Unified Analysis of Thermodynamic and Rheological Properties of High Polymer Solutions. II. Ternary Systems

ISABEL M. IRURZUN, TOMÁS S. GRIGERA, M. SUSANA CORTIZO, RUBÉN V. FIGINI,*
MARIANNE MARX-FIGINI

Instituto de Investigaciones Fisicoqumícas Teóricas y Aplicadas (INIFTA), CONICET, CIC y Universidad
Nacional de La Plata, C.C. 16, suc. 4, La Plata 1900, Argentina

Received 29 January 2001; revised 24 January 2002; accepted 1 March 2002

ABSTRACT: We extend to ternary solutions our previous study of conformational, thermodynamic, and rheological properties of semidilute polymer solutions in good solvent. Osmotic pressure and viscosity measurements were performed in several mixtures of two compatible polymers in a common solvent. Renormalization group results were used to analyze the data, using de Gennes's blobs model to connect dynamic and conformational properties. © 2002 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 40: 1071–1079, 2002

Keywords: heterogeneous polymers; viscosity; thermodynamics

INTRODUCTION

The universal behavior of polymer solutions has been experimentally recognized for a long time. Major manifestations of universality are the power-law relationships (the limiting forms of the most general scaling functions) that hold for a wide range of chemically different systems.[1–3] Universality shows up in that the macroscopic properties of dilute and semidilute polymer solutions are invariant under a redefinition of the monomer unit. Renormalization group (RG) theory exploits this invariance of scale to obtain macroscopic relations from the microscopic model of the system, deriving universal laws.

To date, RG theory has been successfully applied to the description of binary polymer solutions.[4–18] A reasonable understanding of dilute solutions exists, and progress has also been made in the description of thermodynamic and conformational properties of semidilute solutions. The description of dynamic properties is more difficult because of the hydrodynamic interaction, and although there are theoretical approaches to its description, a unified treatment of excluded volume and hydrodynamic screening is still unavailable.

In a previous article,[19] we carried out an extensive study of binary systems (i.e., solvent plus one polymeric species). We measured both the thermodynamic and dynamic properties (osmotic pressure and viscosity) of dilute and semidilute solutions and applied a scheme based on RG theory. Our scheme uses the RG results for osmotic pressure and radius of gyration and extends them to consider also the dynamic properties. Theoretical results agreed with the experimental data. The comparison was made by adjusting a nonuniversal quantity (β) that depends on the chemical nature of the systems and temperature. Once β is experimentally calculated, the behavior of the polymer solution in the whole range from dilute to semidilute limits can be determined. Our previous results indicated that β has different values for static (thermodynamic and conformational) and dynamic properties. Nevertheless, the scheme supports an extensive analysis, and it is

---

Correspondence to: T. S. Grigera (E-mail: tomas.grigera@roma1.infn.it)
*Deceased

Journal of Polymer Science: Part B: Polymer Physics, Vol. 40, 1071–1079 (2002)

useful for the experimental characterization of polymer solutions.

In this article, we extend the analysis to ternary solutions (composed of two different polymeric species in a common solvent). The RG theory has already been extended for such systems, revealing a variety of different limiting situations depending of the quality of the solvent and temperature. Our purpose is to carry out an experimental analysis in the framework of the scheme previously presented for binary systems, thus achieving a unified approach to the description of all these systems. This article is organized as follows. The second section summarizes the relevant RG results, the third section gives details on the samples and experimental measurements, the fourth section presents the results, and the fifth section contains our conclusions.

THEORETICAL BACKGROUND

Some time ago, L. Schäfer developed a renormalization group approach for the description of conformational and thermodynamic properties of polymer solutions.[8–10,15–18] This theory provides a unified treatment of temperature and concentration crossover of the excluded volume interactions. In this scheme, observable macroscopic properties (osmotic pressure, radius of gyration, etc.) are expressed in terms of two variables—f (related to the excluded volume interaction) and w (related to the concentration). In general, these expressions are known as a perturbation series. A mapping (given by the renormalization group equations) is established between f,w on the one hand and the experimental variables (molecular weight and concentration) on the other, thus furnishing an experimentally testable relation. In this mapping, two nonuniversal adjustable quantities have to be introduced.

We have previously[19] applied this scheme to the description of binary systems in which case perturbative results are generally available up to the first order. In this case of ternary systems, however, we find ourselves restricted to order zero (which because of the introduction of renormalized variables does not imply that excluded volume is completely ignored). Because we want to compare results for both systems, in particular the nonuniversal quantities, we must recalculate these for binary systems using the zero-order expressions. At this level of approximation the mapping between the experimental and renormalized variables takes a simpler form. We subsequently summarize the relevant formulas for the binary and ternary cases at zero order, also called tree approximation. Instead of the variable w, it is more convenient to use two variables (c_R and N_R) together with an additional constraint (the so-called renormalization condition). In this way, the formalisms for the binary and ternary cases resemble each other more closely.

Binary Systems

The solution is defined by the experimental variables c_l (monomer concentration) and N (degree of polymerization), or equivalently the mass concentration ($c = m\ c_l/N_A$) and molecular weight ($M = mN$), where m is the monomer's molecular weight and N_A is Avogadro's number. They are related to the renormalized variables through the renormalization group equations[10,16]

$$\frac{1}{N_R} = (1-f)^{-1/\nu\omega} f^2 (s_N N)^{-1} \tag{1}$$

$$C_R = f(1-f)^{(1-3\nu)/\nu\omega} \mu^* S_N S_l^3 C_l \tag{2}$$

$$1 = N_R^{-1} + 2fc_R \tag{3}$$

where s_l and s_N are nonuniversal constants, $\omega = 0.79$ and $\nu = 0.588$ are critical exponents, and $\mu^* = 0.08778$. The last equation is the so-called renormalization condition. From these, the renormalized variables (f, c_R, and N_R) are calculated in terms of the experimental variables c_l and N and the system-dependent s_l and s_N. All the nonuniversal details of the system are contained in these equations. In the case relevant to these experiments, namely, the excluded volume limit $f \rightarrow 1$, from eqs 1 and 2, it follows that

$$s = c_R N_R^{3\nu-1} = \mu^* B^3 c_l N^{3\nu-1} \tag{4}$$

where $B = s_l s_N{}^{v}$. This is the definition of the overlap s. In terms of mass concentration and polymer molecular weight, the overlap reads

$$s = \beta^3 c M_n^{3\nu-1} \tag{5}$$

$$\beta = \sqrt[3]{\mu^* N_A}\,\frac{B}{m} \tag{6}$$

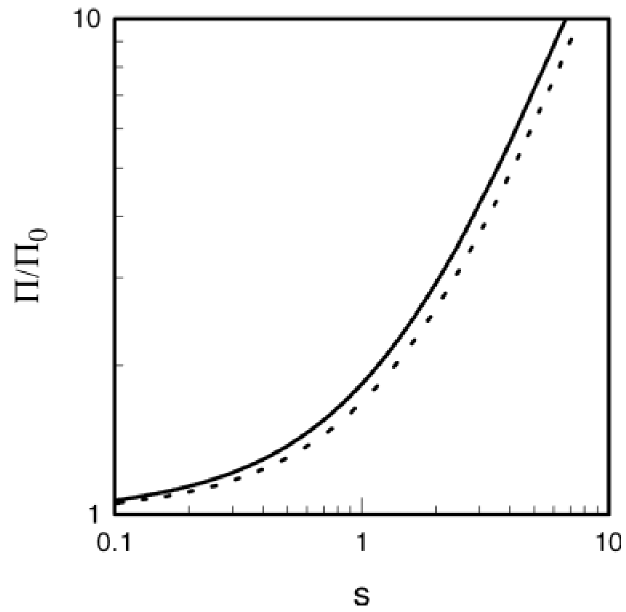


Figure 1. Comparison of RG expressions for osmotic pressure at zero order (dotted line) and first order (continuous line).

so that β (which is the same quantity as in our first article) contains both nonuniversal constants. Equation 3 is still to be used to relate N_R and c_R so that in effect there is only one free variable in the excluded volume limit (s) and one adjustable parameter (β).[20]

The observables are written in terms of f, c_R, and N_R. At zero order, the osmotic pressure is given by

$$\frac{\Pi}{\Pi_0} = 1 + \frac{f}{2} c_R N_R \tag{7}$$

where Π_0 is Van't Hoff's value RTc/M. The radius of gyration S is

$$\frac{S^2}{S_0^2} = N_R^{1-2\nu} \tag{8}$$

where S_0 is the radius of gyration at infinite dilution.

Let us make two remarks before considering the generalization of these results to ternary systems. First, at this level of approximation all polydispersity effects are neglected. Second, apart from these effects, most of the differences between zero and first order can be accounted for by multiplying the overlap by a constant value. In Figure 1 we show the theoretical predictions for osmotic pressure at zero and first order. By contracting the x axis of the order 0 curve [i.e., by transforming s(order 0) $\rightarrow 0.85\ s$ (order 0)], the two curves are almost superimposed. Thus, a reasonable fit is obtained at zero order but with a different value of β.

Ternary Systems

Ternary systems are composed of two chemically different macromolecular species ($a = 1,2$) in a common solvent. The chains are represented with the familiar Gaussian chain model with the excluded volume interactions.[15–18] The polymer chains are characterized by a microscopic length $l \approx l_1, l_2$ and three parameters μ_{ab} ($a,b = 1,2$) representing the strengths of the two-body interaction in the cluster expansion. Hence, we have three renormalized interaction variables f_{ab}, independently ranging between 0 and 1. The renormalization group developments show that eight fixed points govern the behavior of such systems. In this work, we have only analyzed the neighborhood of the symmetric fixed point S, where f_{11} e $= f_{22} = f_{12} = 1$. This is the only stable fixed point, meaning that all systems above the Θ temperatures of the two binary subsystems and where there is some repulsion between the two species reach point S in the limit of infinite molecular weight. Thus, S ultimately governs almost all systems that can be analyzed within RG theory.

By a direct generalization of the binary case, the solution is defined by the experimental variables c_{la} and N_a, or equivalently c_a and M_a, where the subscript refers to the polymer species. The observables are given, as before, in terms of the renormalized concentration (c_{Ra}) and molecular weight (N_{Ra}). The RG equations are more complicated in this case, but we do not need the full equations here because we know that the subsystems of the ternary solutions we are studying are in the good solvent regime. We take the generalization of the renormalization condition that in the case $f_{11} = f_{22} = 1$ reads[15,16]

$$1 = \frac{1}{2N_{R1}} + \frac{1}{2N_{R2}} + \mu^* c_{R1} + \mu^* c_{R2} + \left[\left(\frac{1}{2N_{R1}} - \frac{1}{2N_{R2}} + \mu^* c_{R1} - \mu^* c_{R2}\right)^2 + 4\mu^{*2} f_{12} c_{R1} c_{R2}\right]^{1/2} \tag{9}$$

Here it is allowed that $f_{12} \neq 1$. This is a natural situation because f_{12} reaches its limiting value of 1 more slowly than f_1 and f_2. However, we have found that we can safely assume $f_{12} = 1$ because leaving it as an adjustable parameter does not improve the quality of the agreement with the experiment. This has two of the following advantages: equations become simpler, and no adjustable parameter needs to be used. When $f_{12} = 1$, we obtain from eq 9

$$c_{\mathrm{R1}} = \frac{\left[1 - \frac{1}{2N_{\mathrm{R1}}}\left(\frac{y_{\mathrm{n}}+1}{y_{\mathrm{n}}}\right)\right]^2 - \frac{1}{(2N_{\mathrm{R1}})^2}\left(\frac{y_{\mathrm{n}}-1}{y_{\mathrm{n}}}\right)^2}{2(1+\hat{c})\left[1 - \frac{1}{2N_{\mathrm{R1}}}\left(\frac{y_{\mathrm{n}}+1}{y_{\mathrm{n}}}\right)\right] + \frac{1}{N_{\mathrm{R1}}}\left(\frac{y_{\mathrm{n}}-1}{y_{\mathrm{n}}}\right)} \times (1-\hat{c}) \quad (10)$$

$$y_{\mathrm{n}} = \frac{N_{\mathrm{R2}}}{N_{\mathrm{R1}}} = \left(\frac{\beta_2}{\beta_1}\right)^{1/\nu}\frac{M_{\mathrm{n2}}}{M_{\mathrm{n1}}} \qquad \hat{c} = \frac{c_{\mathrm{R2}}}{c_{\mathrm{R1}}} = \left(\frac{\beta_2}{\beta_1}\right)^{1/\nu}\frac{c_2}{c_1}$$

Here use was made of the RG equations to express y_{n} and ĉ in terms of the experimental variables. β_1 and β_2 are the values of β for the binary polymer-solvent subsystems and can be determined independently from the ternary solution. So now all renormalized variables are given in terms of experimental ones and N_{R1}, which is related to the experiment through the overlap

$$s_1 \equiv c_{\mathrm{R1}}(N_{\mathrm{R1}})^{3\nu-1} = \beta_1^3 c_1 M_{n,1}^{3\nu-1} \quad (11)$$

An overlap s_2 can be similarly defined, as well as an effective overlap, but their physical meaning is rather obscure in this case, so we prefer to avoid them. From these equations, the description of ternary solutions at the fixed point S only requires the molecular weights of the components and their behavior in binary solution (i.e., the value of β_1 and β_2). Then, the comparison between experiments and theory is made without introducing additional adjustable quantities.

Finally, we give the expressions for the physical observables. The osmotic pressure is given by[16]

$$\frac{\Pi}{\Pi_0} = 1 + \frac{c_{\mathrm{R1}}N_{\mathrm{R1}}y_{\mathrm{n}}(1+\hat{c})^2}{2(y_{\mathrm{n}}+\hat{c})} \quad (12)$$

whereas the radius of gyration for each species is written[16]

$$\frac{S_{\mathrm{a}}^2}{S_{\mathrm{a0}}^2} = (N_{\mathrm{Ra}})^{1-2\nu} \quad (13)$$

As before, we use these results also to interpret dynamic properties, using de Gennes's reptation theory to obtain[11,19]

$$\frac{\eta_{\mathrm{sp}}}{[\eta]c} = \left(\frac{S^2}{S_0^2}\right)^{\frac{3\nu-4}{2\nu-1}} \quad (14)$$

where η_{sp} and $[\eta]$ are the specific and intrinsic viscosity, respectively. This equation holds at the same level as the scaling theory. The same remarks apply to eq 14 as to the binary case, as discussed in detail in the literature.[19] As concentration increases, chains begin to overlap, and the intrachain interactions are modified by the presence of the other chains, leading to the screening of the excluded volume and hydrodynamic interactions. This causes a change of behavior in the relaxation times, from a Zimm to a Rouse regime, and, at still higher overlap, to an entangled regime with reptation dynamics (de Gennes). In eq 14 the excluded volume screening is only indirectly considered through the RG treatment of the radius of gyration, which has the effect of smoothly interpolating between the Zimm and de Gennes exponents.

To apply eq 14 to ternary solutions unambiguously, we require that both radii of gyration relative to their respective infinite dilution values be equal. At this level of approximation, according to eqs 8 and 10, this means $y_{\mathrm{n}} = 1$. The molecular weights of the samples were chosen in such a way that their ratio is equal to the ratio of the β values of the corresponding binary systems (eq 10). In the framework of de Gennes's blob picture (see appendix of ref.[19] for details), it means that the number of blobs of both species must be equal because this number determines the relative value of the radii of gyration. Because the number of blobs depends both on the molecular weights and the interactions in the system, one should expect a condition that involves both the values of number-average molecular weight (M_{n}) and the values of β.

EXPERIMENTAL

Materials

To explore the applicability of the theoretical framework previously discussed, we should prepare compatible mixtures of two polymers in a common solvent. Most polymer pairs are incom-

Table 1. Characteristics of the Polymer Samples Used in This Work

Sample	10^{-3} M_n (g/mol)	10^{-3} M_η (g/mol)	M_η/M_n	Solvent	[η] (cm^3/r) at 30 C0
PMMA-336	336 ± 13	577 ± 11	1.72 ± 0.10	Toluene	102 ± 1
PMMA-599	599.7 ± 0.6	1185 ± 8	1.97 ± 0.01	Chloroform	347 ± 2
PMMA-1201	1201 ± 117	1838 ± 28	1.55 ± 0.11	Toluene	246 ± 4
PMMA-801	801 ± 2	1615 ± 10	2.01 ± 0.02	—	—
PS-300	300 ± 4	792 ± 18	2.64 ± 0.09	Toluene[b]	182 ± 3
CTN-188	188 ± 4	353 ± 8	1.88 ± 0.08	Isophorone	911 ± 21
CTN-250	250 ± 6	450 ± 10	1.80 ± 0.08	Isophorone	1088 ± 24
CTN-447	447 ± 11	760 ± 20	1.71 ± 0.09	Isophorone	1778 ± 30
$CoSM_{25/75}$-1078[b]	1078 ± 245	2261 ± 20	2.1 ± 0.23	Toluene	309 ± 2
$CoSM_{25/75}$-2460[b]	2460 ± 954	3650 ± 30	1.48 ± 0.6	Toluene	432 ± 3
$CoSM_{50/50}$-906[c]	906 ± 60	1492 ± 33	1.65 ± 0.09	Toluene	304 ± 5
$CoSM_{50/50}$-945[c]	945 ± 80	1777 ± 35	1.90 ± 0.10	Toluene	346 ± 5
$CoSM_{50/50}$-227[c]	227 ± 47	415 ± 9	1.83 ± 0.22	Toluene	118 ± 2

[a] At 25 °C.
[b] Styrene molar fraction: 0.33.
[c] Styrene molar fraction: 0.51.

patible except at very low concentration. A critical concentration exists, usually in the semidilute regime, beyond which a segregation process takes place. To avoid these difficulties we have chosen pairs of polymers known to be compatible in a wide range of concentrations. We prepared mixtures of polymethylmetacrilate (PMMA) and poly(styrene-*co*-methylmethacrylate) (CoSM) with 50% styrene in toluene,[21] polystyrene (PS) and CoSM with 50% styrene in toluene,[21] cellulose trinitrate (CTN) and poly(methyl methacrylate) in isophorone (3,5,5-trimethylciclohexenone),[22] and cellulose trinitrate and CoSM with 25% styrene in isophorone.[22] Polymer samples were prepared and characterized as previously reported (see the literature[19] and references therein). Table 1 summarizes their characteristics.

Mixtures

Ternary solutions were prepared mixing a pair of polymers in a common solvent and shaking them for 24–72 h at 30 °C. Their average M_n values were determined as

$$M_n = \frac{n_1 M_{n1} + n_2 M_{n2}}{n_1 + n_2} \qquad (15)$$

where n_i is the number of moles of polymer with molecular weight M_i (i = 1,2).

To adequately compare the experimental data with theory, two quantities must be known (see eq 10)

$$y_n = \frac{M_{n2}}{M_{n1}}\left(\frac{\beta_2}{\beta_1}\right)^{1/\nu} \text{ and } \hat{c} = \frac{c_2}{c_1}\left(\frac{\beta_2}{\beta_1}\right)^{1/\nu},$$

where subindices refer to each polymer species.

For each ternary system, y_n can be computed from the molecular weights of the polymers and the values of β (these are independent of molecular weight and concentration). ĉ is kept constant throughout the experiment even when the total concentration ($c_t = c_1 + c_2$) is changed so that c_1 and c_2 are given by

$$c_1 = \frac{c_t}{\hat{c}\left(\frac{\beta_1}{\beta_2}\right)^{1/\nu} + 1} \qquad c_2 = \frac{\hat{c}\left(\frac{\beta_1}{\beta_2}\right)^{1/\nu} c_t}{\hat{c}\left(\frac{\beta_1}{\beta_2}\right)^{1/\nu} + 1} \qquad (16)$$

where ĉ is constant for each ternary system.

Table 2 shows the characteristics of the mixtures used in this work. All calculations are done with the values of β at zero order reported in Table 3.

Measurement

Osmotic pressure was measured with Hewlett-Packard 501 and Knauer membrane osmometers.

Table 2. Characteristics of the Polymer Mixtures Used in This Work

Polymer 1	Polymer 2	Solvent	$y_{\mathrm{n(static)}}$	$\hat{c}_{\mathrm{static}}$	$y_{\mathrm{n(dynamic)}}$	$\hat{c}_{\mathrm{dynamic}}$
PS-300	CoSM$_{50/50}$-906	Toluene	2.70 ± 0.35	0.96 ± 0.05	—	—
PMMA-599	CTN-188	Isophorone	1.24 ± 0.28	1.83 ± 0.37	—	—
PMMA-599	CTN-250	Isophorone	1.65 ± 0.37	1.83 ± 0.37	—	—
PMMA-801	CTN-447	Isophorone	2.21 ± 0.50	1.83 ± 0.37	—	—
CTN-250	CoSM$_{25/75}$-2460	Isophorone	—	—	1.50 ± 1.0	1.01 ± 0.27
CoSM$_{25/75}$-1078	CTN-188	Isophorone			1.14 ± 0.6	1.09 ± 0.29
CoSM$_{50/50}$-945	PMMA-1201	Toluene	1.10 ± 0.2	1.04 ± 0.06	—	—
CoSM$_{50/50}$-227	PMMA-336	Toluene	1.28 ± 0.4	1.04 ± 0.06	1.02 ± 0.33	0.83 ± 0.06
CoSM$_{50/50}$-227	PMMA-1201	Toluene	4.59 ± 1.4	1.04 ± 0.06	—	—
CoSM$_{50/50}$-945	PMMA-1201	Toluene	1.10 ± 0.2	0.43 ± 0.02	—	—
PMMA-1201	CoSM$_{50/50}$-945	Toluene	—	—	1.22 ± 0.31	1.28 ± 0.10
PMMA-1201	CoSM$_{50/50}$-945	Toluene	—	—	1.22 ± 0.31	3.10 ± 0.23

The regenerated cellulose membranes were provided by Sartorius and Schleicher und Schuell.

Intrinsic viscosity $[\eta]$ was determined using Schultz–Blaschke's equation[23]

$$\frac{\eta_{\mathrm{sp}}}{c_{\mathrm{t}}} = [\eta] + [\eta]k_{\mathrm{SB}}\eta_{\mathrm{sp}} \tag{17}$$

where c_{t} is the total concentration, η_{sp} is the specific viscosity, and k_{SB} is the Schultz–Blaschke constant. η_{sp} was measured with Ostwald viscometers, where the flow time of the pure solvent was always higher than 150 s; thus, kinetic energy corrections could be neglected. Intrinsic viscosity was generally measured for the pure components as well as the mixtures, but in some cases, for the mixture, the formula

$$[\eta] = x_1[\eta]_1 + x_2[\eta]_2 \tag{18}$$

was used, where x_i is the molar fraction of component i ($i = 1,2$), and of course $x_1 + x_2 = 1$.

For higher concentrations, Newtonian viscosity was measured with a Haake RV2 rotoviscometer.

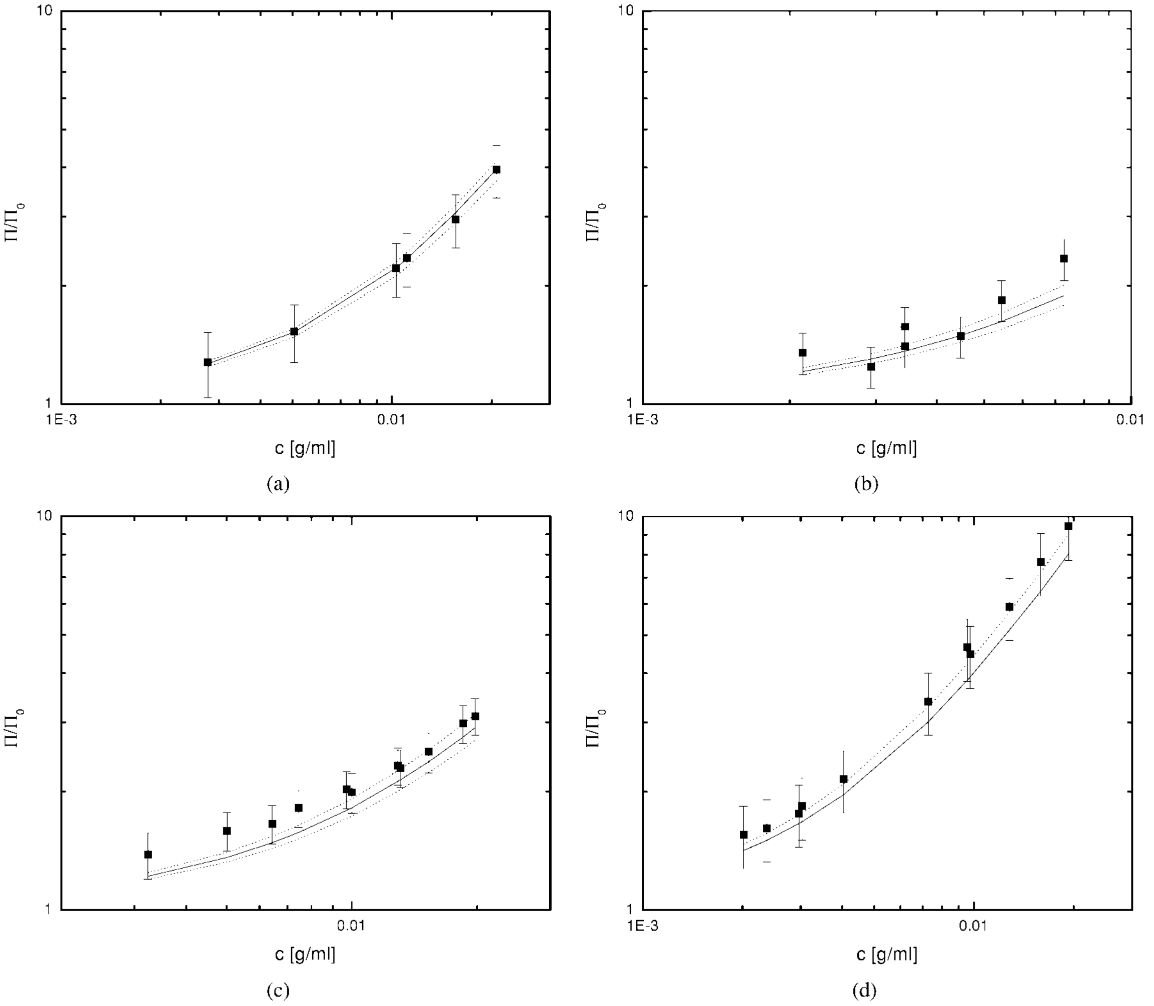
RESULTS

Binary Systems

Before analyzing the ternary systems, values of β for the binary subsystems are needed (see eq 10). For our analysis of binary systems,[19] we used RG results at first order and found that experimental results can be well described with β independent of concentration and molecular weight, but with different values for static and dynamic properties. As previously mentioned, ternary results are available only to order zero; therefore, we have reanalyzed the binary systems at this order to determine β values appropriate for use with the ternary solutions. The preceding conclusions are unaltered, but the adjustable constant takes a different value. Table 3 lists β for binary systems in both cases.

Table 3. Values of β for Binary Systems at Zero Order

			Order Zero		First Order[19]	
Polymer	Solvent	T (°C)	β_{static}	β_{dynamic}	β_{static}	β_{dynamic}
PMMA	Toluene	36	0.193 (1)	0.075 (1)	0.18 (1)	—
PMMA	Isophorone	30	0.147 (4)	—	0.169 (4)	—
PS	Toluene	36	0.2241 (1)	—	0.2137 (2)	— 2
CTN	Isophorone	30	0.33 (3)	0.242 (8)	0.31 (3)	0.27 (2)
CoSM$_{25/75}$	Isophorone	30	—	0.08 (1)	—	0.11 (1)
CoSM$_{50/50}$	Toluene	36	0.210 (6)	0.097 (3)	0.200 (6)	0.118 (5)



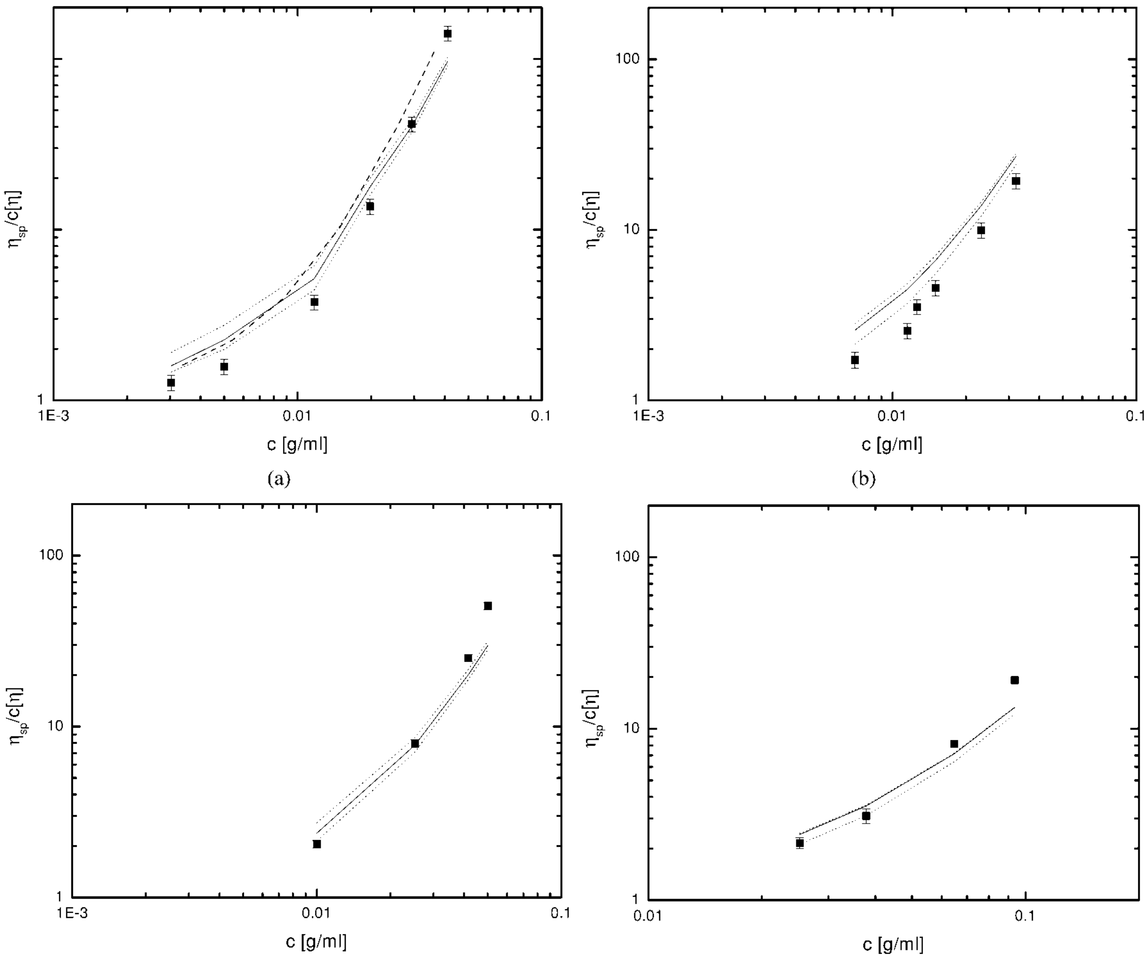
(a) (b) (c) (d)

Figure 2. Typical data for osmotic pressure. The line indicates the theoretical prediction at zero order (eq 12). The dotted line indicates uncertainty intervals. No adjustable parameters were used: (a) CoSM$_{50/50}$-227 + PMMA-1201 in toluene at 36 °C (y_{nstatic} = 4.59, $\hat{c}_{\mathrm{static}}$ = 1.04), (b) PMMA-1201 + CTN-188 in isophorone at 30 °C (y_{nstatic} = 1.24, $\hat{c}_{\mathrm{static}}$ = 1.83), (c) CoSM$_{50/50}$-227 + CoSM$_{50/50}$-336 in toluene at 36 °C (y_{nstatic} = 1.28, $\hat{c}_{\mathrm{static}}$ = 1.04), (d) CoSM$_{50/50}$-945 + PMMA-1201 in toluene at 36 °C (y_{nstatic} = 1.10, $\hat{c}_{\mathrm{static}}$ = 1.04).

Ternary Systems

We measured osmotic pressure and Newtonian viscosity as functions of the concentration for eight and five ternary systems, respectively, from the dilute to the semidilute regime. Figure 2 illustrates the osmotic pressure results for some representative systems. In each case the line indicates the theoretical prediction, eq 12. In eq 10, y_n and $\hat{c}$ involve experimentally determined quantities, so uncertainty intervals can be drawn considering experimental errors. Dotted lines in Figure 2 represent these intervals. Figure 3 shows representative results for the Newtonian viscosity. In each case the line indicates the theoretical prediction, eqs 13 and 14. Uncertainty intervals are indicated with dotted lines.

The osmotic data are predicted rather well by the theory. In the case of viscosity, the theory performs better the nearer y_n is to 1 [Fig. 3(d)], although with deviations at high concentration. Figure 3(b) depicts a systematic shift by a constant factor, most likely due to an error in the determination of the intrinsic viscosity. Figures 3(a,c) show the poorest agreement; these are the mixtures with the highest y_n, where in view of eq 14 some problems might be expected.



(a) (b)

(c) (d)

Figure 3. Typical data for Newtonian viscosity at $T = 30$ °C. The line indicates the theoretical prediction at zero order (eqs 13 and 14). The dotted line indicates uncertainty intervals. No adjustable parameters were used: (a) CTN-250 + CoSM$_{25/75}$-2460 in isophorone ($y_{\text{ndynamic}} = 1.50$, $\hat{c}_{\text{dynamic}} = 1.01$). The dashed line indicates the theoretical prediction when considering the Rouse regime (eq 12 of the literature[19]), (b) CoSM$_{25/75}$-1078 + CTN-188 in isophorone ($y_{\text{ndynamic}} = 1.14$, $\hat{c}_{\text{dynamic}} = 1.09$), (c) PMMA-1201 + CoSM$_{50/50}$-945 in toluene ($y_{\text{ndynamic}} = 1.22$, $\hat{c}_{\text{dynamic}} = 1.28$), (d) CoSM$_{50/50}$-227 + PMMA-336 in toluene ($y_{\text{ndynamic}} = 1.02$, $\hat{c}_{\text{dynamic}} = 0.83$).

As a possible source of disagreement we have considered, as in the literature[19], the fact that our eq 14 does not explicitly consider the Rouse regime. Accordingly, we have also tried to fit the data with an equation (eq 12 in the literature[19]) on the basis of the Doi–Edwards developments that explicitly include the Rouse regime. This equation correctly predicts the power-law relationship between viscosity and molecular weight with a 3.4 exponent. However, as before, we find that without introducing additional adjustable parameters this is not enough to account for the observed deviations. This is clearly seen in Figure 3(a) where the dashed line is the theoretical prediction with the alternative equation. Instead, the approximation $y_n = 1$ seems to be responsible for the disagreement.

DISCUSSION AND CONCLUSIONS

We have measured the osmotic pressure and Newtonian viscosity of mixtures of two compatible polymers in a common solvent, and the results were shown to be described with a renormalization group treatment. Almost all systems are described (in the infinite molecular weight limit) by the symmetric (S) nontrivial fixed point of RG. This corresponds to the case where both binary subsystems are above their Θ temperatures, and there is some repulsion between the two species, which is the case of the solutions here. It follows from the theory that the description of ternary solutions at the fixed point S only requires knowledge of the molecular weights of the components and their binary solution behavior (i.e., the value of the constants β_1 and β_2). Then, the comparison between experiments and theory is made without introducing additional adjustable quantities. Of course, in cases where the interaction between chains of a different kind of f_{12} is still far from the fixed point, an extra constant is needed. However, at the molecular weights considered, we found no improvement in the fits with the introduction of such a constant. Apart from some deviations resulting from molecular weight or intrinsic viscosity uncertainties, osmotic pressure and viscosity data are well accounted for by the zero-order treatment (except for some deviation at high overlap and, for viscosity, at high y_n).

Taking together these results and those of our previous article,[19] this scheme (using the RG results together with de Gennes's blobs model to connect dynamic and conformational quantities) is able to describe thermodynamic and rheological properties of binary and ternary polymer solutions in a unified framework. Binary systems in good solvent are rather accurately described using first-order theoretical results that require the experimental determination of two quantities β (one for static and one for dynamic properties). These quantities were expected (and it was verified) to be independent of molecular weight and concentration. If these values are known for two different polymers in the same solvent, they can be used to predict the ternary system's static properties and its dynamic ones when $y_n \sim 1$.

In conclusion, we feel that the scheme presented in this work could be satisfactorily used to the description of the macroscopic universal properties of polymer solutions. The determination of a few nonuniversal parameters [namely, the Mark–Horowink–Sakurada parameters (k, a) and β] should be enough to describe binary and compatible ternary polymer solutions in the whole range from the dilute to the semidilute limits. Because these parameters are independent of molecular weight, their knowledge would simplify the characterization of polymer solutions in laboratories and industries.

The authors thank F. Amarilla, A. Pesce, and M. A. Sanservino for their very competent technical assistance. This work was funded by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, Argentina), Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC, Argentina), and Universidad Nacional de La Plata. R. V. Figini and M. Marx-Figini are members of the Carrera del Investigador of CONICET, and M. S. Cortizo of the Carrera del Profesional de Apoyo is of the same institution. I. M. Irurzun and T. S. Grigera are research fellows of CONICET.

REFERENCES AND NOTES

1. Yamakawa, H. Modern Theory of Polymer Solutions; Harper and Row: New York, 1971.
2. Doi, M.; Edwards, S. F. The Theory of Polymer Dynamics; Oxford University Press: Oxford, 1986.
3. de Gennes, P. G. Scaling Concepts in Polymer Physics; Cornell University Press: Ithaca, NY, 1979.
4. des Cloizeaux, J.; Jannink, G. Les polymères en solution: leur modélisation et leur structure, Editions de Physique: Les Ulis, 1987.
5. des Cloizeaux, J. J Phys (Paris) 1975, 36, 281.
6. Oono, Y.; Kohomoto, M. J Chem Phys 1983, 78, 1.
7. Oono, Y.; Ohta, T.; Freed, K. F. J Chem Phys 1981, 74, 6458.
8. Schäfer, L. Macromolecules 1982, 15, 652.
9. Schäfer, L. Macromolecules 1984, 17, 1357.
10. Schäfer, L. Excluded Volume Effects in Polymer Solutions; Springer: Berlin, 1999.
11. Irurzun, I. M.; Grigera, J. R.; Figini, R. V.; Marx-Figini, M. Polymer 2000, 41, 725.
12. Shiwa, Y. Phys Rev Lett 1986, 58, 2102.
13. Shiwa, Y.; Oono, Y.; Baldwin, P. R. Macromolecules 1988, 21, 208.
14. Nyström, B. Macromolecules 1993, 26, 3784 and references therein.
15. Kappeler, C.; Schäfer, L. Macromolecules 1990, 23, 2766.
16. Schäfer, L.; Kappeler, C. Colloid Polym Sci 1990, 268, 995.
17. Schäfer, L.; Lehr, U.; Kappeler, C. J Phys (Paris) 1991, 1, 211.
18. Schäfer, L.; Kappeler, C. J Chem Phys 1993, 99, 8.
19. Grigera, T. S.; Irurzun, I. M.; Cortizo, M. S.; Figini, R. V.; Marx-Figini, M. J Polym Sci Part B: Polym Phys 2002, 40, 290 (paper I of this series).
20. In the formulation that introduces w, eq 3 is automatically fulfilled because of the way w is defined.
21. Khol, P. R.; Seifert, A. M.; Hellman, G. P. J Polym Sci Part B: Polym Phys 1990, 28, 1309.
22. Dobry, A.; Boyer-Kawenoki, F. J Polym Sci 1947, 2, 90.
23. Polymer Molecular Weights, Part II; Slade, P. E., Jr., Ed.; Marcel Dekker: New York, 1975.