS) of moderately concentrated solutions of polystyrene and poly(methyl methacrylate) was made by Benoit and Picot.[1] They showed that the Zimm representation displays strong downward curvature in the range of $qR_G < 1$, where $q = 4\pi/\lambda \sin(\theta/2)$ is the wave number, λ the wavelength of the radiation, θ the scattering angle, and R_G the radius of gyration of the macromolecule. However, the behavior of $c/I = f(q^2)$ was found to be linear for $qR_G < 1$ with a slope decreasing with increasing concentration c.

This unexpected phenomenon was the object of many other experimental[2–7] investigations and controversial interpretations. It has been observed for many polymers, polar or nonpolar,[7–9] in classical light-scattering experiments and also in neutron-scattering[3] and small-angle X-ray-scattering measurements.[6] Some dynamic light-scattering data[10–12] recorded for semidilute solutions showed a slow diffusional motion not detectable in dilute solution. This component is thought to be due to particle aggregates and probably has the same origin as anomalies found in elastic small-angle scattering.

From an experimental point of view, this phenomenon has sometimes been considered as an artifact due to poor polymer solubilization. Nevertheless, it has been observed even in carefully prepared solutions, either by concentrating dilute solutions[3] or by diluting more concentrated solution,[2] for polystyrene and polyacrylamide.[7] Moreover, centrifugation was found to decrease this effect.

In the case of polystyrene, Guenet et al.[4] pointed out that the phenomenon depends on the nature of the solvent, and Gan et al.[5] showed that the Flory interaction parameter is not the driving factor. A correlation between the occurrence of anomalous scattering and the potential for physical gelation at low temperature has been demonstrated.[4,5]

The interpretation of this behavior is generally based on the concept of more or less well-defined macromolecule association in the form of "aggregates". In the more recent and convincing approach of Koberstein et al.,[3] the abnormal scattering is attributed to the presence of islands of pure polymer in solution. Consequently the scattered intensity is simply considered as the sum of two terms $I(q) = 1/(1 + q^2\xi^{-2}) + I_{ex}(q)$, where ξ is the screening length[13] and I_{ex} is low-angle excess intensity due to the long-range heterogeneities. In this way they have shown that the correlation length between the inhomogeneities is of the order of magnitude of the radius of gyration of the macromolecule. This result is inconsistent with the starting hypothesis because it shows a very strong correlation between the two phases.

In this report we propose another approach to the scattered behavior of moderately concentrated polymer solutions: First, we use the recent Benoit–Benmouna theory[14] to calculate the light-scattering function and show that this approach gives a good account for the linear parts of the curves $c/I(q,c) = f(q^2)$ in the high-angle range. Second, we introduce a theoretical segment direct correlation function $\Delta(r)$ to renormalize the second virial coefficient A_2 as a sum of a classical short-range excluded volume $v\delta(r)$ and an attractive potential $-fv/r \exp(-r/d)$, where $\delta(r)$ is the known Dirac function, d is a mean distance between inhomogeneties, and f is a constant that should represent the amplitude of the attractive potential. In this approach we do not consider that the solution contains two independent phases, and we show that the change in A_2 can cause an excess of small-angle scattering. The small-angle anomalies observed for the semidilute solution of PS in ref 3 can be described by such an approach.

Linear Behavior at High Angles. The Benoit–Benmouna[14] theory considers a solution containing N chains, of polymerization degree n, per unit volume. The total scattered intensity is defined by

$$I(q) = \frac{Km}{N_A}\sum_{\alpha}^{N}\sum_{\beta}^{N}\sum_{j}^{n}\sum_{l}^{n} \langle \exp(\vec{i}\vec{q}\cdot R_{jl})\rangle \tag{1}$$

K is a constant that characterizes both the apparatus and the type of radiation; m is the molecular weight of a monomer; N_A is Avogadro's number; R_{jl} is the vector distance between monomer j of chain α and monomer l of chain β; and the symbol $\langle ... \rangle$ represents the equilibrium ensemble average.

By extension of the single contact approximation or RPA[14] for chain molecules, $I(q)$ can be written[15,16]

$$K^{-1}I(q) = \frac{Nn^2P(q)}{1 + Nn^2\Delta(p)P(q)} \tag{2}$$

where $K_0 = Km^2/N_A$ and $P(q)$ is the renormalized-chain form and $\Delta(q)$ is the Fourier transform of the segment direct correlation function $\Delta(r)$. Here $\Delta(q)$ is independent of q and equal to the excluded volume v for a pair of monomers. Benoit–Benmouna[14] and Daoud et al.[17] showed

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that eq 2 is still true for semidilute solution if we replace $P(q)$ by $P(q,c)$ and v by $v(c)$, where c is the concentration of polymer. If the chain is assumed to be Gaussian even in the semidilute range, we can write

$$P(q,c) = \frac{2}{u^2(c)}([\exp[-u(c)] + u(c) - 1] \qquad (3)$$

where $u(c) = q^2R_g{}^2(c)$ and the variation of the radius of gyration with concentration is given by Daoud et al.:[17]

$$R_g{}^2(c) = R_g{}^2(0)(c/c^*)^{(1-2\nu)/(3\nu-1)} \qquad (4)$$

where ν is the excluded volume exponent and c^* is the overlap concentration. Of course, eq 4 is restricted to $c \gtrsim c^*$.

By use of the standard notation $A_2 = vN_A/2m^2$, $M = nm$, and $c = Nnm/N_A$, eq 2 can be written in the known form

$$KcI^{-1}(q,c) = \frac{1}{MP(q,c)} + 2A_2(c)c \qquad (5)$$

where $A_2(c)$ is the effective second virial coefficient determined as follows: $A_2(c) = v(c)N_A/2m^2$.

We evaluate $A_2(c)$ by using the classical relation between the scattered intensity at $q = 0$ and the osmotic pressure:

$$KcI^{-1}(0,c) = (RT)^{-1}(\partial\pi/\partial c) \qquad (6)$$

where R is the ideal gas constant and T the temperature. For $c > c^*$, $1/MP(0,c)$ becomes negligible and then

$$2A_2(c)c = (RT)^{-1}(\partial\pi/\partial c) \qquad (7)$$

Many expressions have been suggested to describe the concentration dependence of the osmotic pressure.[18-21] In the semidilute range it was predicted by des Cloizeaux[18] from a scaling argument that the reduced osmotic pressure Z depends only on the dimensionless concentration c/c^*:

$$Z = \pi M/cRT \simeq (c/c^*)^{3\nu/(3\nu-1)} \qquad (8)$$

Other equations allow a continuous crossover between the virial expansion and the des Cloizeaux limit. For example, Schulz and Stockmayer[21] have derived

$$1 - Z^{-1} = G(c/c^*)[1 + k_2{}^{-1}(c/c^*)Z]^{-q'} \qquad (9)$$

With eqs 4, 5, 7, and 8 or 9, we can calculate the scattered intensity for the polymer (in a good solvent) in semidilute solution.

Application 1. We used the experimental data given in ref 22 to calculate the constants of eqs 8 and 9 for polystyrene in benzene. The Des Cloizeaux equation simply becomes

$$\pi/RT = 1.69 \times 10^{-3}c^{9/4} \qquad (10)$$

and for eq 9, $G = 1.36$, $q' = 0.45$, and $k_2 = 1.9$, where c^* is calculated by

$$c^* = 3M/4\pi R_g{}^3N_A \qquad (11)$$

In Figure 1, some experimental LS data obtained by Koberstein et al.[3] for a polystyrene sample ($M_W = 3 \times 10^6$ and $R_g = 1010$ Å) in benzene can be compared with calculated curves. Both eqs 8 and 9 give the same results in $c > c^*$, and the curves (1) correspond to the former relation. In the range of q where $c/I(q,c) = f(q^2)$ is linear, the agreement between experimental and calculated results is quite remarkable. We point out that no adjustable parameter was used in the calculation. This justifies the use of the Benoit–Benmouna[1]14 theory as the basis of the following approach developed to explain the anomalies at small angles.

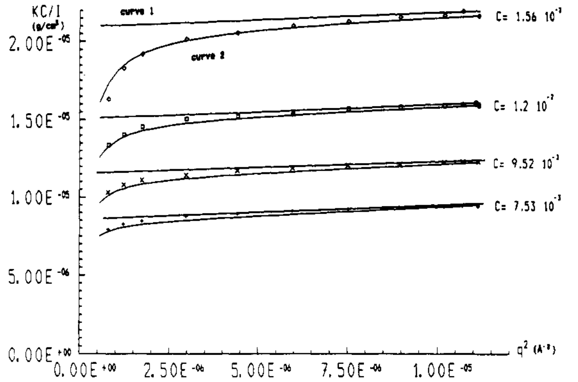

Figure 1. Experimental (from ref 3) and calculated variations of $Kc/I(q)$ versus q^2 for the polystyrene–benzene system at different concentrations c (given in g/cm^3). Curves 1 and curves 2 are obtained from relations 5 and 14 (with $f = 1$), respectively (see text).

Table I
Values of the d and ξ Screening Lengths[a]

c, g/cm^3	c^*, g/cm^3	d, Å	ξ, Å
7.53×10^{-3}	4.84×10^{-4}	3600	93.93
9.57×10^{-3}		3100	87.87
1.2×10^{-2}		2900	67.67
1.56×10^{-2}		2400	56.56

[a] Calculated from experimental data of ref 3 for the polystyrene–benzene system (see text).

Small-Angle Scattered Intensity. Let us assume that the excess of scattered intensity at small angles is caused by inhomogeneities resulting from an attractive potential. We propose to write this potential as

$$\varphi(r) = -fv/r \exp(-r/d) \qquad (12)$$

where d is their mean distance of separation and f is a constant that should represent the amplitude of the potential. Then $\Delta(q,c)$ becomes q dependent:

$$\Delta(q,c) = v(c)[1 - f/(1 + q^2d^2)] \qquad (13)$$

After use of eq 13 in (2), eq 5 becomes

$$KcI^{-1}(q,c) = \frac{1}{MP(q,c)} + 2A_2(c)c\left(1 - \frac{f}{1 + q^2d^2}\right) \qquad (14)$$

In eq 14 there is a renormalized apparent second virial coefficient $A_2(q,c) = A_2(c)G(q)$ with $G(q) = 1 - f/(1 + q^2d^2)$. The case where $f < 1$ is not possible since d^2q^2 cannot be negative, so f must be >1.

We see from eq 14 that for $q^2d^2 = (f - 1)$ the system behaves as in θ conditions. For $q^2d^2 < (f - 1)$, the polymer appears to be in a poor solvent, and for $q^2d^2 > (f - 1)$, the polymer appears to be in a good solvent.

Application 2. The experimental data of ref 3 were fitted with relation 14, by adjusting only the parameter d, within the whole concentration range. The value of f is kept equal to 1 in a first approximation, and a rather good agreement with experimental data is obtained. Table I shows that d is a decreasing function of concentration. In Figure 2, d is plotted versus c/c^* on a logarithmic scale, and the straight line corresponds to the following relationship:

$$d = 15450(c/c^*)^{-0.53} \qquad (15)$$

where d may appear as a screening length of long-range interactions caused by the presence of inhomogeneities.

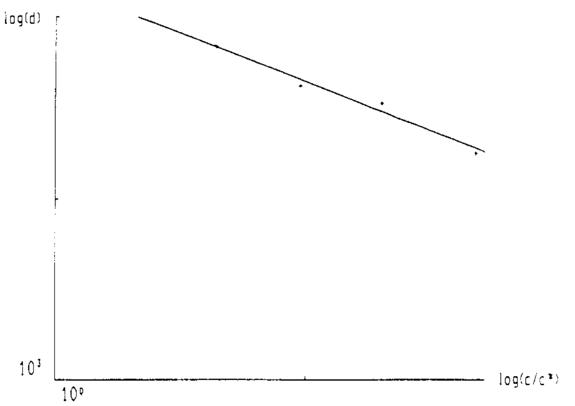

Figure 2. Variation of the parameter *d* (screening length between inhomogeneities) versus c/c^* (see text).

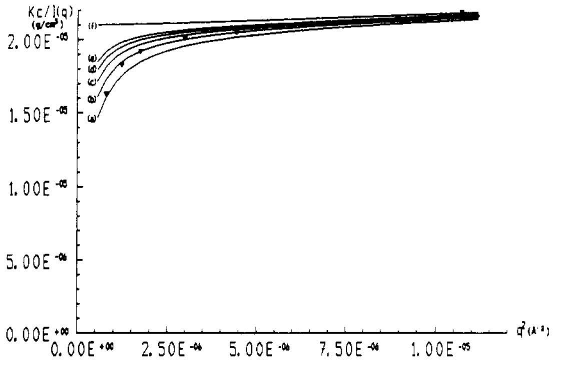

Figure 3. Influence of *d* on the amplitude of the small-angle scattered intensity excess at $c = 1.56 \times 10^{-3}$ g/cm³. Experimental data, ∇. The curves a–f are calculated from relation 14 for d = 2000, 2400, 2800, 3200, and 3600 Å and d → ∞, respectively and $f = 1$.

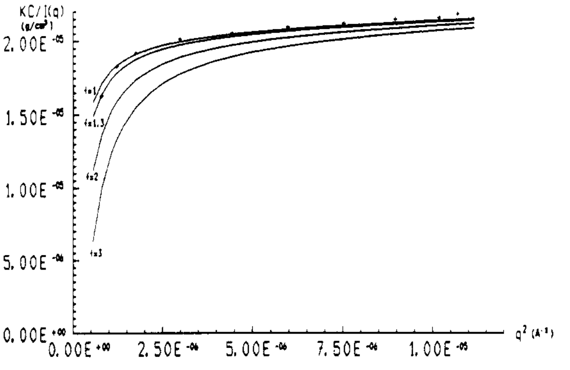

Figure 4. Influence of *f* on the amplitude of the small-angle scattered intensity excess of $c = 1.56 \times 10^{-3}$ g/cm³. Experimental data, +.

Figure 3 shows that a given concentration the calculated rise of intensity at small angles decreases with increasing *d*, the *f* value being constant. We have not tried simultaneously to adjust both parameters *d* and *f*, since the correlation between these parameters is not defined in our model. In fact, the fit cannot be improved by taking $f \neq 1$ if one keeps the $d = f(c)$ values obtained for $f = 1$ (see Figure 4).

Concluding Remarks

The semidilute polymer solution theory of Muthukumar and Edwards[13] considers the effective interactions as the sum of the excluded volume and of an attractive screening potential $-1/r \exp(-r/\xi)$, where ξ is the known screening length. In our attempt, we introduce a new screening length *d* larger than ξ. It has been shown[3,5] that ξ can be measured from the linear part of the plot $1/I(q) = f(q^2)$ at high scattering angles. Indeed, in the range of $R_g^{-1} < q < \xi^{-1}$, the $P(q,c)$ function can be written as

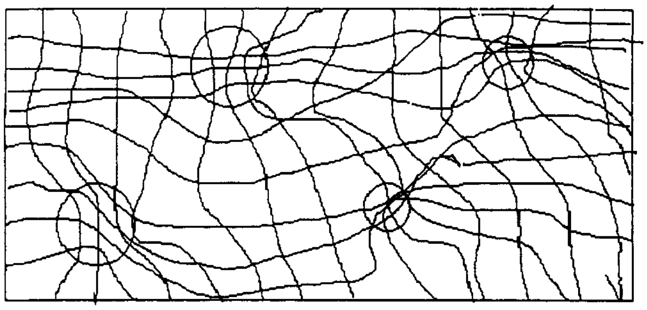

Figure 5. Scheme of an unhomogeneous semidilute solution of polymer.

$$P^{-1}(q,c) = q^2R^2(c)/12 + {}^1/_2 \qquad (16)$$

and thus we obtain

$$I^{-1}(q,c) = \frac{R^2(c)}{12K_0Mc}\left[q^2 + \frac{12}{R^2(c)}[3\nu/(3\nu - 1) \times BMc^{1/(3\nu-1)} - {}^1/_2]\right] \qquad (17)$$

By analogy with the Lorentzian equation ($1/I \simeq 1 + q^2\xi^{-2}$) we can write

$$I^{-1}(q,c) = \frac{R^2(c)}{12KMc}[q^2 + \xi^{-2}(c)] - \frac{2fA_2(c)}{K(1 + q^2d^2)} \qquad (18)$$

This relation shows that ξ can be obtained from the linear behavior of $I^{-1}(q,c) = f(q^2)$ at high scattering angles where the second term tends toward zero. Such treatment of the experimental data of Figure 1 leads to the following scaling law for ξ (see also Table I):

$$\xi = 388(c/c^*)^{-0.74} \qquad (19)$$

This result is in a good agreement with the Lapp et al.[23] law and clearly shows that *d* is much larger than ξ, whatever the *f* value is.

Koberstein et al.[3] found that the excess scattering intensity at small angle can be strongly reduced by centrifuging the solutions. This means that the inhomogeneities are eliminated by centrifugation, and this observation is consistent with their model of two phases of very different density. Dautzenberg,[2] however, found that centrifugation caused only a slight attenuation of the excess scattering, and the same observation was made for aqueous solutions of unhydrolyzed polyacrylamide,[22] in better agreement with our model.

In the case of dilute solutions, the association process implies that molecular weight is an increasing function of concentration. In fact our model must be applied to systems where anomalous scattering is observed only in the semidilute range. Moreover, eq 14 clearly shows that the molecular weight can never be higher than the molecular weight measured at $c = 0$. It is indeed well-known that in the semidilute range the scattered intensity is no longer molecular weight dependent and is a function only of c/c^*.

Nevertheless, two questions should be asked: what exactly are the inhomogeneities, and what is the origin of an attractive potential in polystyrene solutions?

Figure 5 schematizes the possible structure of an inhomogeneous semidilute solution: the inhomogeneities are just domains where the local concentration is higher than the average bulk concentration and one can define two screening lengths: ξ between chains and *d* between heterogeneities. There is no strong association but only attraction between some parts of the macromolecules.

As pointed out by Guenet et al.,[4] such effects for atactic polystyrene have probably the same origin as the physical gelation at low temperature.[24] A series of systematic studies by isotropic and anisotropic light scattering,[5,27] differential scanning calorimetry,[25,26] and rheological measurements support the assumption that the syndiotactic parts of the atactic polystyrene may self-attract and at low temperature form crystallized microdomains acting as reticulation points. Such a description must be checked by numerous other investigations.

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