Miscibility of Styrene/Unsaturated Polyester Quasibinary Systems: Unsaturated Polyester Chemical Composition and Molecular Weight Influence

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Received 18 August 2005; accepted 3 June 2006
DOI 10.1002/app.24943
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Unsaturated polyester prepolymers were synthesized with different chemical compositions and molecular weights. Cloud-point curves (CPC) were measured in St-UP quasibinary solutions, showing UCST behavior in all cases. The miscibility of the first UP samples series in St comonomer was enhanced when AA chemical comonomer concentration in UP prepolymer increased. In the second series, UP prepolymer miscibility increased with the molecular weight up to a maximum and, after that, the miscibility decreased. A thermodynamic analysis of experimental CPCs was performed using the Flory-Huggins (F-H) theory for polydisperse polymer solutions. A simple relationship between the interaction parameter and the temperature inverse could fit the measured CPCs in wide concentrations and molecular weight ranges. In the temperature interval where this fit took place, the positive enthalpic contribution to the interaction parameters determined the miscibility dependence with temperature in both UP sample series. The St-UP miscibility behavior was also correlated with UPs structural chemical parameters as: (a) the final HO— and HOOC— high polar groups concentration, (b) the chain backbone polar adipate and phthalate groups concentration, and (c) the UP size dependent mixing entropy. All these parameters are molecular weight dependent. J Appl Polym Sci 102: 6064–6073, 2006

Key words: unsaturated polyester; miscibility; cloud point curves; Flory-Huggins analysis; interaction parameter

INTRODUCTION

Unsaturated polyester prepolymers (UP) are the most important multifunctional monomer to obtain thermosetting copolymers with the styrene (St) comonomer. At low temperature, St-UP reactive mixtures have low viscosities, that coupled with rapid cure schedules and low cost, make them excellent candidates to be used in the formulation of composites for many structural applications in the industry.[1]

In many applications where the surface quality is an important requirement, the St-UP resins are modified with low-profile thermoplastic additives (LPA), such as poly(vinyl acetate) (PVAc), poly(methylmethacrylate) (PMMA), as well as poly(styrene) (PS) and poly(urethane) (PU), to improve molding compounds with superior surface quality.[2] The low-profile behavior in the cured composite is originated by an open two-phase morphology in the composite polymer matrix. This morphology, with a LPA rich phase and a St-UP copolymer rich phase, is originated by the mechanism of polymerization induced phase separation (PIPS) when the ternary St-UP-LPA system is cured. To achieve suitable morphologies, the miscibility of the three quasibinary systems St-UP, UP-LPA, and St-LPA are important variables to determine the low profile behavior. Poor binary St-UP miscibility has been cited[3,4] as a significant cause of heterogeneous morphologies observed during the cure of St-UP-LPA mixtures at low and at high temperatures.[2,5]

Besides the miscibility importance of the St-UP quasibinary systems to control final morphologies, as well as mechanical properties and low profile behavior, there are not detailed experimental and thermodynamic studies on the miscibility of well-characterized UP prepolymers in open literature. Only qualitative correlations between the experimental liquid–liquid binary and ternary phase diagrams for the initial unreacted system, component concentrations and final morphologies are reported for a few LPA modified systems, most of them with PVAc additive.[6–10]

All reported experimental studies over St-UP quasibinary cloud-point (CP) phase diagrams showed UCST.[7,11,12] St-UP miscibility depends on temperature and UP prepolymer properties such as chemical composition, molecular weight, high polar chain end

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Contract grant sponsors: National Research Council (CONICET, Argentina), National Agency for the Promotion of Science and Technology (ANPCyT, Argentina) and University of Mar del Plata.

groups, polar backbone ester groups, and polydispersity index.[11,12]

In this work, a first series of UP prepolymers with constant molecular weight (≈ 1200 g/mol) were synthesized to study the UP chemical comonomer composition influence on St monomer miscibility. The influence of the molecular weight was analyzed on UP samples with constant chemical composition and different molecular weights. In both cases, the CPCs were experimentally determined.

A Flory-Huggins thermodynamic analysis of measured CPCs allowed determining the binary interaction parameters and their dependence upon UP chemical diacid compositions as well as upon their molecular weights. During thermodynamic calculations, UP prepolymers polydispersities were taken into account.

In a succeeding paper, a thermodynamic analysis of UP chemical composition and molecular weight effects on St-UP-LPA quasiternary systems will be presented.

EXPERIMENTAL PROCEDURE AND RESULTS

UP prepolymers synthesis

UP prepolymers were synthesized by the fusion-melt process[1] in a 2-L stainless steel heated reactor vessel, with moderate stirring and overhead condenser to collect the aqueous by-product. The reaction mixture was precondensed at 90°C during 4.5 h and the temperature was then raised to 190°C. The reaction was stopped when the acid number continuously determined took the characteristic value of the particular molecular weight desired. Typical total reaction times were about 20 h. Preventing discoloration, the reactor was continuously purged with the flow of fresh nitrogen.

In the synthesized first sample series with $M_n \sim 1200$ g/mol, used in UP chemical composition analysis, the UP comonomer constituents maleic anhydride (MA) and ethylene glycol (EG) molar concentrations were fixed, while those of phthalic anhydride (PhA) and adipic acid (AA) were changed according to the following stoichiometric relation in mole number: 1 MA + 2 EG + x AA + (1 − x) PhA. These UPs and their St solutions are identified by AA00, AA25, AA50, AA75, and AA100 in Tables and Figures. The selected molecular weight for this series of UP prepolymers was ~1200 g/mol to compare with similar molecular weights UPs miscibility behavior in St comonomer reported by Lecointe et al.[11]

The second series of UPs were synthesized with a fixed comonomer composition $x = 0.50$ (the AA50 series) and variable molecular weights from 620 to 2740 g/mol. This molecular weight interval was selected because in most industrial applications UPs have molecular weights between 1500 and 2000 g/mol.[1]

The raw chemicals used in the synthesis were maleic anhydride (MA, Maleic S. A, Argentine), ethylene glycol (EG, Química Oeste, Argentine), phthalic anhydride (PhA, Industrias Químicas Wam, Argentine),

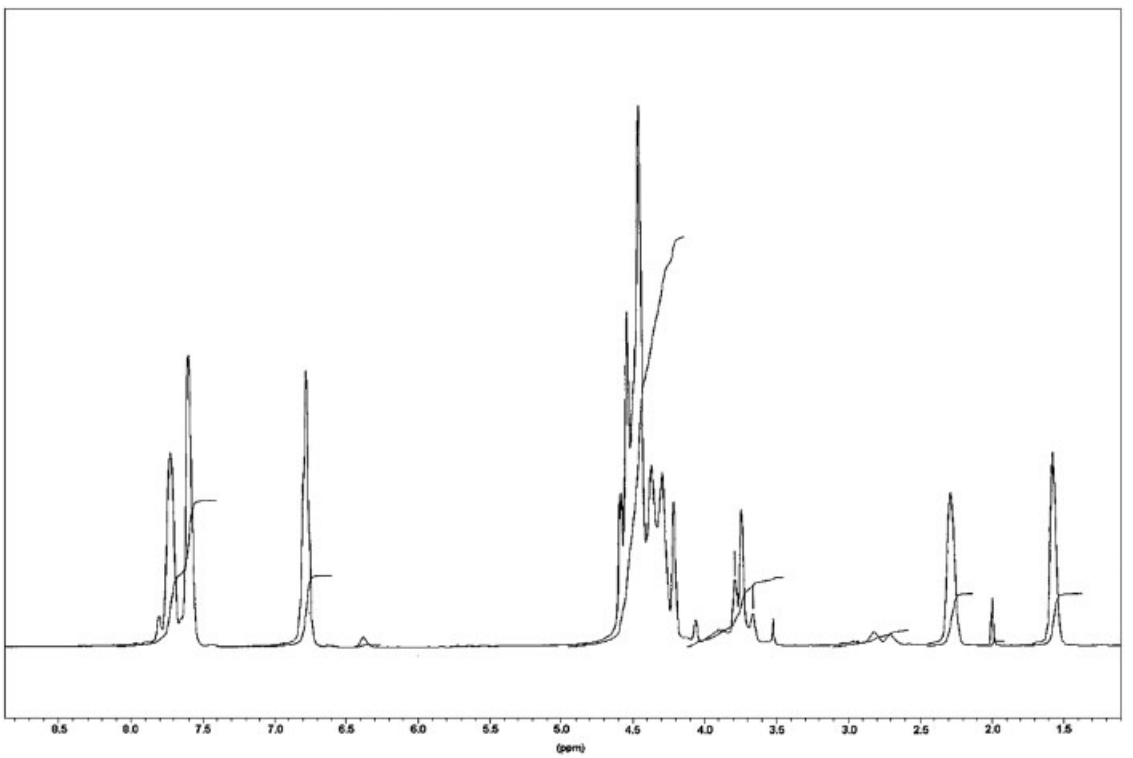

Figure 1 ^{1}H-NMR spectrum of the AA25 UP prepolymer.

and adipic acid (AA, Anedra, Argentine), all under laboratory grade purity. All these chemicals were used without further purifications.

UP prepolymers characterization

^{1}H-NMR spectroscopy

UP prepolymers were analyzed determining their ^{1}H-NMR spectra in acetone-d_6 solutions with a Bruker AC-200 apparatus. Figure 1 shows AA25 UP prepolymer ^{1}H-NMR spectrum. The resonance absorption intensity bands of the *trans*-fumarate double bond structure at 6.83 ppm and *cis*-maleate structure at 6.42 ppm show that this isomerization reaction reaches a conversion degree of 96.2%. In all other UP samples, the isomerization degree is higher than 90%. High conversion in this side reaction is desirable since the fumarate-styrene double bond reactivity is higher than the maleate-styrene one.[13,14] Then, high transformation degrees provide a more reactive UP prepolymer to the styrene comonomer, useful in industrial applications where UP prepolymers with high curing rates are wanted.

Maleate or fumarate double bonds can also react with glycol hydroxyl end groups, forming a lateral branch on UP main chain (2.8 ppm). This is another possible side reaction during the synthesis, named the *Ordelt reaction*. In all synthesized samples, this reaction extent shows low values (< 3%), characteristics of UP prepolymers obtained from primary glycols.[15] The physicochemical parameters of synthesized UP prepolymers are collected in Table I.

The more significant UP prepolymers ^{1}H-NMR bands show that the chemical composition and concentration of each monomer constituent in prepolymers was essentially the same as those charged in the reactor during the synthesis.

SEC analysis

UPs samples molecular weight distribution (MWD) and polydispersity index (PI) were measured by size exclusion chromatography using a Waters Model 510, equipped with a Waters 410 refraction index detector. The apparatus was operated with four columns packed with Ultrastyragel: 10^5, 10^4, 10^3, and 500 A. Polystyrene standards were used for calibration.

TABLE I
Unsaturated Polyester Prepolymers Characteristics

UP	AA%	I_{COOH}	I_{OH}	M_n (g/mol)	PI	δ (g/cm^3)
AA100[a]	100	43.8	48.2	1220	2.14	1.29
AA75[a]	75	36.1	53.6	1250	2.18	1.31
AA50[a]	50	41.1	51.9	1205	2.23	1.30
AA25[a]	25	30.6	59.6	1245	2.04	1.31
AA0[a]	0	32.8	54.2	1290	1.98	1.32
$AA50_{620}$[b]	50	115.6	65.2	620	1.23	1.30
$AA50_{1205}$[b]	50	41.1	51.6	1205	2.23	1.30
$AA50_{1700}$[b]	50	33.6	32.3	1700	2.18	1.31
$AA50_{2740}$[b]	50	28.3	12.6	2740	2.48	1.30

[a] Samples with different chemical compositions.
[b] Samples with different molecular weights.

Density

UP prepolymers densities at room temperature were determined using the picnometric method.

End group analysis

UP prepolymers number average molecular weight, M_n, was determined by measuring the carboxyl and hydroxyl end groups. Carboxyl number (I_{COOH}) was measured by weighing 0.2–0.3 g of each UP, dissolving it in pyridine and titrating with standardized potassium hydroxide solution. To determine hydroxyl number (I_{OH}), 0.2–0.3 g of each sample was refluxed for 1 h with 5 cm^3 of acetylating mixture (pyridine/acetic anhydride, 400/6), and titrating the acetic anhydride excess with KOH solution. Both titration end points were determined by a potentiometric method, and the results were expressed as mg of KOH/g of UP sample. From these results, the number–average molecular weights were calculated by the following equation, assuming the Ordelt reaction being absent, $M_n = 2 \times 56.1 \times 10^3/(I_{OH} + I_{COOH})$.

Cloud-point curves determination

For each particular UP of fixed chemical comonomer composition and molecular weight, the cloud point curve (CPC) was determined by taking a binary mixture series of variable St concentration and introducing them in a cell with a programmed temperature change. The cell was a cylindrical glass jacket tube. The jacket circulating fluid was supplied from an external bath at programmable heating rates. Binary solution cloud point temperatures were determined by averaging three measured values on turbidity onset during slow cooling under moderate stirring to assure uniform temperature.

Figure 2 shows the St-UP cloud-point curves (CPCs) identified by AA00, AA25, AA50, AA75, and AA100 in Table I. Since these UP prepolymer samples molecular weights and polydispersities are similar, it is assumed that the high polar final groups HO— and HOOC— affect the St-UP miscibility of all UP series samples in the same extension, as well as do their average molecular size. Hence, the observed T versus ϕ curves upper displacements were determined by the relative concentrations of polar adipate and phthalate ester groups in the backbone chain, showing that miscibility in St monomer increases when UP samples AA content increases. A similar composition effect

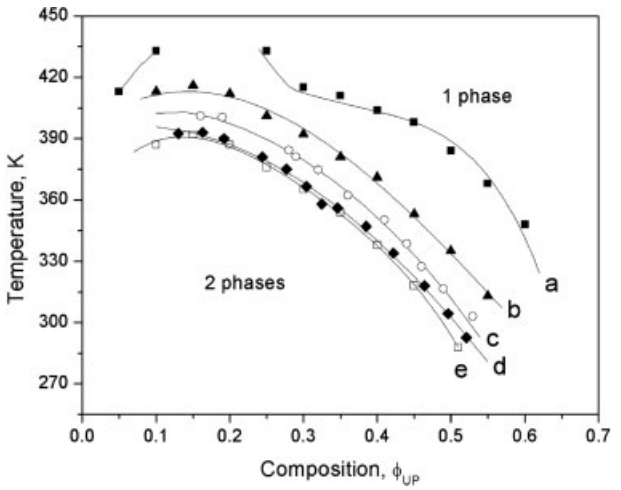

Figure 2 UP chemical composition effect on the experimental T versus ϕ_{UP} cloud point curves: (a) St-AA00, (b) St-AA25, (c) St-AA50, (d) St-AA75, (e) St-AA100.

was experimentally reported by Lecointe et al.,[11] using UP prepolymers of similar molecular weights and distributions, where the polyester backbone chemical structure was changed by using different proportions of neopentyl glycol (NPG) and diethylene glycol (DEG).

Figure 3 shows the CPCs for the AA50 samples of different molecular weights in St. Miscibility increases up to a maximum when the UP molecular weight augments; after that, the miscibility decreases as would be the expected behavior for the higher molecular weight. The CPCs relative positions in this figure show the influence of UP chemical characteristics: the concentration of high polar HO— and HOOC— final groups, the number of adipate and phthalate ester groups in the backbone chains and UP molecules sizes, all of them are UPs molecular weight dependent.

All CPCs represented in Figures 2 and 3 show an UCST behavior, as was found by Lecointe et al.[11] in St-UPs prepolymers solutions with different glycol chemical composition and molecular weights.

THERMODYNAMIC ANALYSIS, RESULTS, AND DICUSSION

Theoretical background

In this work, the simplest version of F-H theory for quasibinary polymer solutions[16–19] was applied considering St-UP binary interaction parameter as composition independent and inversely proportional to the temperature. Despite its simplicity, this thermodynamic model is still suitable to obtain valuable information for these quasibinary solutions. This information can be used later on thermodynamic analysis of St-UP-low profile quasiternary solutions.

The following equation describes the adimensional mixing Gibbs free energy per mole of lattice sites in the quasibinary S-UP solution:

$$\Delta G^{\text{mix}} = \frac{\Delta G^{\text{mix}}}{\text{MRT}} = \frac{\phi_0}{r_0}\ln\phi_0 + \sum_{j=1}^{N_1}\frac{\phi_j}{r_j}\ln\phi_j + \chi_{01}\phi_0\phi_1 \quad (1)$$

Sub index numbers 0,1 represent St solvent and UP prepolymer components, respectively; $j = 1, N_1$ represents the different polymerization degree of UP molecular species inside polydisperse UP molar mass-fraction distribution; ϕ_j is the volumetric fraction of j molecular species in solution, and $\phi_1 = \sum_j \phi_j$ is the total UP prepolymer volumetric fraction; χ_{01} is the composition independent binary interaction parameter given by the equation

$$\chi_{01} = \chi_S + \frac{\chi_H}{T} \quad (2)$$

where χ_S and χ_H are the entropic and enthalpic contributions, respectively.

M represents the lattice sites total mole number in the quasibinary system given by:

$$M = n_0 r_0 + \sum_{j=1}^{N_1} n_j r_j \quad (3)$$

where n_j is the mole number of an UP generic j molecular specie, with size r_j defined by:

$$r_j = \frac{V_j}{V_r} \quad (4)$$

In this equation, V_j is the UP generic j species molar volume, and V_r is the reference volume, taken as the

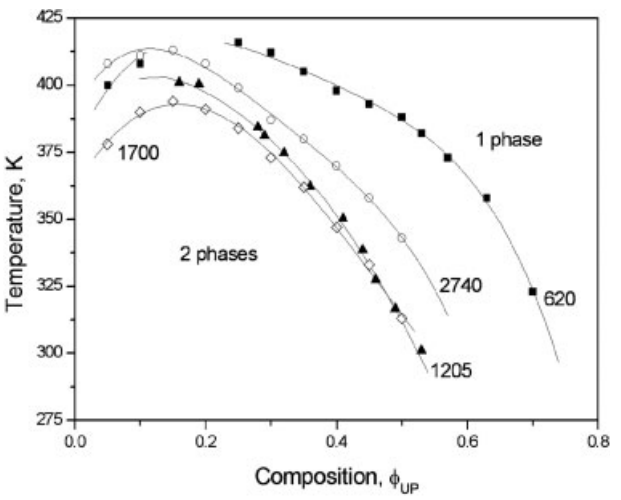

Figure 3 UP molecular weight effect on the experimental T versus ϕ_{UP} cloud point curves for the AA50 samples.

styrene molar volume ($V_r = 115$ cm^3/mol), which gives $r_0 = 1$.

The mass balance for all molecular species in the quasibinary mixture gives,

$$\sum_{j=1}^{N_1} \phi_j = \phi_1 \quad \text{and} \quad \phi_1 + \phi_0 = 1 \tag{5}$$

From the Gibbs free energy expression (1), the dimensionless chemical potential difference, per mol of lattice sites, of a generic j molecular species UP polydisperse prepolymer in quasibinary mixture and in pure amorphous state, $\Delta\mu_{j/RT}$, can be obtained according to its general thermodynamic definition.[18,19] The same procedure is followed to obtain the chemical potential difference for St component, $\Delta\mu_{0/RT}$.

Spinodal curve (SC) in a multicomponent system marks the homogeneous, one phase mixture stability limit in the T versus ϕ CPCs diagrams; crossing this limit, the homogeneous mixture must be separated into two phases.[18,19] SC position is given by the locus of T–ϕ points where the determinant of the matrix of all the mixing free energy second derivatives with respect to all independent composition variables is zero.[19]

The critical solution point (CSP) represents the point in the T versus ϕ phase diagram where both equilibrium phases have the same composition. This position is mathematically determined when the determinant of the matrix of the mixing Gibbs free energy third derivatives with respect to all independent composition variables is zero.[18,19]

The polydispersity effect on T versus ϕ positions of CPC, SC, and CSP are determined by UP polydisperse prepolymers r_{1n}, r_{1w}, and r_{1z} size parameters. Thus, CPC depends on the average number size r_{1n} value, SC on the weight average size r_{1w} value as well as CSP on both r_{1w} and χ and r_{1z} average values.

Under constant temperature and pressure, thermodynamic requirements for liquid–liquid phase equilibrium in a St-UP polydisperse mixture at cloud-point or coexistence conditions, are given by the equations:

$$\Delta\mu_j^\alpha = \Delta\mu_j^\beta \quad \text{from} \quad j = 1 \text{ to } N_1 \qquad \Delta\mu_0^\alpha = \Delta\mu_0^\beta \tag{6}$$

where α and β represent the mother and emergent phases in equilibrium, at the cloud point conditions, respectively.

The phase equilibrium condition (6) together with the expression for UP generic j molecular specie and styrene molecules chemical potential, lead to the following equations for L–L equilibrium calculation in S-UP quasibinary systems,

$$\ln\frac{\phi_0^\beta}{\phi_0^\alpha} - \left[\left(\phi_0 + \sum_{j=1}^{N_1}\frac{\phi_j}{r_j}\right)^\beta - \left(\phi_0 + \sum_{j=1}^{N_1}\frac{\phi_j}{r_j}\right)^\alpha\right] + \chi_{01}\left[\left(\phi_1^\beta\right)^2 - \left(\phi_1^\alpha\right)^2\right] = 0$$

$$\sigma_1 - \left[\left(\phi_0 + \sum_{j=1}^{N_1}\frac{\phi_j}{r_j}\right)^\beta - \left(\phi_0 + \sum_{j=1}^{N_1}\frac{\phi_j}{r_j}\right)^\alpha\right] + \chi_{01}\left[\left(\phi_0^\beta\right)^2 - \left(\phi_0^\alpha\right)^2\right] = 0 \tag{7}$$

where, σ_1 is the separation factor, and its value determines the fractionation extent of each UP molecular species between the two liquid equilibrium phases. Its definition is

$$\sigma_1 = \frac{1}{r_j}\ln\frac{(\phi_j)^\beta}{(\phi_j)^\alpha} \tag{8}$$

where $\phi_j^\alpha = W_j\phi_1^\alpha$ and $\phi_j^\beta = W_j\phi_1^\alpha e^{\sigma_1 r_j}$.

The mass fraction molecular weight distribution, W_j, corresponds to the mother α phase at cloud point condition, where only an emergent β phase infinitesimal amount is present.

The influence of each UP sample molecular weight distribution on the particular CPCs is very important and, in the following thermodynamic calculations, the selected distribution function W_j must represent UP molecules real distribution as accurately as possible. In this work, the information from SEC molecular weight distribution was used. Getting to it, a previous molecular weight scaling of all molecular species in the experimental SEC distribution was needed, since SEC apparatus was calibrated with polystyrene samples. It was expected that the standards polystyrene molecules size exclusion behavior in the packed polystyrene columns would be different to those UP molecules. Here it was assumed that a constant scaling factor would affect all molecular weights of SEC distributions in the same way. This scaling factor was calculated as the ratio between the number average molecular weight values obtained by the chain end group titration method, taken as the accurate values, and the given ones by SEC method with polystyrene standards.

In addition to the equations system (7), a mass balance for the emergent β phase must be included in this analysis. This balance is given by the equation:

$$\sum_{j=1}^{N_1} \phi_1^{\alpha} W_j \quad \exp(r_j \sigma_1) + \phi_0^{\beta} = 1 \qquad (9)$$

Numerical methods to calculate cloud point curves (CPCs), shadow curves (ShCs), spinodal curves (SCs), critical points (CPs), and coexistence curves (CCs), in mixtures with polydisperse components have been proposed and discussed in the literature.[18,19] The procedure developed by Kamide et al.[19] for quasibinary solutions was used in this study.

Equations (7)–(9) were applied to all St-UP quasibinary experimental CPCs, T versus ϕ_1, to obtain the interaction parameter and the emergent β phase composition at a given temperature. In each quasibinary system, the locus of the emergent β phase calculated compositions represents the ShC. SC can be calculated with the interaction parameter at each temperature previously known.[11] At the critical point, CPC and ShC are crossed and SC is tangent to CPC at this point.

UP chemical composition influence on St-UP miscibility

The AA comonomer composition effect on UP prepolymers solubility in styrene, shown by the relative CPCs positions in Figure 2, is well correlated by the χ-parameter values and its temperature dependence, calculated with the simplest version of F-H thermodynamic theory. Table II shows the calculated χ versus $1/T$ linear expressions for all St-UP quasibinaries.

TABLE II
Entropic and Enthalpic Parameters χ_S and χ_H for the St-UP Quasibinary Solutions

UP	M_n (g/mol)	χ_S	χ_H
AA100[a]	1,290	0.236	205.0
AA75[a]	1,250	0.212	215.3
AA50[a]	1,205	0.178	235.7
AA25[a]	1,245	0.094	279.5
AA0[a]	1,220	−0.111	394.8
F80[b]	1,260	0.572	56.56
F90-1[b]	1,245	0.506	87.69
F100[b]	1,250	0.307	163.1
$AA50_{(620)}$[c]	620	−0.099	454.5
$AA50_{(1205)}$[c]	1,205	0.178	235.7
$AA50_{(1700)}$[c]	1,700	0.032	272.3
$AA50_{(2740)}$[c]	2,740	−0.187	351.9

[a] Samples with different chemical compositions (present work results).
[b] Samples with different chemical compositions from the Lecoint et al.[11] results.
[c] Samples with different molecular weights (present work results).

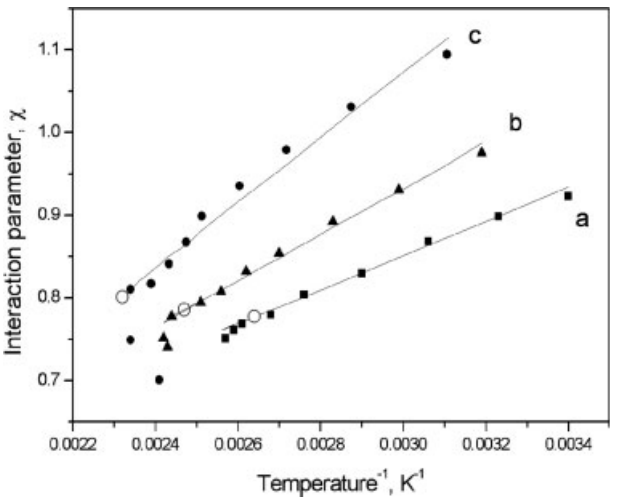

Figure 4 Interaction parameters temperature dependence for the systems: (a) St—AA100, (b) St-AA50 and (c) St-AA00.

As it can be seen, all equations show a characteristic UCST behavior since all enthalpic contributions to the χ-parameters have positive values, meaning that all St-UP quasibinaries miscibilities augments when the temperature increases. Figure 4 shows the calculated χ values for each one CPCs in three selected quasibinaries St-AA100, St-AA50 and St-AA00. The continuous lines represent the χ versus$1/T$ linear behavior that fit the χ calculated values to the χ-parameter equation.

Calculated CPCs, ShCs, and SCs for three selected quasibinary systems are shown in Figure 5. They were obtained from the inverse calculation using the χ-parameter equation. Comparing the experimental and calculated CPCs, it can be observed that this simple model describes the experimental results quite well. The fitting is really satisfactory in the phase diagram concentrated region; though for UP concentrations on the left part of the critical point, the model predicts cloud-points higher than the measured ones. This difference can be explained considering that this simple thermodynamic model is not taking into account the intermolecular association caused by UP high polar groups neither the χ-parameter composition dependence.

In this work, the calculated χ-parameter by the simple linear correlation for any of the St-UP quasibinaries was privileged taking into account its simplicity for a further thermodynamic analysis of the corresponding St-UP-Additive quasiternary polydisperse system in terms of this simple F-H theory.

Besides the similar UP average molecular weight ($M_n \sim 1200$ g/mol) and minor polydispersity differences, all quasibinaries from St-AA100 to St-AA00 could present some residual effect of HO— and HOOC— chain ends, due to these minor differences. Neverthe-

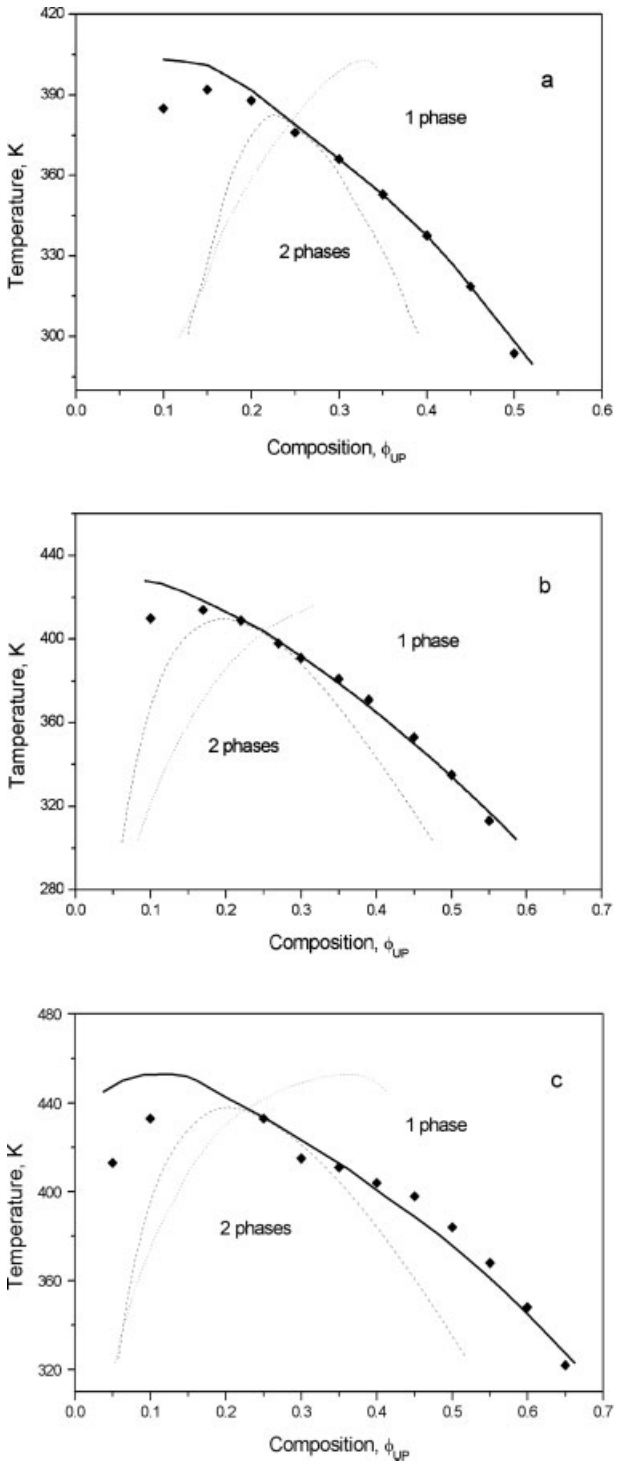

Figure 5 CPC phase diagrams for the systems: (a) St-AA100, (b) St-AA25, and (c) St-AA00: (◆◆◆) experimental CPCs; (——) calculated CPCs; (- - -) calculated spinodal lines; (····) calculated shadow lines.

less, the main reason for regular changes observed in St-UP miscibilities is the different chemical compositions of the UPs internal backbone chains. The only difference between chemical groups that constitute the repetitive unit in this series of UP prepolymers is the AA/PhA content. Then, it can be concluded that the comonomer AA aliphatic chain increases UP miscibility in a higher extension than the comonomer PhA aromatic ring does and, as a consequence, the χ-parameter decreases when UP AA/PhA concentration ratio increases. This observation agrees with the experimental solubility parameter value for the styrene (19 $MPa^{1/2}$) and those calculated with the Small group contribution method for the adipate (19.47 $MPa^{1/2}$) and phthalate (25.06 $MPa^{1/2}$) comonomer groups in UP backbone chain segments. When the AA content increases, the UP solubility parameter decreases conducting to a higher miscibility in St.

Residual entropic and enthalpic contributions to the calculated χ-parameters, obtained from the CPCs experimental results are presented in Figure 6 as χ_S versus χ_H contributions. It displays a linear correlation between the χ_S and χ_H values, showing that they cannot be changed independently, as was shown by different authors for polymer solutions and blends.[20–23] Represented data in Figure 6 for the series of St-UP solutions demonstrate that the more miscible system, St-AA100, has the higher χ_S value and the lower χ_H value, and *vice versa* for the lesser miscible system, St-AA00.

A similar composition effect was experimentally reported by Lecointe et al.[11] on similar molecular weights ($M_n \sim 1200$ g/mol) and distributions of their UP prepolymers, where the polyester backbone chemical structure was changed by using NPG and DEG in different proportions. From the reported CPCs, the interaction parameters were calculated applying the procedure just described. The only difference was the use of two parameters Schultz-Zimm (S-Z) molecular weight distribution function,[18] which took into account the molecular polydispersity effect. The studied samples in this paper are those termed F100, F(90-1),

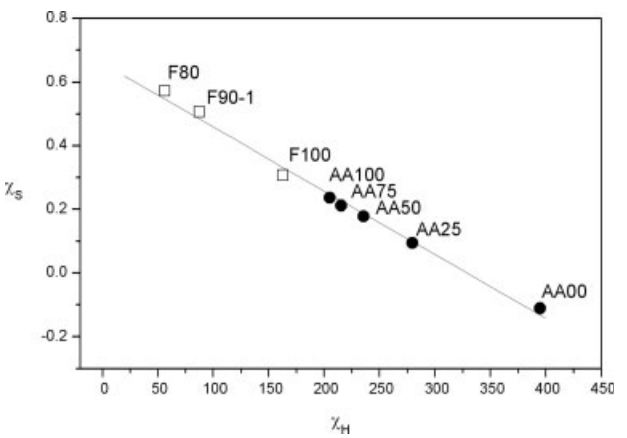

Figure 6 Linear correlation between the χ_S and χ_H contributions to the χ-parameter for the St-UP systems with UP of different composition: (● ● ●) present work results; (□ □ □) Lecointe et al. experimental results; (——) linear correlation.

and F80 in Lecointe et al. original article.[11] These ones content 100, 90, and 80% in DEG molar base, respect to the total glycol comonomers. Calculated χ_S and χ_H contributions to the χ-parameters are presented in Table II and are also represented in Figure 6.

Both UP prepolymers series, those with different NPG/DEG molar ratios (see results in Ref. 11) as well as those with different AA/PhA molar ratios (our results) gave χ_S versus χ_H that are positioned in the same linear correlation. Besides the different UP comonomer compositions and chemical structures in both series, the only common physical parameters of all UP samples in Figure 6 are their average molecular weights ($M_n \sim 1200$ g/mol) and polydispersity values (PI $\sim$ 2). These two common parameters fix the final UPs high polar groups concentration as well as the mixing entropy influence, leaving as the unique cause of this linear correlation those effects that derivate from the comonomers AA/PhA ratio in the UPs backbone chains for our UPs samples and the NPG/DEG ratio for the Lecointe et al.[11] samples. This interesting behavior offers the possibility, for any other member of these two UP series, to obtain χ_S contribution from an independent determination of χ_H, or *vice versa*.

Some solution concentration influence on the interaction parameter and possible intermolecular association caused by the polar UP groups could be present, leading to deviations from the eq. (2). These deviations can be observed in Figures 5 and 7 in the high temperature region, where χ_S and χ_H values could change in an appreciable way from the predicted one by χ-parameter linear correlation.

The χ versus$1/T$ linear correlation in the temperature interval, where χ-parameter equation fits the experimental CPCs, is represented in Figure 8 for all UP samples of similar molecular weight and variable backbone comonomer compositions.

High positive χ_S values mean negative residual entropic contribution to the mixing Gibbs free energy and, as a consequence, low total mixing entropy. This contribution leads to low St-UP miscibility for UP prepolymers of similar molecular weights and polydispersity index but with high AA chemical concentration in the chain. On the other hand, low positive χ_H values lead to a high miscibility and UCST behavior. Moreover, for UPs of similar molecular weights and polydispersity index, the net effect of the chemical composition on the miscibility in styrene will result from a ''proper balance'' of the residual entropic and enthalpic contributions to the mixing Gibbs free energy. This ''proper balance'' of residual contributions for this series of UP prepolymers is expressed through the correlation of χ_S and χ_H values, as is showed in Figure 6.

In Figure 8, the straight lines χ versus$1/T$ slope gives the χ_H values for the St-UP solutions with similar molecular weight. Hence, in UPs with high AA

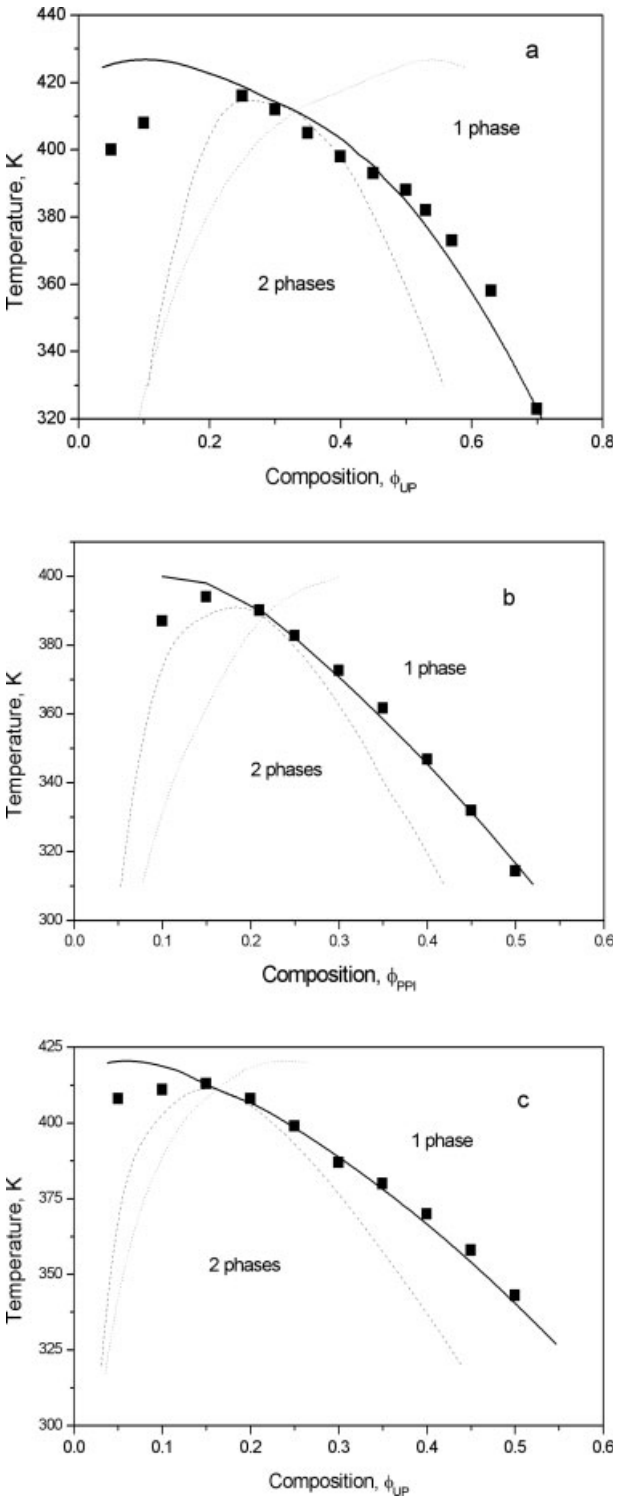

Figure 7 CPCs phase diagrams for the St-UP systems with UP of different molecular weight: (a) $AA50_{620}$, (b) $AA50_{1700}$, and (c) $AA50_{2740}$: (◆◆◆) experimental CPCs; (——) calculated CPCs; (- - -) calculated spinodal lines; (····) calculated shadow lines.

content, their higher miscibility in styrene is caused by the dominant low χ_H value contribution, against the unfavorable entropic contribution from χ_S positive values. Thus, in St-UPs quasibinaries, the miscibility

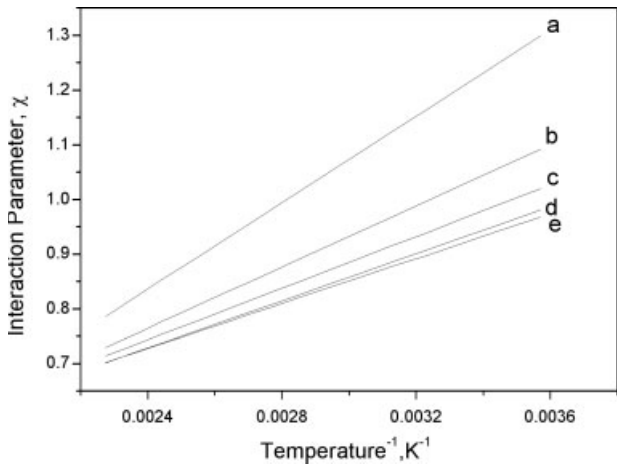

Figure 8 Interaction parameter temperature dependence for systems with UP of different chemical composition and fix molecular weight: (a) AA00; (b) AA25; (c) AA50, (d) AA75, (e) AA100.

increases as the χ_H diminishes, and that is observed when the phthalate backbone group in the UP prepolymers are substituted by the adipate group.

UP molecular weight influence on St-UP miscibility

In regard to St-UP quasibinaries with a fixed AA50 chemical comonomer composition, the UP miscibility depends on the type and number of UP chemical group interactions with the St solvent: if they are favorable, the miscibility increases, and *vice versa* if they are unfavorable. In the present case, the St solvent is non polar and UPs have very high polar carboxylic and/or alcoholic chain end groups, as well as polar adipate and phthalate ester groups in the backbone chain. As consequence, the interactions between St and UPs polar groups are unfavorable in nature and the miscibility should be lower for mixtures with high concentration of any two type of UP polar groups. In fact, both AA100 and AA00 UPs are partially miscible in St monomer. On the other hand, St-UP solution mixing entropy depends on UP molecular weight and, as is well known, high mixing entropy favor polymer solution miscibility. High mixing entropy is characteristic of low molecular weight UP solutions.

The general behavior to be expected when UP sample molecular weight increases at a fixed chemical comonomer composition will result from the relative influence of three UP chemical structure contributions: (1) the lowering concentration of high polar HO— and HOOC— final groups that increase miscibility; (2) the higher concentration of polar ester groups in the backbone chain that diminishe miscibility and; (3) the higher UP average molecular sizes that decrease miscibility. These three simultaneous UP chemical structural contribution effects on the miscibility is the reason of the experimental CPCs relative positions showed in Figure 3. These UP miscibility samples are in the following order: $AA50_{(1700)} > AA50_{(1205)} > AA50_{(2740)} > AA50_{(620)}$. In this order, $AA50_{(1700)}$, $AA50_{(1205)}$, and $AA50_{(620)}$ samples relative positions are justified by the effect of unfavorable interactions between St with HO— and HOOC— end groups increasing number, which diminishes miscibility, against the favorable effects of the increasing mixing entropy and the decreasing number of unfavorable UP polar ester adipate and phthalate backbone groups. The first effect and the other two, change in an opposite way when UP molecular weight increases.

Thus, $AA50_{(620)}$ sample has the lowest miscibility in St because the high polar final group's concentration contribution is the dominant effect. Otherwise, in the highest molecular weight UP sample, $AA50_{(2740)}$, the effect originated by the end polar groups are diluted by the large molecular size and its miscibility decreases due to the unfavorable other two dominant effects, the higher concentration of polar backbone ester groups and the lower mixing entropy.

The $AA50_{(1700)}$ sample show the highest St miscibility as result of a ''proper balance'' between the contributions of mixing entropy, polar backbones adipate and phthalate ester groups interactions, as well as the diluted contribution of final chain high polar groups interactions. Lecointe et al.[11] have published experimental results on the UP molecular weight influence on St miscibility, founding a qualitative behavior according to our results.

CONCLUSIONS

Similar molecular weights UP prepolymers showed miscibilities in St monomer that depend on UP chain segments chemical structure. This miscibility behavior was determined by the enthalpic dominant contribution to the total interaction parameter. Entropic and enthalpic contributions to χ-parameter were linearly correlated for the first St-UP mixtures series with UPs similar molecular weight and different chemical composition, showing that cannot be changed independently. High AA comonomer concentrations in the internal UP backbones led to lower endothermic mixing enthalpy in St solvent, causing high St-UP miscibility.

UP molecular weight influence on miscibility was originated by three contributions: the first caused by the final chain high polar HO— and HOOC— groups concentration, the second was due to the backbone chain polar ester groups concentration and the third by the mixing entropy dependence with chain size. The three contributions depended on UP molecular weight and when the molecular weight increased the first one diminished by the dilution effect, and the

other two increased. The balance of these three contributions for a particular UP molecular weight determined its miscibility in St monomer.

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