

Treatment of Poly(styrene-*co*-methacrylic acid)/Poly(4-vinylpyridine) Blends in Solution Under Liquid–Liquid Phase-Separation Conditions. A New Method for Phase-Separation Data Attainment from Viscosity Measurements

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Received 7 April 2006; accepted 29 June 2006

DOI 10.1002/app.25082

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Phase diagrams are contributed for polymer mixture systems in solution. One polymer has proton-acceptor character and the other has growing proton-donor nature, which is reflected in the phase diagrams. Usually, these diagrams are obtained from size-exclusion chromatographic (SEC) measurements. A totally novel application, which is exposed in this report, is the construction of the phase diagram from the viscometric experiments of polymer mixtures. The evaluated binodal or cloud-point isotherms so built agree well with those from SEC. The results indicate an augmentation in the dimensions of donor polymer B, in the presence of acceptor polymer C, intensifying with the concentration of C, which is inter-

preted as an B-C association growing as the number of hydrogen bonds increases. An increment in the Huggins constant for BC, as the proportion of methacrylic acid in the donor copolymer increases, means an augmentation in the interaction for BC, indicating an extension of compatibility. Viscometric experiments evidence hydrogen bonds, intensifying as greater proportion of donor groups has polymer B, equal to that observed in the phase diagrams. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5039–5049, 2006

Key words: ternary polymeric system; compatibility between polymers

INTRODUCTION

A number of advanced materials, tailored for specific applications,^{1,2} are based on mixtures of two or three polymers. Studies of miscibility and phase separation of polymer blends are of usual interest, because they

provide information needed to develop advanced materials for technological applications. Experimentally, it is well known that mixtures of most polymer pairs are incompatible enough, and the obtained phase diagrams consist of two-phase regions.^{3–9} In multi-component polymer systems, the boundary between two- and single-phase regions can be experimentally established from cloud-point,¹⁰ critical-point,^{11,12} spinodal-curve,¹² or coexistence-curve^{13,14} measurements. As compatibility of polymers in solution is a rare occurrence,¹⁵ several authors proposed a method for increasing the compatibility of polymers, which consists in introducing interacting polar groups into the polymeric chain.^{15–17} These groups increase polymer compatibility in organic solution; usually these groups induce the formation of hydrogen bonding interactions.^{15,18–20} In most works devoted to the study of mixtures of polymers in solution, Gibbs ternary phase diagrams were represented, which sometimes were built with vitreous transition temperatures²¹ and, some other times, binodal equilibrium curves of dif-

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Contract grant sponsor: Dirección General de Investigación of the Spanish MEC; contract grant number: CTQ2004-07,768-C02-01/BQU.

Contract grant sponsor: Generalitat Valenciana; contract grant numbers: DGEUI INF01-051 and INFRA03-047, OCYT GRUPOS03-173.

Contract grant sponsor: Dirección General de Enseñanza Superior of the Spanish MEC; contract grant number: MAT2003-0068.

Contract grant sponsor: Sotssecretaria de l'Oficina de Ciència i Tecnologia; contract grant number: CTIDIB-2002-284.

Contract grant sponsor: Universitat de València-Mediscovery.

ferent polymer mixtures were approximated by cloud-point isotherms^{7-9,15,22} or under liquid-liquid phase-separation conditions.

In earlier publications,⁶⁻⁸ an extension of the Flory-Huggins formalism to ternary solvent/polymer/polymer systems has been developed. Briefly, our proposal required accurate phase-composition data, from liquid-liquid phase-separation experiments at constant temperature. Liquid-phase microextraction, in conjunction with size-exclusion chromatography (SEC), provides a suitable way to generate proper experimental data. From each microextraction experiment, one finds the composition of two points in the ternary phase diagram, each one located at the intersection of a given tie line with each branch of the phase-separation curve. Thus, phase-separation results have been used simultaneously to obtain theoretical results. Polymer pairs with equal molecular weights cannot be treated with this method, since drastic experimental conditions are necessary and, under these extreme conditions, SEC experiments cannot be performed.

The present report represents an experimental extension of earlier publications with polymer pairs without union by hydrogen bonding⁶⁻⁸ and polymers with possibilities of union by hydrogen bonding,⁹ developing new strategies to obtain the composition of two points in the ternary phase diagram (each one located at the intersection of a given tie line), based on viscosity measurements of ternary solutions. The proposed experimental method to obtain compositions of phases in equilibrium is completely new, so that with a technique as attainable as viscometry, ternary phase diagrams can be plotted in solvent/polymer/polymer systems, which, as it has been said, are a powerful tool to know the compatibility between two polymers; moreover, the study of these diagrams allows deducing the compatibility between the two polymers as a function of the mixture composition between the two, aspects that could be also deduced with a theory as that of association equilibria applied to a blend of polymers in solution (work in preparation).²⁰ Two types of ternary diagrams, those obtained from SEC measurements and those obtained from viscometry, are compared for chloroform (CHCl₃) (A)/poly(styrene-*co*-methacrylic acid) (PS-MAA) (B)/poly(4-vinylpyridine) (PVPy) (C) systems, with different propor-

tions of MAA for the B component in each case. The obtained results are quite similar, which show that the viscometric method could be a useful procedure for these requirements, being so this method of measuring the compatibility between polymers within the reach of any laboratory.

MATERIALS AND METHODS

The source of chloroform (CHCl₃) was Prolabo (Fontenay-sous-Bois, France) of analytical grade, distilled in the presence of P₂O₅ before use to eliminate ethanol. Poly(4-vinylpyridine) (PVPy) has been obtained by fractionation of a commercial sample from Polysciences (Warrington, PA). Such fractionation has been performed by ultrafiltration with an equipment Millipore Corp. (Bedford, MA), consisting of a cell HIFLUX V-F of 142 mm in diameter, as well as membranes of Pellicon PTHK 10⁵ and PTGC 10⁴. Solutions at 2% (w/v, g dL⁻¹) of commercial PVPy in a water-methanol mixture 30/70 (v/v) underwent ultrafiltration at a constant pressure of 3 kg cm⁻². The obtained fraction was precipitated with ether being reprecipitated after dissolution in CHCl₃. Finally, it was vacuum dried up to constant weight.

The styrene-methacrylic acid (PS-MAA) copolymers have been prepared with different percentages of the MAA polar group. The PS-MAA has been synthesized by radical copolymerization of 40 g of styrene and methacrylic acid, in a methanol 50% (w/w) solution at 65°C under nitrogen atmosphere N_{2(g)}, in the presence of 0.3 g of α,α' -azobisisobutyronitrile (AIBN). The reaction yielded 10% of conversion (12 h) enough to form random copolymers. The solution was precipitated twice with tetrahydrofuran (THF)-ethanol mixtures and the precipitate was vacuum dried up to constant weight.

The PS used as reference was obtained by the same procedure from 50 g of styrene in 150 mL of toluene at 60°C under N_{2(g)}, with 0.2 g of AIBN during 48 h.

Characterization of the PS-MAA samples

The PS-MAA solutions in benzene-ethanol 90/10 (v/v) were titrated with sodium ethoxide in the same mixture, using the potentiometric technique. The compositions of the PS-MAA are detailed in Table I.

TABLE I
Composition of the Poly(styrene-*co*-methacrylic acid) (PS-MAA) Copolymers

Copolymer	MAA content				
	Initial mixture of monomers		Final composition		
	% (w/w)	% (mol/mol)	% (w/w)	% (mol/mol)	mmol g ⁻¹
PS-MAA (3%)	2.4	2.9	3.0	4.0	0.45
PS-MAA (6%)	4.8	5.7	6.0	7.5	0.70
PS-MAA (7%)	5.8	6.6	7.0	8.7	0.80

The PS and PS-MAA characterizations have been carried out via chromatographic experiments. The liquid chromatograph consisted of a solvent-delivery system model 590, and an U6K universal injector from Waters (Milford, MA). Detection was performed with a refractive index (RI) detector model 2410 from Waters. The system was equipped with three complete sets of TSK columns, with pore size name TSK Gel H_{XL} and appropriate range of pore diameter. The mobile phase (THF) was adjusted to 1 mL min⁻¹. The injection volume of samples was 100 μ L. The eluents were always filtered and degassed via regenerated cellulose 0.45 μ m pore diameter filters, from Micro Filtration Systems (Dublin, CA). For all the samples whose characteristics have been given in Table I and PVPy, the molecular weights averaged in number M_n and polydispersity indices I are shown in Table II. Such results have been obtained via previous calibration of the columns ($\log M_n$ versus elution volume V_e) in THF, with polystyrene standards.

Viscosity measurements

An automatic AVS 440 Ubbelohde-type capillary viscometer from Schott Geräte (Hofheim, Germany) was used to perform viscometric experiments, at (25.0 \pm 0.1) $^\circ$ C. The stock solutions were made by dissolving the polymer samples in the corresponding solvents, up to a concentration of about 1.0 g dL⁻¹. At least five dilutions were obtained by adding the appropriate aliquots of solvent. The efflux time of the solvent or binary mixture was always above 100 s. To minimize drainage errors, a 12 mL sample of each solution was loaded into the viscometer, and placed in the thermostatic bath. Measurements started after an equilibration time of 5–10 min; they were continued until several flow-time readings agreed within 0.5%. The elution time of each solution was then determined as the average of several readings. The dilution and subsequent measurements were stopped when the difference in viscosity between the sample solution and pure solvent dropped below 10%. The viscometer was previously calibrated with different solvents; the obtained data indicated there was no need to apply, for this particular viscometer, end correction to the

length of the capillary and kinetic energy correction. For each copolymer in the CHCl₃/PS-MAA/PVPy ternary system, the specific and intrinsic coefficients of viscosity have been determined via infinite-dilution extrapolation of the copolymer, with the CHCl₃/PVPy binary mixture. For CHCl₃/PS-MAA/PVPy mixtures and their dilutions with CHCl₃, the elution times of each phase (to obtain phase diagrams from viscometry) have been determined with the described viscometers.

Binodal or cloud-point isotherms from SEC measurements

To build the binodal or cloud-point isotherms in the ternary phase diagrams, copolymer/homopolymer mixtures have been prepared with different compositions, covering a range of molar fractions from zero to one. Upon them, CHCl₃ has been added drop by drop up to dissolution after appearance of turbidity. About 15 mL of solution has been prepared in each case. After repose of 24 h two phases appear, which compositions are analyzed by liquid chromatography. Using CHCl₃ as eluent, RI as detector and the system equipped with three complete sets of TSK columns (with pore size names TSK Gel Super AW 2500, TSK Gel Super AW 3000 and TSK Gel Super AW 4000, suitable for any eluent,²³ and able to completely separate PS with $M_n = 38,000$ g mol⁻¹ or PS-MAA with $M_n = 33,000$ g mol⁻¹ from PVPy with $M_n = 25,000$ g mol⁻¹, cf. Table II), copolymer and homopolymer have been calibrated separately (peak height versus quantity of injected polymer). Later and separately, 50 μ L of both phases have been injected (storing the rest up to 15 mL for further viscometry), finding out the quantity in weight of both polymers in each phase, as well as the quantity of CHCl₃ by difference of weights. The procedures used with this technique have been described elsewhere in detail.^{6–8} In this way, the compositions of both phases in equilibrium have been evaluated via size-exclusion chromatography (SEC). The repetition of the operation, with additional CHCl₃ in the ternary system, allows assessing the composition of those phases in equilibrium that are more diluted with solvent. When in the homopolymer/copolymer mixture, CHCl₃ is added up to dissolution and disappearance of turbidity, the respective composition corresponds to the maximum of the phase separation diagram (*cloud point*). All the titrated diagram was isothermal at room temperature; its determination has been limited to a homopolymer + copolymer content lower than 30% (w/w) in the ternary system since, at greater concentrations, the excessive viscosity of the mixture prevents the clear physical separation between the two phases and, so, the accurate calculation of the equilibrium compositions.

TABLE II
Molecular Weights and Polydispersity Indices
for the Employed Samples

Polymer	M_n (g mol ⁻¹)	I
PS	38,000 \pm 3000	1.4
PS-MAA (3%) (B)	33,000 \pm 3000	1.4
PS-MAA (6%) (C)	33,000 \pm 3000	1.4
PS-MAA (7%) (D)	33,000 \pm 3000	1.4
PVPy	25,000 \pm 3000	1.5

Binodal or cloud-point isotherms from viscosity measurements

To build the binodal or cloud-point isotherms in the ternary diagrams from viscometry, the 15 mL of solution in which two phases appear have been taken, whose composition has been already analyzed by SEC. The solution with both phases is prepared in a graduated test tube, with a key that allows rapidly separating both phases. Immediately, each phase with known volume is also put into two different viscometers of already-reported analogous characteristics, measuring the flux time at least twice in each case. Then, the solution is diluted in each viscometer by multiplying the original volume by four, and the flux time is evaluated at least twice in each case. Next, the solution is diluted in each viscometer by multiplying the previous volume by two (or the original by eight), and the flux time is assessed at least twice in each case. The calculation of the composition of both polymers in the original solution from these measurements is detailed in the latter section.

RESULTS

Binodal isotherms from SEC measurements

The calculation of c_B and c_C (concentrations of polymers B and C) in each phase, when these are in equilibrium, is simple; it has been reported in the latter

section and explained elsewhere.^{6–8} Basically one starts by preparing a set of SEC columns by where CHCl_3 eludes at 25°C , which have been always calibrated by injecting $50\ \mu\text{L}$ of polymer i ($i = \text{B}, \text{C}$) at known concentration c_i . In the calibrations, h_i (peak height obtained with a detector of differential refractometry, refractive index) is represented versus c_i (in g dL^{-1}). The calibrations have been always linear in the investigated range of concentrations, as it usually happens.²⁴ Then, $50\ \mu\text{L}$ of one of the phases in equilibrium are injected. Two peaks appear corresponding to polymers B and C, respectively. From the height of such peaks and the calibration, c_B and c_C are evaluated for one of the phases, repeating the procedure to assess c_B and c_C for the other phase in equilibrium with the first one. In Table III, they are given the c_B and c_C values obtained for each system from SEC measurements, as well as the values of the specific volumes v_i ($i = \text{A}, \text{B}, \text{C}$) for the three components of each studied system. They are also given (Table III) the values of the ternary weight fractions for the three system components ω_i^T ($i = \text{A}, \text{B}, \text{C}$), as well as those of the binary weight fractions of the B and C polymeric components ω_i ($i = \text{B}, \text{C}$).

The calculation procedure of the later magnitudes follows. Taking as reference 1 dL of solution, the volumes of the three components are

$$c_B (\text{gdL}^{-1}) v_B (\text{mLg}^{-1}) = (\text{mLdL}^{-1}) \text{ of B}$$

TABLE III
Values of Ternary and Binary Weight Fractions Obtained from SEC Measurements^a

System	c_B (g dL^{-1})	c_C (g dL^{-1})	v_A (mL g^{-1})	v_B (mL g^{-1})	v_C (mL g^{-1})	ω_A^T	ω_B^T	ω_C^T	ω_B	ω_C
CHCl_3 (A)/PS (B)/PVPy (C)	3.2343	1.1741	0.6740	0.9170	0.8200	0.9700	0.0220	0.0080	0.7337	0.2663
	0.4548	2.4985				0.9800	0.0031	0.0169	0.1540	0.8460
	2.1192	1.5625				0.9750	0.0144	0.0106	0.5756	0.4244
	0.8120	1.9932				0.9810	0.0055	0.0135	0.2895	0.7105
CHCl_3 (A)/PSMAA (3%) (B)/PVPy (C)	19.0910	3.1916	0.6740	0.9019	0.8200	0.8422	0.1352	0.0226	0.8568	0.1432
	0.7881	4.9315				0.9611	0.0054	0.0335	0.1378	0.8622
	11.9240	3.0045				0.8961	0.0830	0.0209	0.7988	0.2013
	1.0514	3.6933				0.9678	0.0071	0.0251	0.2216	0.7784
	5.2993	2.7299				0.9450	0.0363	0.0187	0.6600	0.3400
	1.9751	2.9281				0.9667	0.0134	0.0199	0.4028	0.5972
CHCl_3 (A)/PSMAA (6%) (B)/PVPy (C)	19.0190	4.2825	0.6740	0.8867	0.8200	0.8353	0.1344	0.0303	0.8162	0.1834
	2.2277	8.3390				0.9276	0.0153	0.0572	0.2108	0.7892
	15.4360	4.2855				0.8617	0.1083	0.0300	0.7827	0.2173
	3.4588	7.3861				0.9256	0.0237	0.0507	0.3189	0.6811
	7.9036	5.7871				0.9053	0.0547	0.0400	0.5773	0.4227
	5.2688	6.5459				0.9187	0.0363	0.0450	0.4460	0.5540
CHCl_3 (A)/PSMAA (7%) (B)/PVPy (C)	22.9510	3.0974	0.6740	0.8817	0.8200	0.8148	0.1632	0.0220	0.8811	0.1189
	1.0571	10.4440				0.9211	0.0073	0.0716	0.0919	0.9081
	10.1340	4.7691				0.8967	0.0703	0.0331	0.6800	0.3200
	4.0549	7.7377				0.9189	0.0279	0.0532	0.3439	0.6562

^a Each phase composition is given by c_B and c_C ; each two consecutive phase compositions conform a tie line. In each system the tie lines are disposed from bottom to top in accordance with Figure 5039–50491.

$$\begin{aligned}
 c_C \text{ (gdL}^{-1}\text{)} v_C \text{ (mLg}^{-1}\text{)} &= \text{(mLdL}^{-1}\text{) of C} \\
 100 \text{ (mLdL}^{-1}\text{)} - c_B v_B \text{ (mLdL}^{-1}\text{)} - c_C v_C \text{ (mLdL}^{-1}\text{)} & \\
 &= \text{(mLdL}^{-1}\text{) of A} \\
 c_B \text{ (gdL}^{-1}\text{)} + c_C \text{ (gdL}^{-1}\text{)} & \\
 + \frac{100 - c_B v_B - c_C v_C \text{ (mLdL}^{-1}\text{)}}{v_A \text{ (mLg}^{-1}\text{)}} & \\
 = \text{total weight of 1 dL of solution} = w_T &
 \end{aligned}$$

$c_B \text{ (gdL}^{-1}\text{)} / w_T \text{ (gdL}^{-1}\text{)} = \omega_B^T$, $c_C \text{ (gdL}^{-1}\text{)} / w_T \text{ (gdL}^{-1}\text{)} = \omega_C^T$, $(100 - c_B v_B - c_C v_C) / v_A w_T = \omega_A^T$, $\omega_B^T / 1 - \omega_A^T = \omega_B$, $\omega_C^T / 1 - \omega_A^T = \omega_C$. Operating in this way $\sum_{i=A,B,C} \omega_i^T = 1$, and $\sum_{i=B,C} \omega_i = 1$. For the calculations the specific volume of PS has been taken as 0.917 mL g⁻¹,²⁵ that of polyMAA, as 0.412 mL g⁻¹ (water/NaCl pH = 12),²⁶ that of PVPy, as 0.820 mL g⁻¹,²⁵ and that of CHCl₃, as 0.674 mL g⁻¹ at 25°C.

Binodal isotherms from viscosity measurements

In the framework of the formalism developed by Krigbaum and Wall²⁷ and Cragg and Bigelow,²⁸ the reduced coefficient of viscosity of a polymer *i* in solution follows the linear relationship given by the Huggins equation:

$$\frac{(\eta_{sp})_i}{c_i} = [\eta]_i + b_{ii}c_i \tag{1}$$

where $b_{ii} = k_H[\eta]_i^2$, and $[\eta]_i = c_i \lim_{c_i \rightarrow 0} \frac{(\eta_{sp})_i}{c_i}$, being $(\eta_{sp})_i$, $[\eta]_i$, c_i , b_{ii} and k_H the specific coefficient of viscosity, intrinsic coefficient of viscosity, polymer concentration, viscometric interaction parameter, and Huggins constant, respectively.

For a mixture of neutral (uncharged) polymers in a common solvent, the extension of eq. (1) leads to:

$$\frac{(\eta_{sp})_m}{c_m} = [\eta]_m + b_m c_m \tag{2}$$

where the subscript *m* denotes *mixture*. Equation (2) can also be expressed in a weight-average form, since the reduced coefficient of viscosity is an additive property:

$$\frac{(\eta_{sp})_m}{c_m} = \sum_i \frac{(\eta_{sp})_i}{c_i} \omega_i \tag{3}$$

with $\omega_i = c_i/c_m$ being the weight fraction of polymer *i* (*i* = B, C), and $c_m = c_B + c_C$. A combination of eqs. (1) and (3) renders:

$$\begin{aligned}
 \frac{(\eta_{sp})_m}{c_m} &= \sum_i ([\eta]_i + b_{ii}c_i)\omega_i \\
 &= \sum_i [\eta]_i \omega_i + c_m \sum_c b_{ii} \omega_i^2 \tag{4}
 \end{aligned}$$

TABLE IV
Values of the Flux Times Obtained by Viscometry for Each Phase in Equilibrium and Its Dilutions Assessed in This Work^a

System	<i>t</i> ⁽¹⁾ (s)	<i>t</i> ⁽²⁾ (s)	<i>t</i> ⁽³⁾ (s)	<i>k</i>	$[\eta]_B$ (dL g ⁻¹)	$[\eta]_C$ (dL g ⁻¹)
CHCl ₃ (A)/PS (B)/PVPy (C)	247.96	133.42	115.84	1.3390	0.29	0.34
	190.79	123.23	111.17	0.9868		
	219.33	127.96	113.34	1.1458		
	180.41	121.20	110.22	0.9132		
CHCl ₃ (A)/PSMAA (3%) (B)/PVPy (C)	441.28	211.07	157.13	4.8686	0.20	0.34
	301.37	145.75	122.43	1.8464		
	359.35	177.31	138.93	3.3180		
	261.08	136.22	118.03	1.4838		
	316.02	150.08	123.21	1.9637		
	277.59	135.83	116.71	1.3728		
CHCl ₃ (A)/PSMAA (6%) (B)/PVPy (C)	468.53	206.53	153.69	4.5223	0.16	0.34
	324.35	172.87	137.21	3.2028		
	405.46	191.53	146.28	3.9284		
	326.50	171.02	135.61	3.0741		
	348.52	175.26	138.10	3.2501		
	333.71	171.37	135.76	3.0734		
CHCl ₃ (A)/PSMAA (7%) (B)/PVPy (C)	480.33	202.30	151.22	4.2664	0.14	0.34
	331.15	182.31	142.33	3.6767		
	350.11	172.11	136.08	3.0682		
	333.01	173.05	137.14	3.1836		

In the table the values of *k* are given, obtained taking into account eqs (12)–(14).

^a The given data are in the same order as those in Table III.

TABLE V
Values of c_B , c_C , and t for Three Mixtures in Solution Whose c_B and c_C Are Related by the Corresponding k (Table IV)

c_B (g dL ⁻¹)	c_C (g dL ⁻¹)	t (s)
3.2001	1.2089	247.61
3.3002	1.1236	247.71
3.5001	0.9530	247.94

First phase in the first system exposed in Tables III and IV.

By comparison of eqs. (2) and (4), as well as $i = B, C$, it is deduced that:

$$[\eta]_m = \sum_i [\eta]_i \omega_i = [\eta]_B \omega_B + [\eta]_C \omega_C \quad (5)$$

On the other hand²⁹

$$(\eta_{sp})_m = \frac{t_{c_B, c_C}}{t_o} - 1 \quad (6)$$

where t_{c_B, c_C} and t_o are the flow times of a solution with concentrations c_B and c_C of polymers B and C, as well as of the pure solvent, respectively.

By substituting eqs. (5) and (6) in eq. (2), it is obtained:

$$\frac{\frac{t_{c_B, c_C}}{t_o} - 1}{c_B + c_C} = [\eta]_B \frac{c_B}{c_B + c_C} + [\eta]_C \frac{c_C}{c_B + c_C} + b_m(c_B + c_C) \quad (7)$$

since

$$b_m = \frac{\frac{t_{c_B, c_C}}{t_o} - 1 - [\eta]_B c_B - [\eta]_C c_C}{(c_B + c_C)^2} \quad (8)$$

If a solution of polymers B and C is considered in the same solvent with concentrations c_B and c_C , respectively, and it is diluted, e.g., up to $(1/4)c_B$ and $(1/4)c_C$, as well as, then, up to $(1/8)c_B$ and $(1/8)c_C$, for the three solutions, it follows, respectively, taking into account eq. (8):

$$b_m(c_B + c_C)^2 = \frac{t^{(1)}}{t_o} - 1 - [\eta]_B c_B - [\eta]_C c_C \quad (9)$$

TABLE VI
Values of c_B , c_C , and t for Four Mixtures in Solution Whose c_B and c_C Are Related by the Corresponding k (Table 4)

c_B (g dL ⁻¹)	c_C (g dL ⁻¹)	t (s)
18.0003	3.7312	443.22
18.3001	3.5547	441.65
18.3402	3.5312	441.44
18.3701	3.5135	441.27

First phase in the second system exposed in Tables III and IV.

TABLE VII
Values of c_B , c_C , and t for Four Mixtures in Solution Whose c_B and c_C Are Related by the Corresponding k (Table IV)

c_B (g dL ⁻¹)	c_C (g dL ⁻¹)	t (s)
19.0002	4.3597	470.34
19.4001	4.1715	468.95
19.5002	4.1244	468.59
19.5201	4.1150	468.52

First phase in the third system exposed in Tables III and IV.

$$b_m(c_B + c_C)^2 = \frac{\frac{t^{(2)}}{t_o} - 1 - \frac{1}{4}[\eta]_B c_B - \frac{1}{4}[\eta]_C c_C}{(1/4)^2} \quad (10)$$

$$b_m(c_B + c_C)^2 = \frac{\frac{t^{(3)}}{t_o} - 1 - \frac{1}{8}[\eta]_B c_B - \frac{1}{8}[\eta]_C c_C}{(1/8)^2} \quad (11)$$

being $t^{(i)}$ ($i = 1, 2, 3$) the flux times of the original solution and its successive dilutions.

Equalling eqs. (9) and (10), (9) and, (11) as well as (10) and, (11) it is obtained, respectively:

$$[\eta]_B c_B = \frac{16 t^{(2)}}{3 t_o} - \frac{1 t^{(1)}}{3 t_o} - 5 - [\eta]_C c_C \quad (12)$$

$$[\eta]_B c_B = \frac{64 t^{(3)}}{7 t_o} - \frac{1 t^{(1)}}{7 t_o} - 9 - [\eta]_C c_C \quad (13)$$

$$[\eta]_B c_B = 16 \frac{t^{(3)}}{t_o} - 4 \frac{t^{(2)}}{t_o} - 12 - [\eta]_C c_C \quad (14)$$

The same result would be obtained with any dilutions, although $t^{(i)}$ and their coefficients should be varied accordingly in the equations. Generally, it is obtained

$$[\eta]_B c_B = k - [\eta]_C c_C \quad (15)$$

being k a constant whose value can be written in different forms according to eqs. (12)–(14). From eq. (15) in a mixture of two polymers in solution with unknown concentrations of both, if they are mea-

TABLE VIII
Values of c_B , c_C , and t for Five Mixtures in Solution Whose c_B and c_C Are Related by the Corresponding k (Table 4)

c_B (g dL ⁻¹)	c_C (g dL ⁻¹)	t (s)
22.9901	3.0818	479.33
22.9503	3.0982	479.40
22.6002	3.2424	480.07
22.5003	3.2835	480.26
22.4701	3.2959	480.32

First phase in the fourth system exposed in Tables III and IV.

sured $t^{(1)}$, $t^{(2)}$, and $t^{(3)}$ (flux times of the solution as well as its dilutions to 1/4 and 1/8, respectively), k ($t_o = 99$ s for CHCl_3 at 25°C) can be evaluated as well as, so, the relationship between c_B and c_C can be assessed provided $[\eta]_B$ and $[\eta]_C$ are known.

Returning to the already-reported method of measurement, each phase with known volume is rapidly put into a viscometer measuring $t^{(1)}$ at least twice. Then the dilutions up to 1/4 and 1/8 of the initial concentration are performed in the viscometer, as it has been already described. The corresponding flux times (mean of two replications) are given in Table IV, following the same order in systems and *tie lines* exposed in Table III. From such times, the value of k is calculated as average of the three values of such a constant given in eqs. (12)–(14). In Table IV, k is consigned for each system, with which the relationship between c_B and c_C that exist in each phase will be evaluated via eq. (15). The values of $[\eta]_B$ and $[\eta]_C$ are also given in Table IV for each ternary system. To know the accurate values of c_B and c_C in each phase, it was operated in the following way. It is prepared a solution that keep the known relationship between c_B and c_C . If the phase to be evaluated corresponds to those zones richer in component B (at the left of the ternary phase diagram), with lower density, it will be the upper phase in the equilibrium with greater c_B (cf., e.g., the first entry in Table III). In this way, a mixture in which

$c_B \gg c_C$ is initially prepared in solution. If nothing is known about these solutions, one tries until the flux time be close to the $t^{(1)}$ of the problem solution. As examples for those c_B and c_C of the first entry in Tables III and IV, the assessed values of flux time are reported in Table V.

As it can be shown for the last entry in Table V, $t = 247.94$ s, practically equal to $t^{(1)}$ of the problem solution (cf. Table IV), so that the corresponding concentrations will be those of the problem solution (first entry in Tables III and IV). In practice, these concentrations can be found without performing so much trial solutions in the following way. For the first entry in Table V, $t = 247.61$ s, already close to $t^{(1)} = 247.96$ s (cf. Table IV). With this mixture, b_m can be calculated following eq. (8). As the remaining trial solutions contain c_B and c_C similar between themselves, one can assume that b_m is common to all of them (b_m depends on some particular starting c_B and c_C , as well as on their divisors); by substituting this value ($b_m = 0.00,834$) in eq. (7), making $t_{c_B, c_C} = t^{(1)}$ and writing c_C as a function of c_B following eq. (15), c_B can be evaluated and, so, also c_C , for which the flux time is $t^{(1)}$, which is that of the problem solution.

In Tables VI–VIII, the same magnitudes as in Table V are consigned as an example for the first phase composition in each system, written following the order established in Tables III and IV. In each of the

TABLE IX
Values of Ternary and Binary Weight Fractions Obtained from Viscometry^a

System	c_B (g dL ⁻¹)	c_C (g dL ⁻¹)	v_A (mL g ⁻¹)	v_B (mL g ⁻¹)	v_C (mL g ⁻¹)	ω_A^T	ω_B^T	ω_C^T	ω_B	ω_C
CHCl ₃ (A)/PS (B)/PVPy (C)	3.5001	0.9530	0.6740	0.9170	0.8200	0.9702	0.0238	0.0065	0.7993	0.2177
	0.4602	2.5100				0.9799	0.0031	0.0170	0.1548	0.8449
	3.0502	0.7685				0.9740	0.0207	0.0052	0.7962	0.2009
	0.2002	2.5152				0.9816	0.0014	0.0170	0.0736	0.9250
CHCl ₃ (A)/PSMAA (3%) (B)/PVPy (C)	18.3702	3.5135	0.6740	0.9019	0.8200	0.8452	0.1299	0.0248	0.8391	0.1602
	0.7003	5.0188				0.9611	0.0047	0.0341	0.1223	0.8766
	10.6001	3.5223				0.9007	0.0745	0.0247	0.7503	0.2487
	0.7700	3.9111				0.9682	0.0052	0.0266	0.1644	0.8352
	6.7002	1.8344				0.9414	0.0460	0.0126	0.7846	0.2148
2.5401	2.5435	0.9657	0.0170	0.0173	0.4955	0.5038				
CHCl ₃ (A)/PSMAA (6%) (B)/PVPy (C)	19.5201	4.1150	0.6740	0.8867	0.8200	0.8327	0.1381	0.0291	0.8257	0.1739
	2.2301	8.3706				0.9273	0.0153	0.0574	0.2103	0.7894
	15.3803	4.3165				0.8618	0.1079	0.0303	0.7807	0.2191
	3.5048	7.3920				0.9252	0.0240	0.0508	0.3212	0.6787
	8.0901	5.7522				0.9044	0.0560	0.0398	0.5854	0.4162
5.2550	6.5665	0.9186	0.0362	0.0452	0.4448	0.5554				
CHCl ₃ (A)/PSMAA (7%) (B)/PVPy (C)	22.4699	3.2959	0.6740	0.8817	0.8200	0.8169	0.1596	0.0234	0.8716	0.1279
	0.8998	10.4432				0.9222	0.0062	0.0716	0.0793	0.9206
	10.7003	4.6182				0.8937	0.0743	0.0321	0.6985	0.3015
	3.7501	7.8194				0.9205	0.0258	0.0537	0.3241	0.6758

^a Each phase composition is given by c_B and c_C ; each two consecutive phase compositions conform a tie line. In each system the tie lines are disposed from bottom to top in accordance with Figures 5039–50491–3.

Tables VI–VII, the last consigned trial solution has a flux time equal to the corresponding $t^{(1)}$; so, the c_B and c_C of such solutions are those that are taken for the problem solution (representative of a phase), in each case. In such a way, using viscometry, c_B and c_C have been evaluated for every phase in every system studied in this report.

In Table IX they are given all these values, as well as the values of the ternary ω_i^T ($i = A, B, C$) and binary ω_i ($i = B, C$) weight fractions given rise by such concentrations, operating in the same way as when the concentrations have been obtained from SEC (cf. Table III).

To compare the results obtained from both techniques, in Figures 5039–50491 and 2 a ternary diagram is presented, with the results obtained for every system proceeding from SEC and viscometry, respectively. The way of representing each phase composition has consisted in the intersection of a perpendicular to the ω_A^T axis, with a straight line that joins ω_C with the upper vertex of the triangle. As it can be seen in both figures, a *tie line* joins the compositions of two phases in equilibrium. It can also be shown in such figures, how the zones of one phase (unclosed or external part to each curve) are becoming greater as the percentage of MAA in PS-MAA increases, which is logical, because hydrogen bonding between PS-MAA and PVPy increases as the participation of MAA in the proton-donor copolymer is greater, augmenting system stability. In Figure 5039–50493, the results obtained with both techniques are superimposed, showing that they are similar as well as, surprisingly, the concordance between the two techniques is emphasized, as the union between the PS copolymer and PVPy is more intense.

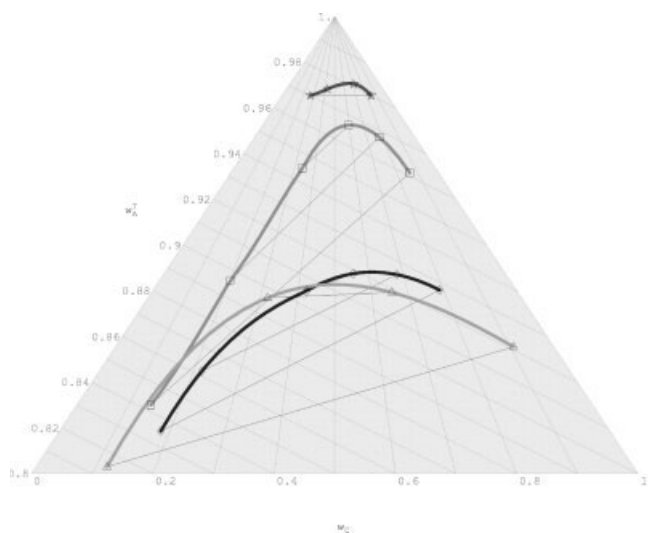


Figure 1 Binodal isotherms obtained from SEC measurements: $\text{CHCl}_3/\text{PS}/\text{PVPy}$ (\star), $\text{CHCl}_3/\text{PS-MAA (3\%)/PVPy}$ (\square), $\text{CHCl}_3/\text{PS-MAA (6\%)/PVPy}$ (\diamond), and $\text{CHCl}_3/\text{PS-MAA (7\%)/PVPy}$ (\triangle).

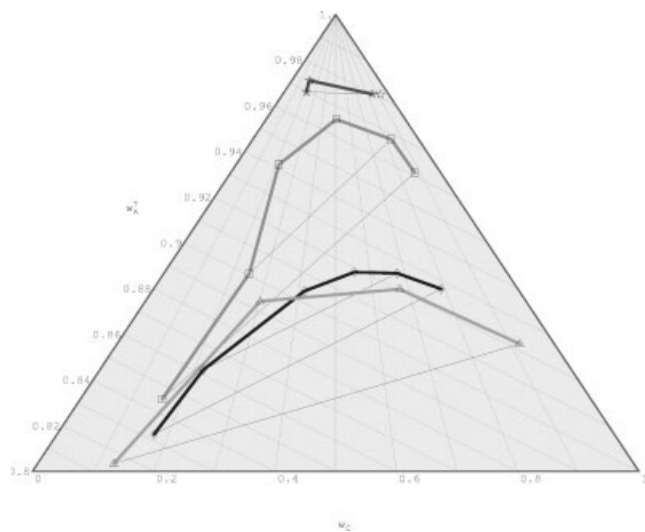


Figure 2 Binodal isotherms obtained from viscometry: $\text{CHCl}_3/\text{PS}/\text{PVPy}$ (\star), $\text{CHCl}_3/\text{PS-MAA (3\%)/PVPy}$ (\square), $\text{CHCl}_3/\text{PS-MAA (6\%)/PVPy}$ (\diamond), and $\text{CHCl}_3/\text{PS-MAA (7\%)/PVPy}$ (\triangle).

Corroboration with the viscometric technique of the global results obtained in phase diagrams

In the preceding subsections, it has been demonstrated that with two different techniques we obtain identical results. In the present subsection, we corroborate, exclusively via viscometry, the results obtained with the studied series of copolymers.

To power even more the advantages of using viscometry in this type of studies, one can remind a procedure used, in the past and nowadays, for estimating the compatibility of two polymers in solution,^{29–31} as it is the determination of the intrinsic coefficient of vis-

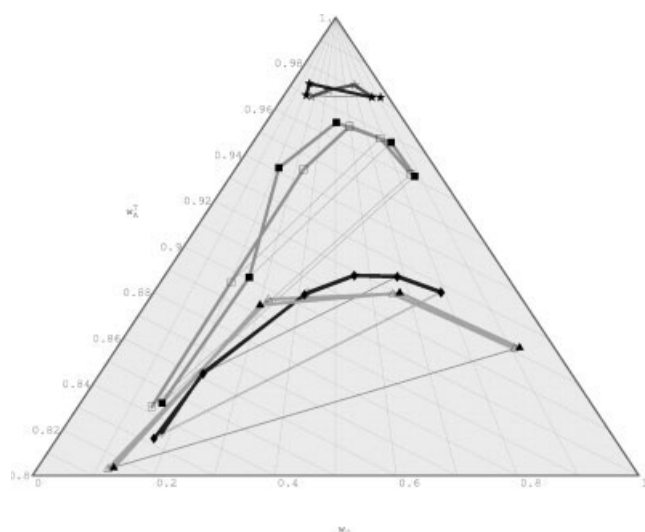


Figure 3 Comparison between binodal isotherms obtained from SEC (\star , (\square), (\diamond), (\triangle)) and viscometry (\star), (\blacksquare), (\blacklozenge), (\blacktriangle). The same symbols that in Figures 5039–50491 and

cosity for polymer B, in a binary mixture formed by a dilute solution of polymer C in solvent A. This procedure is based on that the difference between the intrinsic coefficients of viscosity for polymer B in pure solvent A, $[\eta]_B$, and in the solvent (A)/polymer (C) mixture with concentration c_C , $[\eta]_{B,c_C}$, lies in the change in dimensions of polymer B in the absence and presence of polymer C. The variation of flux time t_{c_B,c_C} with the c_B and c_C concentrations, in a dilute solution of both polymers, can be written taken into account in eq. (4):

$$\eta_{\text{red},m} = \frac{(\eta_{\text{sp}})_m}{c_m} = [\eta]_B c_B + [\eta]_C c_C + c_m (b_{BB} \omega_B^2 + b_{CC} \omega_C^2 + 2b_{BC} \omega_B \omega_C) = [\eta]_m + b_m c_m \quad (16)$$

where $(\eta_{\text{sp}})_m$ and $\eta_{\text{red},m}$ are the specific and reduced coefficients of viscosity of the polymer mixture, respectively, as well as b_m , the parameter of viscometric interaction for the polymeric mixture. From eq. (16) it can be deduced:

$$(\eta_{\text{sp}})_m = [\eta]_B c_B + [\eta]_C c_C + b_{BB} c_B^2 + b_{CC} c_C^2 + 2b_{BC} c_B c_C = \frac{t_{c_B,c_C}}{t_0} - 1 \quad (17)$$

From eq. (17), it can be written:

$$t_{c_B,c_C} = t_0 (1 + [\eta]_B c_B + [\eta]_C c_C + b_{BB} c_B^2 + b_{CC} c_C^2 + 2b_{BC} c_B c_C) \quad (18)$$

and so:

$$t_{c_C} = t_0 (1 + [\eta]_C c_C + b_{CC} c_C^2) \quad (19)$$

Taking into account the latter expressions and the definition of intrinsic coefficient of viscosity, it can be written:

$$[\eta]_{B,c_C} = c_B \lim_{c_C \rightarrow 0} \frac{t_{c_B,c_C} - 1}{c_B} = \frac{[\eta]_B + 2b_{BC} c_C}{1 + [\eta]_C c_C + b_{CC} c_C^2} \quad (20)$$

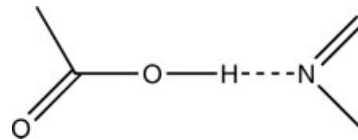
where b_{ii} ($i = B, C$) are terms that take into account the interactions between similar molecules, being related to the Huggins constant k_i ($i = B, C$) via the equality $b_{ii} = k_i [\eta]_i^2$ ($i = B, C$). The b_{BC} is an interaction parameter, representing the thermodynamic and hydrodynamic interactions between polymers B and C in a common solvent, being its value as a function of the Huggins constant: $b_{BC} = k_{BC} [\eta]_B [\eta]_C$. Taking into account eq. (20) it can be written:

$$\frac{[\eta]_{B,c_C}}{[\eta]_B} = \frac{1 + 2 \frac{b_{BC}}{[\eta]_B} c_C}{1 + [\eta]_C c_C + b_{CC} c_C^2} = \frac{1 + 2k_{BC} [\eta]_C c_C}{\eta_{\text{re},C}} \quad (21)$$

where $\eta_{\text{re},C}$ is the relative coefficient of viscosity for a solution of polymer C at concentration c_C . Finally, eq. (21) can be represented by:

$$\frac{[\eta]_{B,c_C}}{[\eta]_B} \eta_{\text{re},C} = 1 + 2k_{BC} [\eta]_C c_C \quad (22)$$

In Figure 5039–50494, eq. (22) is represented for the four systems studied here. From the slope of such representation, k_{BC} is obtained. In Table X, the results necessary for the representation of eq. (22) are shown. If the results of Table X and Figure 5039–50494 are analyzed, it can be shown how for each system as c_C increases $[\eta]_{B,c_C}$ and $[\eta]_{B,c_C} \eta_{\text{re},C} / [\eta]_B$ also grow, which indicates an augmentation in dimensions for polymer B in the presence of C, which intensifies with c_C , and that can be interpreted as a sign of association between the two polymers. In turn, in the same Table X it can be seen how for a given c_C , $[\eta]_{B,c_C} \eta_{\text{re},C} / [\eta]_B$ increases as greater proportion of MAA has the proton-donor PS-MAA copolymer, which can be interpreted as an association between the two polymers, growing as the number of unions by hydrogen bond



increases. Finally, an increment in k_{BC} as the proportion of MAA in the donor copolymer increases means an augmentation in the b_{BC} parameter in the same direction, which, in these cases and according with the theory, indicates an extension of the compatibility between the two polymers. Notice in Table X how $[\eta]_B$ decreases as the proportion of the polar group increases. This is usual in an organic solvent as CHCl_3 . In such a way, this type of viscosity measurements evidence unions by hydrogen bond, which

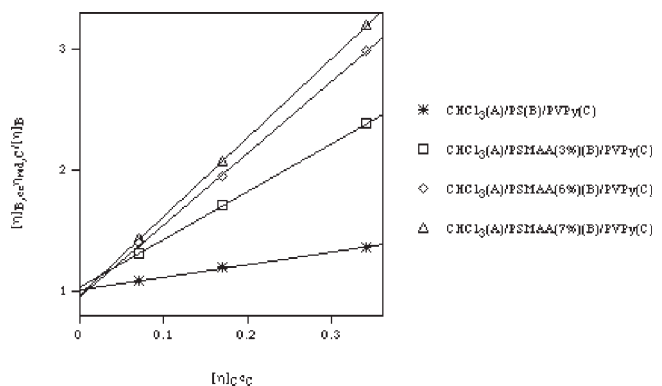


Figure 4 Variation of $[\eta]_{B,c_C} \eta_{\text{re},C} / [\eta]_B$ versus $[\eta]_C c_C$: $\text{CHCl}_3/\text{PS}/\text{PVPy}$ (*), $\text{CHCl}_3/\text{PS-MAA (3\%)}/\text{PVPy}$ (\square), $\text{CHCl}_3/\text{PS-MAA (6\%)}/\text{PVPy}$ (\diamond), and $\text{CHCl}_3/\text{PS-MAA (7\%)}/\text{PVPy}$ (\triangle).

TABLE X
Viscometric Data Related to Viscosity Measurements of Polymer B in the Presence of Polymer C
at Constant c_C Concentration

System	$[\eta]_B$ ($\text{dL} \cdot \text{g}^{-1}$)	$[\eta]_C$ ($\text{dL} \cdot \text{g}^{-1}$)	b_{c_C} ($\text{dL}^2 \cdot \text{g}^{-2}$)	c_C ($\text{g} \cdot \text{dL}^{-1}$)	$[\eta]_{c_C}$	$[\eta]_{B,c_C}$ ($\text{dL} \cdot \text{g}^{-1}$)	$\eta_{\text{red},C}/[\eta]_B$	k_{BC}
CHCl ₃ (A)/PS (B)/PVPy (C)	0.29	0.34	0.02	0.2	0.07	0.293	1.08	0.53
				0.5	0.17	0.294	1.19	
				1.0	0.34	0.290	1.36	
CHCl ₃ (A)/PSMAA (3%) (B)/PVPy (C)	0.20	0.34	0.02	0.2	0.07	0.245	1.31	2.10
				0.5	0.17	0.291	1.71	
				1.0	0.34	0.351	2.38	
CHCl ₃ (A)/PSMAA (6%) (B)/PVPy (C)	0.16	0.34	0.02	0.2	0.07	0.208	1.39	2.90
				0.5	0.17	0.264	1.94	
				1.0	0.34	0.350	2.98	
CHCl ₃ (A)/PSMAA (7%) (B)/PVPy (C)	0.14	0.34	0.02	0.2	0.07	0.187	1.43	3.20
				0.5	0.17	0.247	2.07	
				1.0	0.34	0.329	3.19	

are intensified as greater proportion of donor groups has polymer B, exactly equal to that observed in the ternary phase diagrams (cf. Figs. 5039–50491–3).

CONCLUSIONS

In this study, phase diagrams are contributed for polymer mixture systems in solution. One of the polymers has proton-acceptor character, and the other has growing proton-donor nature, which is reflected in the ternary phase diagrams. A novelty, as we know, full of applications is the construction of the phase diagram from the viscosity measurements of polymer mixtures, being the viscometric technique accessible to any laboratory. The evaluated binodal isotherms agree well with those contributed from SEC measurements, the latter method being more traditional in this type of measurements.

The results contributed by the ternary phase diagrams agree in their conclusions with other type of measurements, derived from the viscometry of the donor polymer in binary solutions of the acceptor polymer, at constant concentration in the solvent.

The chromatographic technique has been used repetitively by the authors, in previous works, to build polymer–polymer–solvent ternary diagrams by using the gel permeation chromatographic (GPC) technique, though for some systems different from the donor/acceptor ones.^{6–8} The utilization of the viscometric technique in this case comes, in part, from our experience in the utilization of viscometric theories in mixtures of polymers.^{29,30,32} However, from a practical point of view, the viscometric technique is much more economic and attainable for any laboratory and, as is demonstrated in the present report, the results obtained with both techniques are similar. The numerical example used to solve viscometrically the compo-

sition of the phases in equilibrium is extendible to any mixture, as can be easily demonstrated.

Figure 5039–50494 shows a representation that indicates that the intrinsic and relative viscosity measurements used in the present report are right, so that it is an indirect form of showing that the results obtained with ternary diagrams have been accomplished with adequate viscometric measurements.

The results obtained with phase diagrams via GPC have the same form that those obtained viscometrically, so that a discussion with these diagrams would be possible but, in this case, we would not have polymer–polymer interaction parameters. Perhaps, with a help technique as light scattering, at the same studied compositions, they could be related the forms of the graphs to thermodynamic interaction parameters between polymers, obtained in an independent way.

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