# Light Scattering from Ternary Polymer Solutions: An Analysis of the Apparent Radius of Gyration

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ABSTRACT: Using a renormalized form of the random-phase approximation (RPA) for ternary solutions, we analyze hitherto unpublished data on the apparent radius of gyration for the system polystyrene-poly(methyl methacrylate)-bromobenzene. The microscopic parameters for this system being known from previous analysis of the zero-angle scattering intensity, the theory yields a parameter-free prediction, which fits the data very well. To show the influence of renormalization, we also analyze the data by an unrenormalized version of RPA.

## 1. Introduction

During the last years both the experimental and the theoretical tools available for an analysis of ternary polymer solutions have been greatly improved. On the experimental side, the optical $\Theta$-method has been invented,[1,2] which allows for a compensation of contributions to the scattering intensity which hold little information on the interaction of the two chemically different polymer species in the solution. On the theoretical side, the application of the renormalization group directed attention to possible scaling and power law behavior.[3-6] The parameter region governed by such simple behavior is known[7] to be quite restricted, however, and in general we expect the data to be taken in some crossover region where a power law analysis is not justified. We therefore need a theory of measurable quantities in the crossover region among different asymptotic scaling limits. A lowest order calculation of the crossover functions for both scattering intensity and thermodynamic quantities recently has been presented,[8] which in combination with a higher order representation of the renormalization group is expected to give a semiquantitative fit of experimental data. For some thermodynamic quantities also first-order results for scaling functions are available.[9]

The experimental test of the new theoretical developments is only at its beginning. Some asymptotic power laws are supported by experiment,[10] but it is at least not obvious that the data reach the appropriate scaling limits. It is well-known that a restricted set of data taken in a crossover regime often simulates a power law with some effective exponent. An example pertaining to the semidilute limit of ternary solutions may be found in ref 7 (Figure 1). An unambiguous test of the theory therefore needs an extensive set of measurements covering a large region of concentrations and molecular weights and including data on the binary polymer-solvent subsystems.

A light scattering experiment conforming to these criteria recently has been carried through[1,2] for the system polystyrene (PS)-poly(methyl methacrylate) (PMMA)-bromobenzene (BB), and the resulting zero-angle scattering intensity, $R_0$, has been analyzed by renormalization group theory.[8] The system was found to be close to the excluded-volume limit for both binary subsystems PS-BB or PMMA-BB. In such a situation the theory involves only three microscopic parameters, which by construction are independent of molecular weight or concentration. Furthermore, two of these parameters can be determined by independent measurements on the binary subsystems. In ref 8 it was found that the remaining ternary parameter can be adjusted so that the theory gives a reasonable fit of the molecular weight and concentration dependence of $R_0$.

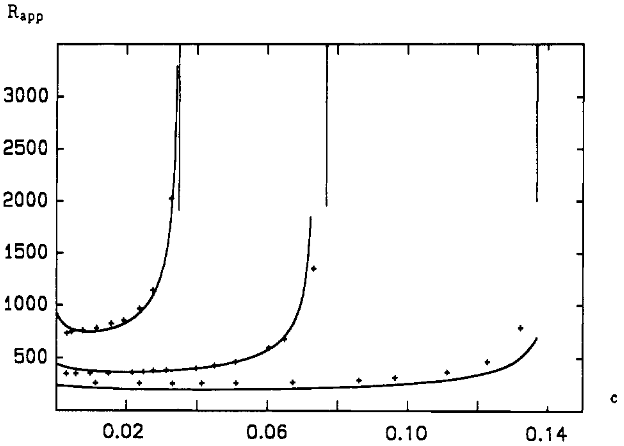

**Figure 1.** $R_{app}$ in cm$^{-8}$ as a function of total polymer concentration $c$ in g/mL: (upper curve) PC200-75M, (middle curve) F80-78M, (lower curve) 49H-31M. Vertical lines indicate the spinodal concentrations and crosses the data points. Full curves are our theory.

Once the microscopic parameters are fixed, the theory yields quantitative predictions for a wealth of other experimental observables. To test the theory and to demonstrate its predictive power, it therefore is of interest to analyze more data on the same system. This paper is devoted to that task. We analyze hitherto unpublished data on the "apparent radius of gyration", $R_{app}$, which derives from the slope of the scattering intensity at small angles. We indeed find reasonable agreement between theory and experiment. (See Figure 1.) Since this test involves no new adjustable parameter, this result strongly supports the validity of the theory.

In section 2 we define $R_{app}$ and we recall the standard unrenormalized random-phase approximation[11] (RPA) for this quantity. To lowest order, the renormalized theory essentially replaces all parameters of the RPA by effective quantities, the concentration and molecular weight dependence of these quantities being given by the renormalization group. A detailed presentation of the resulting equations has been given in ref 8 (see also ref 7), and we therefore only summarize the somewhat involved equations in the Appendix. In section 3 we compare the experimental data to the results of renormalized and unrenormalized theory.

## 2. Apparent Radius of Gyration

To define $R_{\mathrm{app}}$, we write the scattering intensity $R_\vartheta$ at angle $\vartheta$ as

$$\frac{R_\vartheta}{K^*} = N_{\mathrm{Av}} \sum_{a,b=1}^{2} \nu_a I_{ab}(q) \nu_b \tag{1}$$

$$\nu_a = \partial n/\partial c_a, \quad a = 1, 2 \tag{2}$$

$$K^* = 4\pi^2 n^2/(N_{\mathrm{Av}} \lambda_0^4) \tag{3}$$

$$q^2 = (4\pi/n\lambda_0)^2 \sin^2 \vartheta/2 \tag{4}$$

Here $N_{\mathrm{Av}}$ is Avogadro's number, $n$ denotes the refractive index of the solution, and $\lambda_0$ is the wavelength of the light in vacuo. The monomer number concentration, $c_a$ (i.e., weight concentration divided by monomer molecular weight), is measured in number per cubic centimeter. $I_{ab}(q)$ is the correlation function of the fluctuating densities of monomer species $a$ and $b$. With our conventions, it is normalized such that

$$I_{ab}(0) \underset{c_a, c_b \to 0}{\longrightarrow} c_a N_{\mathrm{w}a} \delta_{ab} \tag{5}$$

where $\delta_{ab}$ denotes Kronecker's symbol and $N_{\mathrm{w}a}$ is the weight-averaged polymerization index of species $a$. We now can define $R_{\mathrm{app}}$ as

$$R_{\mathrm{app}}^{\ 2} = -3 \frac{\partial}{\partial q^2}\bigg|_0 \ln (R_\vartheta/K^*) = -3 \left. \frac{\sum_{ab} \nu_a \frac{\partial}{\partial q^2} I_{ab}(q) \nu_b}{\sum_{ab} \nu_a I_{ab}(0) \nu_b} \right|_{q=0} \tag{6}$$

Clearly this quantity is directly observable in a scattering experiment but has no simple interpretation in terms of the properties of the individual macromolecules. It rather gives some weighted average of the length scales characterizing our system. In the dilute limit it reduces to the weighted average of the radii of gyration:

$$R_{\mathrm{app}}^{\ 2} = \frac{\sum_a \nu_a^2 c_a N_{\mathrm{w}a} R_{\mathrm{g}a}^{\ 2}}{\sum_a \nu_a^2 c_a N_{\mathrm{w}a}}, \quad c_1, c_2 \to 0 \tag{7}$$

Close to the spinodal of the two-fluid phase separation, which typically occurs for strongly overlapping systems of chemically different chains, it diverges proportional to the correlation length of the composition fluctuations driving the phase separation.

The RPA for the scattering intensity is most easily formulated in terms of the matrix $\tilde{I}_{ab}$ inverse to $I_{ab}$. We use the expression

$$\tilde{I}_{ab} = \delta_{ab}[c_a N_a D_a(q^2 R_{\mathrm{g}a}^{\ 2})]^{-1} + u_{ab} \tag{8}$$

Table I

| sample | $10^3 N_{\mathrm{w}}$ | $N_{\mathrm{w}}/N_{\mathrm{n}}$ | $(R_{\mathrm{g}}^2)_z$, Å | $10^4 A_2$, (mol cm$^3$)/g$^2$ |
|---|---|---|---|---|
| | | PS | | |
| PC200 | 23.3 | 1.30 | 770 | 2.05 |
| F80 | 7.44 | 1.01 | 370 | 2.71 |
| 49H | 2.72 | 1.10 | | |
| | | PMMA | | |
| 75M | 21.3 | 1.35 | 660 | 1.57 |
| 78M | 6.26 | 1.45 | 334 | 2.33 |
| 31M | 2.11 | 1.27 | | |

where $N_a$ is the number-averaged polymerization index, $R_{\mathrm{g}a}$ is the radius of gyration of an isolated chain of species $a$ and polymerization index $N_a$, and $u_{ab}$ is the interaction constant for monomers of species $a$ and $b$. $D_a(x)$ stands for the Debye function, generalized to arbitrary polydispersity

$$D_a(x) = \frac{2}{x^2}[\tilde{p}_a(x) - 1 + x] \tag{9}$$

Here $\tilde{p}_a(x)$ is the Laplace transform of the chain-length distribution function, of which we will need only some low order moments

$$\frac{\partial^2}{\partial x^2}\tilde{p}_a(x)\bigg|_0 = \frac{N_{\mathrm{w}a}}{N_a}$$

$$-\frac{\partial^3}{\partial x^3}\tilde{p}_a(x)\bigg|_0 = \frac{N_{za} N_{\mathrm{w}a}}{N_a^{\ 2}} \tag{10}$$

Equation 8 can be derived as a lowest order approximation of the cluster expansion, ignoring all nontrivial correlations. Some correlation effects can be taken into account[11] by replacing $D_a(q^2 R_{\mathrm{g}a}^2)$ by the total scattering $J_a(q^2)$ of a single chain in the solution and taking $u_{ab}$ as effective chain-length- and concentration-dependent parameters. In the absence of independent information of $J_a(q^2)$, this, however, for the quantities considered here essentially amounts to a reparametrization of the data with no predictive power. In the analysis of the data using the unrenormalized formalism, we therefore follow ref 12, taking the result (8) as unrenormalized RPA, with $u_{ab}$ and $R_{\mathrm{g}a}^2$ taken as concentration independent, but chain-length-dependent, parameters.

To lowest order, the renormalized theory yields a result of the same structure (8), but with $c_a$, $N_a$, $R_{\mathrm{g}a}^2$, and $u_{ab}$ being replaced by renormalized counterparts $c_{\mathrm{R}}^{(a)}$, $N_{\mathrm{R}}^{(a)}$, etc. The expression, given in the Appendix, can be interpreted as scattering due to chains composed of $N_{\mathrm{R}}^{(a)}$ excluded-volume blobs, the blob concentrations, blob size, and interactions depending on molecular weights and concentrations in the solution. This dependence is given by the renormalization group equations, which for the present system depend on only three microscopic parameters, independent of chain lengths and concentrations. Since this theory is discussed at length in ref 8, we do not repeat the lengthy derivation here. With regard to the discussion given above, it may be sufficient to note that the renormalized theory yields definite results for the chain-length and concentration dependence of the parameters occurring in the renormalized form of eq 8, which are summarized in the Appendix. Note that the use of the renormalization group flow equations for these parameters goes far beyond the substitution of simple power law expressions advocated by scaling theories. It gives an expression for the crossover among the different scaling limits.

## 3. Comparison between Theory and Experiment

The molecular characteristics of the polymer samples as given in ref 2 are collected in Table I, where we use the

**Table II**

| | $\nu_a$, cm$^3$/g | $\rho_a$, mol/cm$^3$ |
|---|---|---|
| PS | 0.0484 | 0.0103 |
| PMMA | −0.0501 | 0.0121 |

**Table III**

| sample | $x_{\rm PS}$ | $x_{\rm PMMA}$ | $c^*$, g/cm$^3$ |
|---|---|---|---|
| PC200–75M | 0.457 | 0.543 | 0.0350 |
| F80–78M | 0.426 | 0.574 | 0.0769 |
| 49H–31M | 0.408 | 0.592 | 0.1370 |

polymerization index instead of the molecular weight. Except for the shortest chains, the $z$-averaged radius of gyration determined in bromobenzene is also given.

In the ternary solutions the relative concentrations of PS and PMMA were chosen according to the (unrenormalized) optical Θ-condition, which reads in the present notation

$$0 = \nu_1 N_{\rm w1} \frac{c_1}{\rho_1} + \nu_2 N_{\rm w2} \frac{c_2}{\rho_2} \tag{11}$$

Here $\rho_a$ is the density in moles of monomer per cubic centimeter of polymer species $a$ in the pure state. Condition (11) is constructed such that the light scattering second virial coefficient is directly proportional to the parameter $\chi_{12}$, which in Flory–Huggins theory characterizes the interaction of the two polymer species. An analysis of this condition on the basis of the renormalization group is given in ref 7.

To evaluate condition (11), we need values of $\nu_a$ and $\rho_a$ that are given in Table II. There is a weak concentration dependence of $\nu_a$ (compare eq 26 of ref 2), which we ignore. In Table III we give the experimentally chosen values of $x_a = c_a/(c_{\rm PS} + c_{\rm PMMA})$. We also include the spinodal concentrations $c^* = c^*_{\rm PS} + c^*_{\rm PMMA}$, which are determined by extrapolating the inverse zero-angle scattering intensity $K^*/R_0$ to zero. For each sample the experiment covers all the range of concentration $c = c_{\rm PS} + c_{\rm PMMA}$ up to $c^*$. More details on the experiment can be found in refs 1 and 2.

In ref 8 data on the zero-angle scattering intensity $R_0/K^*$, both for the ternary system as well as for the two binary subsystems, have been analyzed. The data of the binary subsystems fix two of our parameters ($B_a$, $a = 1$ and 2, in eqs A3 and A4). The third parameter ($s_{\rm I}^{(12)}$, eq A5) was fixed by simultaneously adjusting the position of the spinodal for all three ternary samples.

With the nonuniversal parameters fixed, the only unknown quantity needed for the evaluation of $R_{\rm app}$ is the $z$-averaged molecular weight. In the absence of further information, we assumed that the chain-length distribution is well approximated by a Schulz distribution, thus taking $N_{za}/N_{wa} = 2 - N_a/N_{wa}$. Figure 1 compares our theoretical result for $R_{\rm app}$ to experiment. The overall agreement is quite satisfactory. The most serious deviation occurs in the dilute limit $c \rightarrow 0$ for the system of highest molecular weight. Supposedly, this is an artifact of the present lowest order calculation of $I_{ab}$. It is well-known that this approximation underestimates the interpenetration ratio $\psi^* \sim A_2/R_g^3$ in binary solutions by a factor of 2. Since our parameters have been determined by fitting to $R_0/K^*$ and thus nicely reproduce the second virial coefficient $A_2$, our calculation should overestimate the zero concentration radius of gyration by a factor of $2^{1/3} \sim 1.26$, which might explain the observed deviation. A first-order calculation of $I_{ab}(q)$ is in progress.

We furthermore note that our calculation does not incorporate critical fluctuations of the phase separation close to the spinodal. An evaluation of the Ginzburg criterion[3] for the present system suggests that such effects influence the region $0.9c^* \leq c \leq c^*$. It is clear that the present data points in this concentration region are too few to show a systematic deviation from the theory.

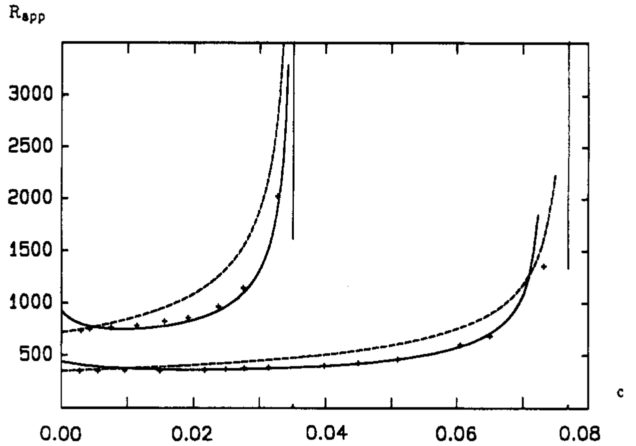

**Figure 2.** $R_{\rm app}$ in cm$^{-8}$ as a function of total polymer concentration $c$ in g/mL: (upper curves) PC200–75M, (lower curves) F80–78M. Full lines result from renormalized and broken lines from unrenormalized theory. Vertical lines indicate the spinodal concentrations and crosses the data points.

To illustrate the effect of renormalization, we in Figure 2 compare our results to those of unrenormalized RPA (eq 8). $R_{ga}$ is taken to be the experimentally determined radius of an isolated chain, and $u_{11}$ and $u_{22}$ are fixed by fitting the second virial coefficients of the binary solutions. These data are available only for the first two samples and can be taken from Table I. The parameter $u_{12}$ is determined by adjusting to the spinodal concentration for each sample separately. We stress that with this evaluation of the data we have five parameters ($R_{g1}$, $R_{g2}$, $u_{11}$, $u_{22}$, $u_{12}$) for each experimental system separately, which are determined to fit the $c \rightarrow 0$ and the $c \rightarrow c^*$ behavior. As is shown in Figure 2, nevertheless, this ansatz for intermediate concentrations does not give a fit of the data of the same quality as the renormalized theory. This clearly stresses the importance of the incorporation of the renormalization group flow for the effective parameters of the random-phase approximation.

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## Appendix: Renormalized RPA

Renormalized RPA yields for the matrix $I_{ab}(q)$ of scattering intensities (see ref 8, section 3.2)

$$I_{ab}(q) = \left( \frac{c_a N_a}{c_{\rm R}^{(a)} N_{\rm R}^{(a)}} \frac{c_b N_b}{c_{\rm R}^{(b)} N_{\rm R}^{(b)}} \right)^{1/2} I_{{\rm R}ab}(q) \tag{A1}$$

where $I_{{\rm R}ab}$ is given in terms of its inverse matrix

$$I_{{\rm R}ab} = \delta_{ab}[c_{\rm R}^{(a)} N_{\rm R}^{(a)} D_a(q^2 l_{\rm R}^2 N_{\rm R}^{(a)})]^{-1} + g^* f_{ab} \tag{A2}$$

For the present system the binary subsystems are in the excluded-volume limit, which implies $f_{aa} = 1$, with $a = 1$ and 2. The "fixed point coupling" $g^*$ takes the value $g^* \approx 5.7$ to the order considered. $l_{\rm R}$ is of the order of the size of a concentration blob and is to be determined by the implicit eq A6. The other renormalized parameters are to be calculated from the equations

$$N_{\mathrm{R}}^{(a)} = (B_a/l_{\mathrm{R}})^{1/\nu} N_a, \quad \nu \approx 0.588 \tag{A3}$$

$$c_{\mathrm{R}}^{(a)} = (B_a/l_{\mathrm{R}})^{1/\nu} l_{\mathrm{R}}^{\mathrm{d}} c_a, \quad \nu \approx 0.588 \tag{A4}$$

$$\frac{s_l^{(12)}}{l_{\mathrm{R}}} = f_{12}^{\;1/\omega_{12}(0)} (f_{12} - 1)^{1/\omega_{12}}; \quad \frac{1}{\omega_{12}(0)} \approx -2.49, \quad \frac{1}{\omega_{12}} \approx 2.70 \tag{A5}$$

Here $B_a$ ($a$ = 1 and 2) and $s_l^{(12)}$ are the microscopic parameters of the theory. Equations A3–A5 give the number $N_{\mathrm{R}}^{(a)}$ of blobs per chain, the blob concentration $c_{\mathrm{R}}^{(a)}$, and the effective blob interaction $f_{12}$ in terms of the blob size $l_{\mathrm{R}}$, which is determined implicitely by the equation

$$1 = \frac{1}{2N_{\mathrm{R}}^{(1)}} + \frac{1}{2N_{\mathrm{R}}^{(2)}} + g^*(c_{\mathrm{R}}^{(1)} + c_{\mathrm{R}}^{(2)}) + \left[\left(\frac{1}{2N_{\mathrm{R}}^{(1)}} - \frac{1}{2N_{\mathrm{R}}^{(2)}} + g^*(c_{\mathrm{R}}^{(1)} - c_{\mathrm{R}}^{(2)})\right)^2 + 4g^{*2} f_{12}^{\,2} c_{\mathrm{R}}^{(1)} c_{\mathrm{R}}^{(2)}\right]^{1/2} \tag{A6}$$

As mentioned in the main text, these equations result from the general scheme of the renormalization group under the assumption that the binary subsystems are found in the excluded-volume limit.

In ref 8 data on the zero-angle scattering intensity $R_0/K^*$ of the present system have been analyzed. The data on the binary subsystems yield parameter values $B_{\mathrm{PS}} = 2.49 \times 10^{-8}$ cm and $B_{\mathrm{PMMA}} = 2.31 \times 10^{-8}$ cm. The analysis of the location of the spinodal of the ternary solution data resulted in a value $s_l^{(12)} = 1.06 \times 10^{-11}$ cm.

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