Measurement of coil contraction by total-intensity light scattering from isorefractive ternary solutions*

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The radius of gyration of a guest polymer (polystyrene) has been measured in the presence of a host polymer (poly(methyl methacrylate)) in a solvent (ethyl benzoate) which is good for both polymers and isorefractive with the host polymer. A range of host concentrations from dilute to semidilute has been studied for a guest and host pair with similar molecular weights. It is found that no change in coil size occurs in the dilute regime, and at host concentrations greater than c^*, the guest chain contracts in the same manner as observed for chains in binary solutions by neutron scattering. There is no evidence that the small, unfavourable interaction between polystyrene and poly(methyl methacrylate) leads to a steeper contraction with increasing host concentration or to an onset of contraction at lower concentrations of host polymer. It is shown that conflicting results obtained in previous experiments of this type probably result from improper extrapolation to infinite dilution, due to non-negligible non-linear thermodynamic terms, or to small scattering contributions from the host polymer.

(Keywords: coil contraction; ternary solution; isorefractive; interaction parameter)

INTRODUCTION

The increasing role of polymer mixtures and copolymers in technological applications has motivated many studies of their solution properties. The spatial dimension of a polymer coil, and any changes in coil size which occur as a result of solution conditions, are of fundamental importance. The particular problem of the change in coil dimensions with polymer concentration has received some attention both theoretically[1–9] and experimentally[1,10–17]. The problem is fairly well understood for the case of a single polymer in a good solvent. Several theoretical approaches[1–5] have led to the prediction that the radius of gyration scales with $c^{-1/8}$ in the semidilute regime; this dependence has received some experimental support from small-angle neutron scattering measurements[1,10]. However, the effect of an unfavourable interaction between unlike monomers in the case of polymer mixtures has not been clearly established.

The notion that a polymer will contract to a greater extent or at lower concentrations when surrounded by a host polymer with which it is immiscible in the melt, can be relevant in the interpretation of various physical processes, such as diffusion in polymer mixtures, transport of polymers in solution through pores, and the kinetics of reactions between macromolecules. It is the goal of this study to determine if a positive binary interaction parameter, χ, between polymers in a ternary polymer–polymer–solvent mixture leads to different behaviour for the contraction of a guest chain than is observed for a binary polymer–solvent system.

This question can be studied by total-intensity light scattering from ternary polymer–polymer–solvent systems in which the host polymer and solvent are chosen to be isorefractive. The solvent should be good for both polymers, so that the guest is expanded and to enable the dissolution of both polymers. Since there is no contrast between the host polymer and the solvent, the properties of the dilute guest chain can, in principle, be determined as in binary solutions. In practice, however, there are some difficulties unique to this experiment which must be handled carefully to obtain accurate results and provide a meaningful comparison with the results of the neutron scattering experiments in binary solutions.

In this work, we have identified two important experimental difficulties and show how each affects the determination of the radius of gyration, R_g, from light scattering data. It is likely that these provide major contributions to discrepancies which have arisen among previous experiments of this type[11–17]. The first is a slight mismatch between host polymer and solvent refractive index, and the second involves the range of guest polymer concentration employed. Using the system polystyrene–poly(methyl methacrylate)–ethyl benzoate, we have eliminated both problems and studied both dilute and semidilute regimes, enabling a close comparison with the neutron scattering data[1,10] for binary solutions to determine the role of a positive χ between polymers on the coil dimensions of the guest chain.

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* Dedicated to Professor W. Burchard on the occasion of his 60th birthday

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RESULTS FROM SCALING THEORY

Scaling predictions for $R_g(c)$ have been worked out in detail for both binary[1,3] and ternary solutions[6–9]. Daoud *et al.*[1] used a scaling approach to derive the concentration dependence of the radius of gyration of polymer chains in binary solutions. They considered three concentration regimes, corresponding to separated chains (dilute), overlapping chains (semidilute), and concentrated systems, respectively. Assuming that contraction begins to occur when the overlap concentration is reached, their analysis yields the relation:

$$R_g \sim c^{-1/8} \tag{1}$$

in the semidilute regime, with the chains reaching theta dimensions in the concentrated regime. The $-1/8$ power can be derived from simple arguments. In the semidilute regime, the solution is viewed as having a correlation length or mesh size, ξ, which is the only relevant length scale in the problem. The guest is viewed as a renormalized chain of blobs equal in size to the correlation length. On distances less than ξ, the chain is expanded, but on distance scales greater than ξ, the excluded volume interaction is screened out, and the renormalized chain of blobs has a Gaussian distribution. The scaling analysis is based on the assumptions that the correlation length is equal to the radius of gyration at the crossover concentration c^*, and that the correlation length scales as some power of the reduced concentration (c/c^*) and is independent of molecular weight above c^*.

These assumptions lead to the result that $\xi \sim c^{-3/4}$ in the semidilute regime. Since the chain of renormalized subunits has a Gaussian distribution, the mean square radius of gyration is proportional to the number of subunits times the square of the size of the subunits:

$$R_g^2 \approx (N/N_b)\xi^2 \tag{2}$$

where N = the total number of monomers and N_b = the number of monomers in a subunit or blob. The $-1/8$ power results since $\xi \sim N_b^{3/5}$ and $\xi \sim c^{-3/4}$. This result was subsequently derived through a combination of path integral and field theoretic techniques[4], and by a renormalization group technique[5]. As mentioned in the Introduction the $-1/8$ power has received some experimental support from neutron scattering[1,10], although King *et al.* claim that the difference between their reported slope of -0.078 and the predicted -0.125 is beyond experimental error.

De Gennes[6] and Joanny *et al.*[7,8] extended the scaling approach to consider ternary solutions containing two polymers and a solvent good for both, where the two polymers differed only in molecular weight. They found an additional regime of higher concentration dependence ($-1/4$ power) when $N > P$ and $1 < c_P/c_P^* < (N/P)^{4/5}$, where N and P are the degree of polymerization of the guest and host polymers, respectively. At concentrations such that $c_P/c_P^* > (N/P)^{4/5}$, the contraction of the guest again goes with the $-1/8$ power of the host concentration. The additional regime of higher concentration dependence results because the renormalized guest chain experiences excluded volume interactions between its subunits if the number of subunits per chain is high enough (or greater than the number in a thermal blob). Nose[9] has further extended the scaling analysis to include the effect of thermodynamic interactions between the two polymer types. In his analysis, a positive χ between the polymers influences the effective excluded volume interaction between renormalized subunits. For $N/P \gg 1$, a collapse of the guest chain is predicted around c_P^* for large χ. When $N = P$, the effect of χ becomes significant when $c_P/c_P^* > 1$ and:

$$\chi > (c_P/c_P^*)^{-5/8} \tag{3}$$

where a $-1/3$ power law is predicted. For the system PS/PMMA, phase separation occurs before this condition is attained, and thus scaling theory predicts the same behaviour as for binary solutions in the experimentally accessible region.

EXPERIMENTAL

The light scattering measurements were performed on a commercial multiangle light scattering photometer from Wyatt Technologies. The instrument was of the flow-through type, and was modified to allow temperature control. The uncertainty in the measurement of cell temperature was estimated at ±1°C, since the temperature was measured not in the light scattering cell itself, but in a large aluminum block in which the cell rested. The instrument allowed data to be acquired at 15 angles simultaneously, and of these, 13 were commonly used in the data analysis, covering an angular range from 30° to 140°. A typical sample volume was 2.5 ml. The source was a He–Ne laser with $\lambda_0 = 633$ nm.

The detector gains were normalized by measuring the excess scattering from a low molecular weight polystyrene standard ($M_w = 17\,500\ \mathrm{g\,mol^{-1}}$), assumed to scatter isotropically, in the same solvent as used in the ternary solutions. Dark current offsets were determined by measuring the voltage from the detectors when the laser source was turned off. The scattered intensity of a binary solution of the host polymer and solvent relative to the dark current was always used as the solvent offset. However, for the experiments in ethyl benzoate, in no case was the intensity from the binary solution measurably higher than the scattered intensity from the pure solvent. The excess scattering from a ternary solution was determined by subtracting the solvent and dark current contributions from the measured intensities at each angle, and multiplying the resulting values by the normalization constants. The absolute calibration constant was determined from pairs of pure solvents with known Rayleigh ratios by measuring the scattered intensities at 90°. The solvents and corresponding Rayleigh ratios are given in *Table 1*. The values determined from three solvent pairs agreed to within ±2%. As the photometer used was a recently developed instrument, several polystyrene standards were measured in toluene before the work on ternary solutions, and the molecular weight, radius of gyration, and second virial coefficient of these were found to agree very well with literature data[18–20] for the same system, as shown in

Table 1 Rayleigh ratios of solvents used to determine instrument calibration constant ($\lambda_0 = 633$ nm)

Solvent	Rayleigh ratio ($\mathrm{cm^{-1}}$)	Reference
Toluene	1.406×10^{-5}	27
Tetrahydrofuran	4.28×10^{-5}	28
Acetone	4.28×10^{-5}	27
Methanol	2.85×10^{-5}	27

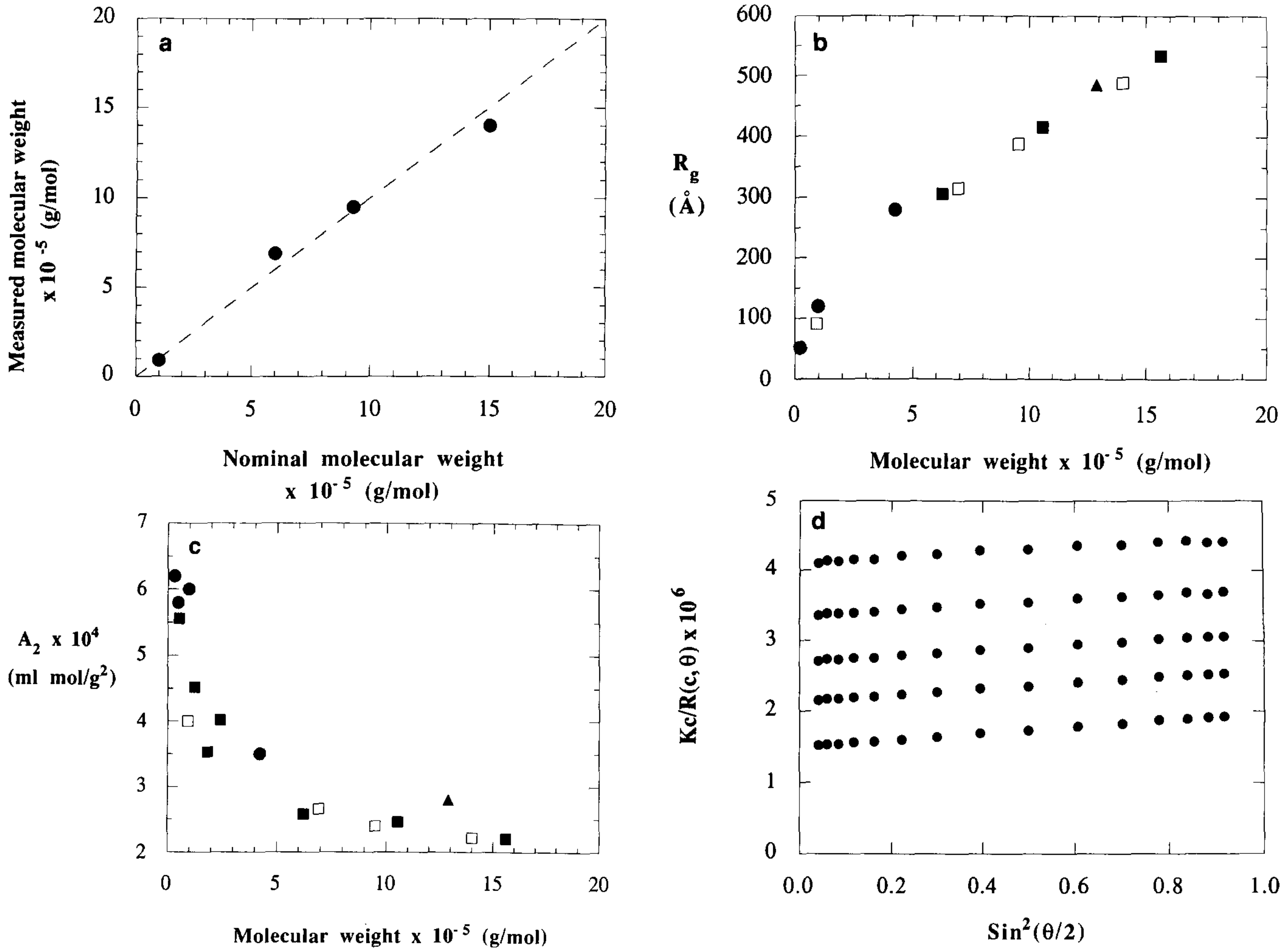

Figure 1 (a) Measured M_w *vs* nominal M_w. (b) R_g *vs* M_w. (c) A_2 *vs* M_w for polystyrene standards in toluene at room temperature obtained with the Dawnflow photometer. (d) Sample scattering data obtained with the Dawnflow photometer for polystyrene (nominal $M_w = 930000$) in toluene. Concentrations: 0.00091, 0.0019, 0.0026, 0.0035, 0.0043 g/ml. In (b) and (c), the symbols ●, ■, and ▲ represent the data of references 18, 19, and 20, respectively, and □ represents the data of this work

Figures 1a–c. An example of a typical scattering plot is shown in *Figure 1d*.

The polymers used were monodisperse standards and the details are given in *Table 2*. The h.p.l.c. grade solvents used were ethyl benzoate, methyl benzoate, and *o*-xylene (Aldrich), toluene and tetrahydrofuran (Fisher Scientific), and acetone and methanol (Mallinckrodt). All were filtered several times before use. The solutions were delivered into the instrument using a peristaltic pump and an injection loop. An in-line filter placed just before the instrument allowed the solutions to be injected without exposure to the atmosphere after filtration. Reasonable precautions were taken to avoid exposure to water vapour, which was found to affect the measurement of refractive index increments.

The refractive index increments were measured using a modified Brice-Phoenix differential refractometer with a He–Ne laser source. The refractometer was modified by removing the optical microscope, inserting two lenses to magnify the deflection, and casting the exiting beam on a scale fixed to a wall some 6 m from the refractometer. For most of the measurements, five concentrations were used, but for the measurements closest to the matching condition, only one concentration—around 4%—was used. It was found that sufficiently accurate measurements of small deflections could be made with these modifications.

Table 2 Characteristics of polymers

Polymer	Nominal M_w (g/mol)	$\frac{M_w}{M_n}$	Source
PS	930 000	1.14	Scientific Polymer Products
PMMA	840 000	1.12	Scientific Polymer Products
PMMA	1 300 000	1.06	Polymer Labs

Data analysis

Two aspects of the experimental procedure demand particular attention to obtain reliable data on index-matched ternary solutions.

The first is the effect of a slight visibility of the host polymer. Following Stockmayer's theory[21] for scattering from multicomponent solutions, the scattered intensity at zero angle is given by the following expression (which includes only terms up to second order in concentration):

$$\frac{R^*_{\theta=0}}{K/v_N^2} = (M_N c_N - 2A_{NN} M_N^2 c_N^2) v_N^2 - (2A_{NP} M_N M_P c_N c_P) v_N v_P + (M_P c_P - 2A_{PP} M_P^2 c_P^2) v_P^2 \qquad (4)$$

where:

$R^*_{\theta=0}$ = the Rayleigh ratio at zero angle (* indicates that

$R_{\theta=0}$ includes the scattering from the pure solvent);
K = a collection of optical constants given in the Appendix;
A_{NN}, A_{NP}, A_{PP} = the binary virial coefficients;
v_N, M_N, c_N = the refractive index increment, molecular weight and concentration of the guest;
v_P, M_P, c_P = the refractive index increment, molecular weight, and concentration of the host.
If $v_P = 0$ exactly, the second and third terms vanish and the molecular weight, radius of gyration, and apparent second virial coefficient of the guest can be determined in the same manner as in binary solutions. For small but finite values of v_P, the second and third terms contribute to the total scattering.

If an attempt is made to remove the small contribution from the host polymer by measuring the scattered intensity from a binary solution of the host polymer and solvent, and subtracting this as the solvent offset, only the third term from equation (4) is removed and the second term, which may be the larger of the two, remains. This cross term will be significant unless:

$$\frac{2\mathrm{A}_{NP}M_N M_P c_N c_P v_P}{(M_N c_N - 2A_{NN}M_N^2 c_N^2)v_N} \cong \frac{2A_{NP}M_P c_P v_P}{v_N} \ll 1 \qquad (5)$$

Notice that this ratio depends on the concentration and molecular weight of the host polymer as well as the refractive index increments. Since the host concentration c_P can be large, v_P must be extremely small to ignore the contribution of the cross term.

We have estimated the effects of a non-zero v_P on the measured molecular weight, apparent second virial coefficient, and radius of gyration of the guest chain by starting with the first two terms of Stockmayer's equation (equation 2.16 of ref. 21) and substituting expressions for the chemical potentials. It is assumed that the third term has been subtracted as the solvent offset. The effect on the radius of gyration is less clear, as it involves the form of the intermolecular scattering function. Using the expression of Benoit and Benmouna[22,23], we find (see Appendix):

$$M_N(\mathrm{app}) = M_N(1 - X) \qquad (6)$$

$$A_2(\mathrm{app}) = \frac{A_{NN} - \dfrac{A_{NP}^2 M_P c_P}{2(1 + 2A_{PP}M_P c_P)}}{1 - X} \qquad (7)$$

$$\langle R_g^2(\mathrm{app})\rangle_N = \langle R_g^2\rangle_N\left(1 - X\left(1 + \frac{\langle R_g^2\rangle_P}{\langle R_g^2\rangle_N}\right) + Y\frac{\langle R_g^2\rangle_P}{\langle R_g^2\rangle_N}\right) \times (1 - X) \qquad (8)$$

where:

$$X = 2\left(\frac{v_P}{v_N}\right)\frac{A_{NP}M_P c_P}{1 + 2A_{PP}M_P c_P};$$

$$Y = 8\left(\frac{v_P}{v_N}\right)A_{NP}A_P M_P^2 c_P^2;$$

$A_2 = (1 - X)A_2(\mathrm{app})$ is the apparent second virial coefficient for a perfectly matched system. Notice that the sign of the correction term in each case depends on the sign of v_P/v_N. These expressions may be used to estimate how precise the index match must be for a particular concentration range, pair of molecular weights, and set of virial coefficients. For example, for $c_P = 0.001$ g ml^{-1}, $v_N = 0.11$, $v_P = 0.01$, $A_{NN} = A_{PP} = 0.5A_{NP} = 0.00025$ cm^3 mol g^{-2}, $M_N = M_P = 1\,000\,000$ g mol^{-1}, and $\langle R_g^2\rangle_N^{1/2} = \langle R_g^2\rangle_P^{1/2} = 40$ nm, which constitutes a realistic set of values, $M_N(\mathrm{app})/M_N = 0.90$, $A_2(\mathrm{app})/A_2 = 1.06$, and $\langle R_g^2(\mathrm{app})\rangle_N/\langle R_g^2\rangle_N = 0.87$, but if $v_P = 0.001$, $M_N(\mathrm{app})/M_N = 0.99$, $A_2(\mathrm{app})/A_2 = 1.01$, and $\langle R_g^2(\mathrm{app})\rangle_N/\langle R_g^2\rangle_N = 0.99$. While equations (6), (7) and (8) are only estimates involving leading terms, the importance of an order of magnitude decrease in v_P is clear. From the above, it is also clear that subtracting the excess scattering from a binary solution of the host polymer and solvent as the solvent offset does not necessarily remove the effects of a small mismatch.

The second and probably more significant error in experiments of this type is due to improper extrapolation to infinite dilution of the guest polymer. The conventional form for plotting light scattering data from binary solutions is described by the following equation:

$$\frac{Kc}{R_\theta} = \frac{1}{M}(1 + 2A_2Mc + 3A_3Mc^2 + \cdots) \times \left(1 + \frac{q^2\langle R_g^2\rangle}{3} + \cdots\right) \qquad (9)$$

where q is the scattering vector, and A_2 and A_3 are the second and third virial coefficients, respectively.

It was recognized many years ago[19,24] that for high molecular weight polymers in good solvents, extremely low concentrations must be used to ignore non-linear terms in the virial expansion. This is illustrated in *Figure 2*, which shows scattering data for a binary solution of polystyrene (Nominal $M_w = 930\,000$) in toluene. *Figure 2a* shows that a linear regression through data points that actually contain upward curvature will result in extrapolated values which are too low. *Figure 2b* shows the extrapolated points for all angles using linear and quadratic regressions. While the slope is virtually the same, the radius of gyration (determined from the slope divided by the intercept) will be too large if linear extrapolations are used, since the intercept is too low. For very high molecular weight polymers, the range of concentration which is sufficiently low to allow linear extrapolations may be too low to provide measurable scattering above the background. In binary solutions, this difficulty is handled by using square-root plots[19]. By approximating the third virial coefficient in terms of the second as $A_3 = A_2^2M/3$, one obtains:

$$\frac{Kc}{R_\theta} = \frac{1}{M}(1 + 2A_2Mc + A_2^2M^2c^2 + \cdots) \times \left(1 + \frac{q^2\langle R_g^2\rangle}{3} + \cdots\right) \qquad (10)$$

or:

$$\left(\frac{Kc}{R_\theta}\right)^{1/2} \cong \left(\frac{1}{M}\right)^{1/2}(1 + A_2Mc)\left(1 + \frac{q^2\langle R_g^2\rangle}{6}\right) \qquad (11)$$

which is appropriate for an experimentally accessible concentration range and allows a linear extrapolation to infinite dilution when the square root of Kc/R_θ is taken as the ordinate.

This difficulty is more critical in isorefractive ternary solution experiments because as the concentration of host polymer is increased, the thermodynamic environment or the 'solvent quality' experienced by the guest polymer changes, and that change alone may lead to an apparent

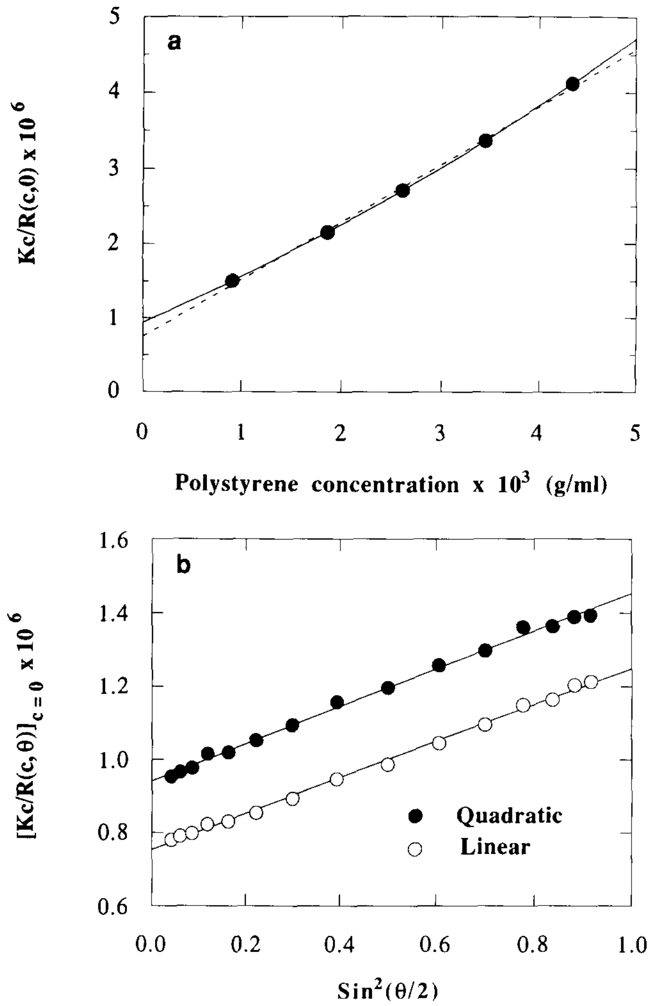

Figure 2 Effect of non-linear thermodynamic terms on measured radius of gyration for the binary solution, polystyrene (nominal $M_w = 930\,000$) in toluene. (a) Scattering data extrapolated to $\theta = 0$, concentration dependence fit with linear (dashed line) and quadratic (solid line) regressions. (b) Infinite dilution values for all measured angles where extrapolations were made with linear and quadratic regressions. Concentration range is below c*, yet still too high to use a linear extrapolation to infinite dilution. Linear extrapolation leads to a measured radius of gyration which is too high

change in the radius of gyration if accurate extrapolation to infinite dilution in the guest is not obtained. This is illustrated in *Figure 3a–c* for the ternary system PS ($M_w = 930\,000$)–PMMA ($M_w = 840\,000$)–toluene where the concentration range of the guest PS chains is below c^* yet still too high to use the conventional Zimm plot. *Figure 3a* shows that as the concentration of host polymer increases, the initial slope or apparent second virial coefficient decreases; in addition, there is also a decrease in the curvature, i.e. in the apparent third virial coefficient. This is illustrated more clearly in *Figure 3b* in which the data of *Figure 3a* have been normalized to have the same initial slope. The decrease in the apparent third virial coefficient can be understood from Stockmayer's fluctuation theory for multicomponent systems when terms of order c^3 are retained (equation (A.7)). This decrease in the apparent third virial coefficient will result in an apparent change in R_g if linear extrapolations are used. With no host polymer present, linear extrapolations will result in infinite dilution values which are too low and thus in radii of gyration which are too large, but at higher concentrations of host polymer, linear extrapolations will result in infinite dilution values which are too

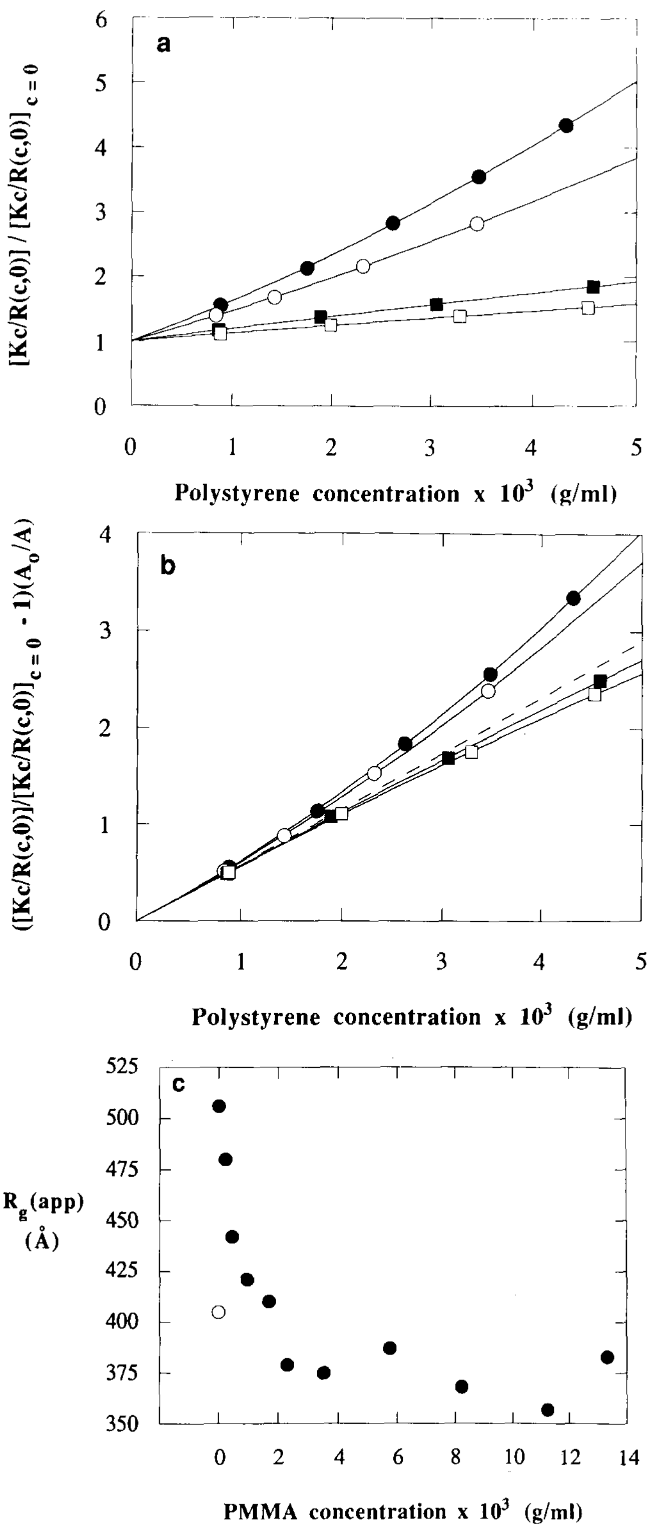

Figure 3 Effect of non-linear thermodynamic terms on measured radius of gyration for the nearly isorefractive ternary solutions, PS ($M_w = 930\,000$)–PMMA ($M_w = 840\,000$)–toluene at 23°C. (a) Scattering data extrapolated to $\theta = 0$ *vs* c_{PS} for PMMA concentrations: ●, 0.0, ○ 0.0010, ■ 0.0057, □ 0.0082 g/ml. Apparent second virial coefficient (initial slope) decreases with c_{PMMA}. (b) Scattering data of (a) where the initial slope of each curve has been normalized to have the same value as for $c_{PMMA} = 0$. A_0 and A are the initial slopes for $c_{PMMA} = 0$ and for each corresponding curve in (a), respectively. The dashed line is a straight line. Curvature or apparent third virial coefficient decreases with c_{PMMA} (see Appendix). (c) Measured radius of gyration of the polystyrene guest *vs* c_{PMMA} obtained from Zimm plots, ●. Also shown, ○, is the radius of gyration of the guest in pure toluene obtained when the concentration extrapolation is performed in the square-root mode. The decrease in curvature shown in (b) leads to an apparent decrease in R_g at low c_{PMMA} if conventional Zimm plots are used when the concentration range of the guest is too high

high and thus radii of gyration which are too low. Errors in extrapolation to infinite dilution should be more significant the steeper the slope, or when the apparent second virial coefficient is furthest from zero.

Figure 3c shows the apparent radius of gyration of the guest *versus* host concentration obtained from conventional Zimm plots. Also shown is the value of the radius of gyration of the guest in pure toluene obtained when the concentration extrapolation is performed in the square-root mode (the infinite dilution values, $[Kc/R(c,\theta)]_{c=0}$, for all angles were then squared so that the radius of gyration could be obtained from the angular dependence in the same manner as in the Zimm plots). It should be noted that no angular distortions were observed in any of the Zimm plots. Since v_P/v_N is positive for this system, the effect of an index mismatch can only decrease the apparent radius of gyration from the true value. Since the apparent radii of gyration at low concentrations of PMMA in *Figure 3c* are significantly greater than the value obtained from a square-root plot in binary solution, it is clear that the curvature in the concentration dependence has led to apparent radii of gyration which are too high at low concentrations of host polymer, and that most of the apparent 20–30% decrease in the radius of gyration is due to improper extrapolation to infinite dilution. A 20% error is substantial in this experiment and demonstrates the significance of this problem. Unfortunately, the higher-order terms cannot be represented in a simple manner in ternary solutions as they are in the square-root plot for binary solutions, since the thermodynamics of ternary solutions is complicated. It should be emphasized that the difficulty of extrapolating to infinite dilution of the guest is completely separate from the slight visibility of the host polymer, and will be present even when $v_P = 0$.

To eliminate these two sources of error, a solvent and host polymer pair must first be found for which the conditions for an exact refractive index match are experimentally accessible. The degree of mismatch will then depend only on the accuracy of the dn/dc measurements and on the precision of temperature control. The results of dn/dc measurements for PMMA in toluene and o-xylene as a function of temperature and for two different wavelengths are shown in *Figure 4a*. Several of the previous experiments have used PMMA as the host polymer in either toluene or benzene (which falls between toluene and o-xylene in *Figure 4a*) at $\lambda_0 = 436$ nm. From our measurements, we conclude that an exact match at the wavelength of the present experiments ($\lambda_0 = 633$ nm) can not be achieved near room temperature with either toluene or benzene. In addition, it seems unlikely that an exact match was achieved in the previous experiments ($\lambda_0 = 436$ nm). *Figures 4b,c* show that at $\lambda_0 = 633$ nm, PMMA can be exactly matched with either a mixture of methyl and ethyl benzoate at room temperature (23°C) or with pure ethyl benzoate at around 15°C. We have chosen the latter for our experiments. We estimate the degree of mismatch to be $< \pm 0.3\ \mathrm{mm^3\,g^{-1}}$ from the scatter in the dn/dc measurements and our uncertainty of ±1°C in estimating the temperature in the light scattering cell. Throughout the experiments, the degree of mismatch was monitored by looking for a change in the apparent molecular weight with host concentration and for any appreciable scattering of the host over the solvent.

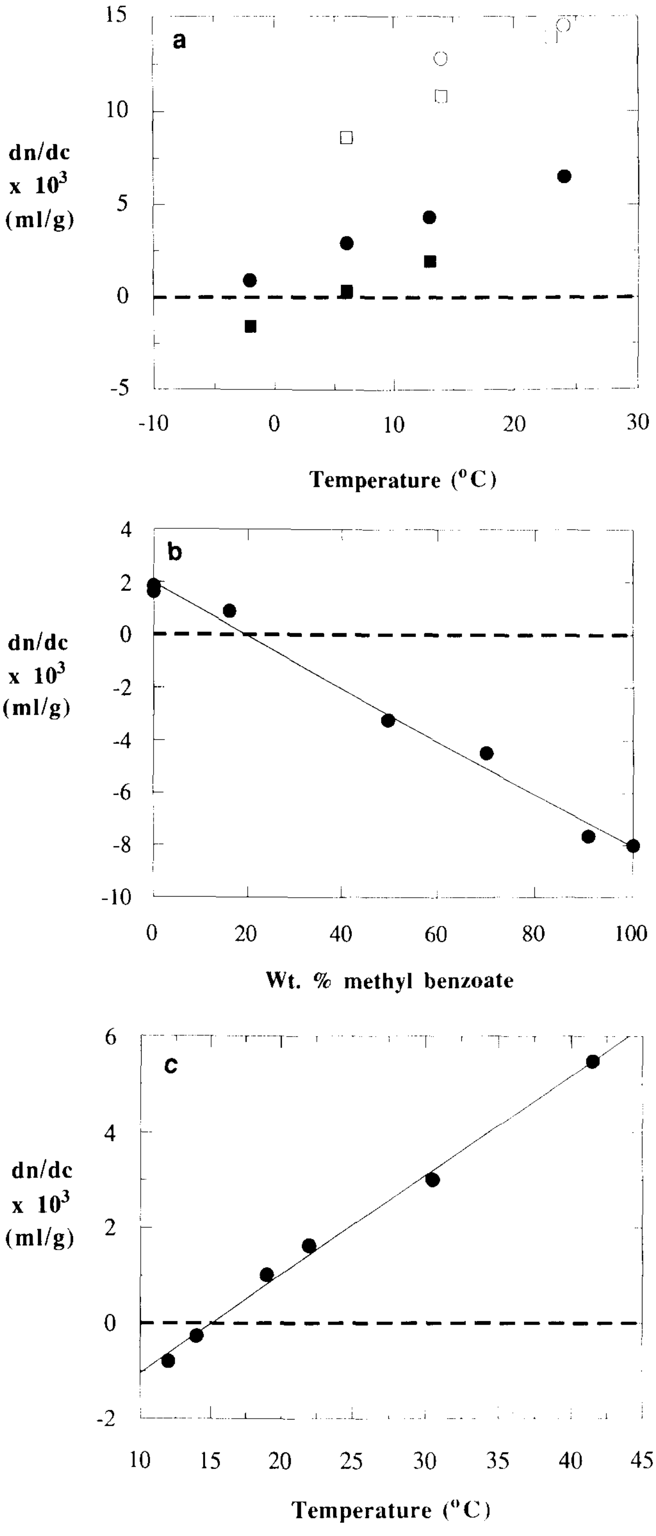

Figure 4 Refractive index increments for PMMA in: (a) toluene for: ○ $\lambda_0 = 633$ nm, □ $\lambda_0 = 546$ nm, o-xylene for: ● $\lambda_0 = 633$ nm, ■ $\lambda_0 = 546$ nm *vs* temperature; (b) mixtures of methyl and ethyl benzoate for $\lambda_0 = 633$ nm at 23°C; (c) pure ethyl benzoate for $\lambda_0 = 633$ nm *vs* temperature

The difficulty of obtaining the correct extrapolation to infinite dilution may be dealt with in two ways. First, many concentrations of the guest can be measured over a wide range and fitted to a polynomial. The meaning of the coefficients of the polynomial will not be obvious as they are in the binary solution case, but an accurate extrapolation to infinite dilution should be obtainable, which is all that is required to extract R_g. Alternatively, very low concentrations of guest polymer can be used and non-linear terms can be neglected. However, it must be possible to judge when the guest polymer concentration is low enough. Also, the lower the concentration of the guest, the more precise must be the match in refractive indices of the host polymer and the solvent. Given our ability to match the host polymer refractive index with ethyl benzoate to a very high degree of precision, we have chosen the latter alternative for our experiments and in all cases the guest polymer concentrations were < 1.25 g l^{-1}. This is roughly $0.2c^*$, where c^* is estimated from the formula $c^* = M/(4\pi R_g^3 N_A/3)$ and appears from *Figure 3b* to be low enough to neglect any curvature in the concentration dependence.

RESULTS

The apparent molecular weight *versus* host polymer concentration is shown in *Figure 5a*. Nearly all of the data fall within $\pm 5\%$ and there is no trend with host polymer concentration. This is contrasted with experiments in toluene which show a clear trend in the apparent molecular weight of the guest. Since the concentration of the guest was higher in the experiments in toluene, extrapolations to infinite dilution for those data were made with quadratic regressions. The remaining decrease in the apparent molecular weight of the guest must be due to the refractive index mismatch between PMMA and toluene, as described earlier. We believe that the absence of a change in the apparent molecular weight of the guest chain with host polymer concentration is strong evidence that the index match between PMMA and ethyl benzoate is sufficiently precise over the entire concentration range of these experiments.

The radius of gyration and apparent second virial coefficient of the guest are shown *versus* host polymer concentration in *Figures 5b* and *5c*, respectively. The concentration of the guest polymer was below 1.25 g l^{-1} for all the measurements in ethyl benzoate and we believe this to be sufficiently low, since for host concentrations up to 10 g l^{-1}, virtually no change in the radius of gyration or apparent molecular weight of the probe is observed while the apparent second virial coefficient has decreased to zero. As demonstrated in *Figures 3a,b*, the apparent third virial coefficient changes sign by the time the apparent second virial coefficient reaches zero, and so it is clear that the values of the radius of gyration and molecular weight in *Figure 5* are not affected by changes in the non-linear thermodynamic terms. In *Figure 3c*, where the concentration of the guest was much higher (1–5 g l^{-1}), the radius of gyration showed an apparent decrease of more than 20% over the range of host polymer concentration up to 10 g l^{-1} when linear extrapolations were used.

Having established that the two sources of error described above have been eliminated, we can make a close comparison with the neutron scattering data[1,10] for binary solutions to determine if the unfavourable interaction between PS and PMMA leads to any additional effects. The contraction seems to begin around 10 g l^{-1}, which is roughly c^* for the guest. The contraction occurring at concentrations higher than c^* is consistent with the -0.125 power law, although the concentration range is rather limited. These results are very similar to those observed in binary solutions by neutron scattering, where contraction seems to begin around c^* and power law exponents of -0.125[1] and -0.078[10] have been observed. Therefore, we conclude that the small positive χ between the polymers has little, if any, effect on the contraction of the guest for similar molecular weights of the guest and host. We point out that a much different

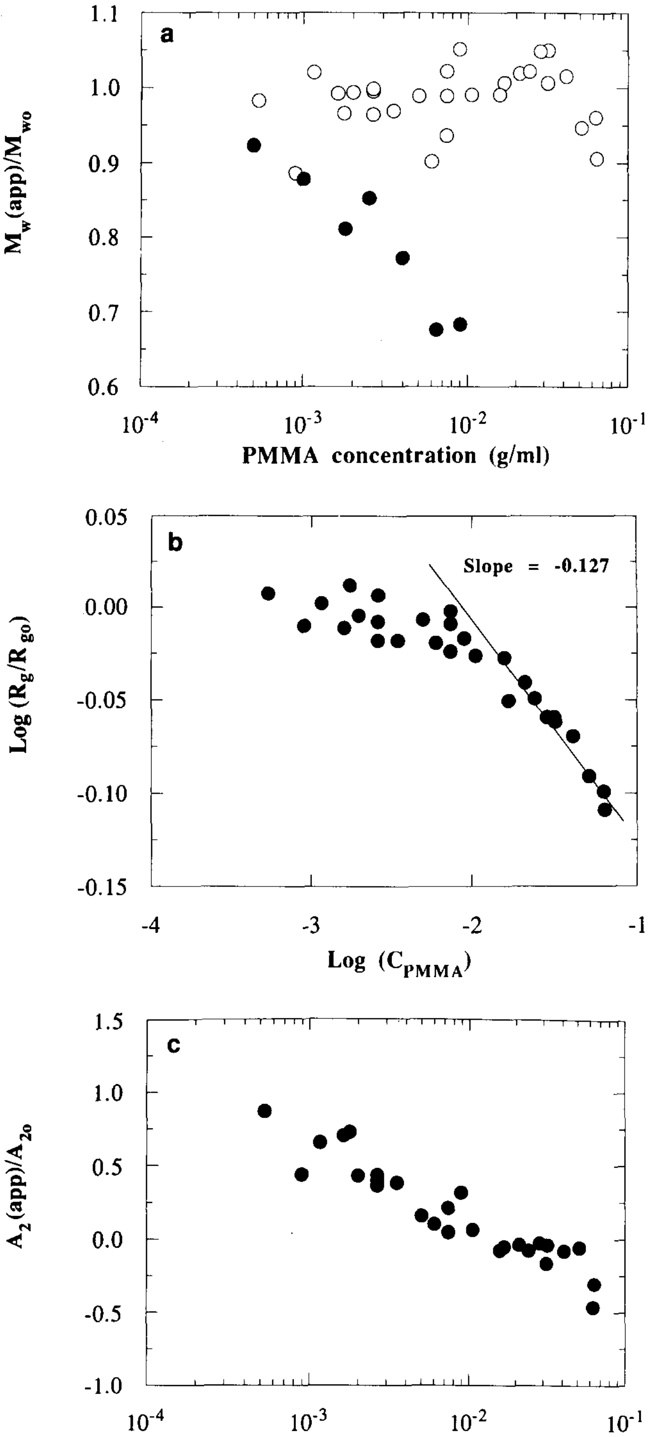

Figure 5 (a) Apparent M_w/M_{w0} of polystyrene *vs* c_{PMMA} in: ● toluene ($M_{w_{PMMA}} = 840000$) at 23°C, and ○ ethyl benzoate ($M_{w_{PMMA}} = 1300000$) at 15°C. M_{w0} (970000 g mol^{-1}) is the value measured in binary solution. Decrease observed in toluene is due to non-negligible dn/dc_P. (b) Reduced radius of gyration and (c) apparent second virial coefficient *vs* c_{PMMA} in ethyl benzoate at 15°C. ($M_{w_{PMMA}} = 1300000$, $R_{g0} = 39$ nm, $A_{2_0} = 0.00019$ ml mol g^{-2}.) No change in R_g or M_w below $c_{PMMA} = 0.01$ g ml^{-1}, where A_2 has decreased to zero, indicates accurate extrapolation has been made to infinite dilution in the guest. At concentrations of host polymer greater than 0.01 g ml^{-1}, contraction is consistent with the -0.125 power law over a limited concentration range.

conclusion could result if the extrapolations to infinite dilution were not performed correctly. A small difference between the values of the apparent power law exponents in semidilute binary and ternary solutions may still exist, but would be no larger than the difference between the results of the two neutron scattering experiments on similar binary solutions.

In a subsequent paper, we report results for the same PS guest polymer in lower molecular weight PMMA host polymers which will enable a more detailed comparison with the scaling picture for ternary solutions.

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APPENDIX

To determine the effects of a small mismatch in refractive index of the host polymer and solvent, we begin with Stockmayer's equation (equation 2.16 of ref. 21):

$$\frac{R^*_{\theta=0}}{K'} = \frac{v_N^2 a_{PP} - 2v_N v_P a_{NP} + v_P^2 a_{NN}}{|a_{ij}|} \tag{A.1}$$

where subscripts N and P refer to guest and host polymer, respectively, $K' = KRT/v_N^2$, $K = 2\pi^2 n^2 v_N^2/N_A\lambda_0^4$, and $R^*_{\theta=0}$ is the Rayleigh ratio at zero angle (* indicates that $R_{\theta=0}$ includes the scattering from the pure solvent), with:

$$a_{ij} = \frac{\partial\mu_i}{\partial c_j}, \quad \text{and} \quad |a_{ij}| = \left(\frac{\partial\mu_N}{\partial c_N}\right)\left(\frac{\partial\mu_P}{\partial c_P}\right) - \left(\frac{\partial\mu_N}{\partial c_P}\right)\left(\frac{\partial\mu_P}{\partial c_N}\right)$$

where μ_N and μ_P are chemical potentials.

If the following form is assumed to be adequate for the osmotic pressure:

$$\frac{\Pi}{RT} = \frac{c_N}{M_N} + \frac{c_P}{M_P} + A_{NN}c_N^2 + A_{PP}c_P^2 + A_{NP}c_N c_P + A_{NNN}c_N^3 + A_{PPP}c_P^3 + A_{NNP}c_N^2 c_P + A_{PPN}c_N c_P^2 \tag{A.2}$$

the a_{ij} may be written as[25]:

$$\frac{\partial\mu_N}{\partial c_N} = \frac{RT}{M_N}\left\{\frac{1}{c_N} + 2A_{NN}M_N + 3A_{NNN}M_N c_N + A_{NNP}M_N c_P\right\}$$

$$\frac{\partial\mu_N}{\partial c_P} = \frac{RT}{M_N}\{A_{NP}M_N + A_{NNP}M_N c_N + A_{PPN}M_N c_P\}$$

$$\frac{\partial\mu_P}{\partial c_N} = \frac{RT}{M_P}\{A_{NP}M_P + A_{NNP}M_P c_N + A_{PPN}M_P c_P\}$$

$$\frac{\partial\mu_P}{\partial c_P} = \frac{RT}{M_P}\left\{\frac{1}{c_P} + 2A_{PP}M_P + 3A_{PPP}M_P c_P + A_{PPN}M_P c_N\right\}$$

When $c_N \to 0$, the third term in equation (A.1) approaches the excess scattering of a binary solution of the host polymer and solvent over the scattering of the solvent alone, i.e.:

$$\frac{a_{NN}}{|a_{ij}|} \cong \frac{1}{a_{PP}}$$

The third term may then be removed by subtracting the intensity from the binary solution as the solvent offset, which gives:

$$\frac{R_{\theta=0}}{K'} \simeq \frac{v_N^2 a_{PP} - 2v_N v_P a_{NP}}{|a_{ij}|} \tag{A.3}$$

Keeping only terms of order c^2 in the expansion of $\frac{\Pi}{RT}$:

$$\frac{R_{\theta=0}}{K'} = \frac{v_N^2 M_N c_N - 2v_N v_P \dfrac{A_{NP}M_N M_P c_N c_P}{1 + 2A_{PP}M_P c_P}}{RT\left\{(1 + 2A_{NN}M_N c_N) - \dfrac{A_{NP}^2 M_N M_P c_N c_P}{1 + 2A_{PP}M_P c_P}\right\}}$$

then:

$$\frac{Kc_N}{R_{\theta=0}} = \frac{1 + 2A_{NN}M_N c_N - \dfrac{A_{NP}^2 M_N M_P c_N c_P}{1 + 2A_{PP}M_P c_P}}{M_N - \dfrac{2v_P}{v_N}\dfrac{A_{NP}M_N M_P c_P}{1 + 2A_{PP}M_P c_P}} \tag{A.4}$$

Note that if only lowest order terms are retained, equation (A.4) gives:

$$\frac{R_{\theta=0}}{K/v_N^2} = (M_N c_N - 2A_{NN}M_N^2 c_N^2)v_N^2 - 2A_{NP}^2 M_N M_P c_N c_P v_N v_P + \cdots$$

which is equation (4) of the text when the term involving

v_P^2 has been subtracted. If the data are plotted in the conventional form $\left(\frac{Kc_N}{R_{\theta=0}}\ vs\ c_N\right)$, then:

$$\text{Intercept} = \frac{1}{M_N\left(1 - 2\frac{v_P}{v_N}\frac{A_{NP}M_Pc_P}{1+2A_{PP}M_Pc_P}\right)}$$

thus:

$$M_N(\text{app}) = M_N\left(1 - 2\frac{v_P}{v_N}\frac{A_{NP}M_Pc_P}{1+2A_{PP}M_Pc_P}\right) \qquad (A.5)$$

$$\text{Slope} = \frac{2A_{NN}M_N - \dfrac{A_{NP}^2M_NM_Pc_P}{1+2A_{PP}M_Pc_P}}{M_N - 2\dfrac{v_P}{v_N}\dfrac{A_{NP}M_NM_Pc_P}{1+2A_{PP}M_Pc_P}}$$

thus:

$$A_N(\text{app}) = \frac{A_{NN} - \dfrac{A_{NP}^2M_Pc_P}{2(1+2A_{PP}M_Pc_P)}}{1 - 2\dfrac{v_P}{v_N}\dfrac{A_{NP}M_Pc_P}{1+2A_{PP}M_Pc_P}} \qquad (A.6)$$

Note that the higher order terms in (A.4) must be retained to describe the decrease in the apparent second virial coefficient with host polymer concentration.

If terms of order c^3 are retained in the expansion of Π/RT:

$$\frac{Kc_N}{R_{\theta=0}} = \frac{1 + (2A_{NN}M_N + A_{NNP}M_Nc_P)c_N + 3A_{NNN}M_Nc_N^2 - \dfrac{(A_{NP} + A_{NNP}c_N + A_{PPN}c_P)^2M_NM_Pc_Nc_P}{1 + 2A_{PP}M_Pc_P + 3A_{PPP}M_Pc_P^2 + A_{PPN}M_Pc_Nc_P}}{M_N - 2\dfrac{v_P}{v_N}\dfrac{(A_{NP} + A_{NNP}c_N + A_{PPN}c_P)M_NM_Pc_P}{1 + 2A_{PP}M_Pc_P + 3A_{PPP}M_Pc_P^2 + A_{PPN}M_Pc_N}} \qquad (A.7)$$

The decrease in the apparent third virial coefficient observed in *Figure 3c* is described by the numerator of equation (A.7).

Kratochvil[26] has also attempted to include terms of order c^3. His expression, however, is limited to concentrations such that all terms are much less than unity. Equation (A.7) is valid as long as (A.2) is an adequate description of the osmotic pressure.

For an estimate of the error in R_g, scattering factors are included according to the theory of Benoit and Benmouna[22,23]:

$$\frac{Kc_N}{R_\theta} = \frac{1 + 2A_{NN}M_NP_Nc_N - \dfrac{A_{NP}^2M_NM_PP_NP_Pc_Nc_P}{1+2A_{PP}M_PP_Pc_P}}{M_NP_N - 2\dfrac{v_P}{v_N}\dfrac{A_{NP}M_NM_PP_NP_Pc_P}{1+2A_{PP}M_PP_Pc_P}} \qquad (A.8)$$

For $c_N \rightarrow 0$ and $P_i \cong (1 - q^2\langle R_g^2\rangle_i/3)$:

$$\frac{Kc_N}{R_\theta} = \frac{1}{M_N}\left[1 + X + \frac{q^2}{3}(\langle R_g^2\rangle_N - X(\langle R_g^2\rangle_N + \langle R_g^2\rangle)_P) + Y\langle R_g^2\rangle_P)\right] \qquad (A.9)$$

where

$$X = 2\left(\frac{v_P}{v_N}\right)\frac{A_{NP}M_Pc_P}{1+2A_{PP}M_Pc_P}, \quad \text{and} \quad Y = 8\left(\frac{v_P}{v_N}\right)A_{NP}A_PM_P^2c_P^2$$

If the data are plotted in the conventional form $\left(\frac{Kc_N}{R_\theta}\ vs\ \frac{q^2}{3}\right)$, then:

$$\langle R_g^2(\text{app})\rangle_N = \langle R_g^2\rangle_N\left(1 - X\left(1 + \frac{\langle R_g^2\rangle_P}{\langle R_g^2\rangle_N}\right) + Y\frac{\langle R_g^2\rangle_P}{\langle R_g^2\rangle_N}\right)(1 - X) \qquad (A.10)$$

valid for X, Y, and $2A_{PP}M_Pc_P \ll 1$.