**Summary:** A model system, consisting of a linear polymer dissolved in a bifunctional monomer/co-monomer solvent, was selected to test the applicability of the Flory-Huggins (FH) theory in the absence of the usual assumptions present in the analysis of modified thermosetting polymers. Solutions of two almost monodisperse polystyrenes (PS, $\overline{M}_n = 83\,000$ or $217\,000$), in diglycidyl ether of bisphenol A (DGEBA) and in stoichiometric DGEBA/BA (benzylamine) solutions, exhibited an upper critical solution temperature (UCST) behavior. Cloud-point curves (CPC) were fitted with the FH model using an interaction parameter depending on both temperature and concentration, $\chi = (a + b/T)/(1 - c\phi_2)$, where ϕ_2 represents the volume fraction of PS. A group-contribution method provided a reasonable explanation of the observed trends. Cloud-point times in the course of the DGEBA/BA stepwise polymerization, carried out at 70 °C and 80 °C, were determined for solutions containing 2.5 to 15 wt.-% PS ($\overline{M}_n = 83\,000$). Times were transformed to conversions using kinetic curves determined by Fourier Transform Infrared Spectroscopy (FT-IR) and Size Exclusion Chromatography (SEC). The analysis of cloud-point conversions with the FH model was performed considering the (ideal) distribution of epoxy/amine species generated as a function of conversion. An empirical fitting of cloud-point curves was possible with

the use of an interaction parameter decreasing with conversion. Possibilities of improving the thermodynamic description of a polymerization-induced phase separation are discussed.
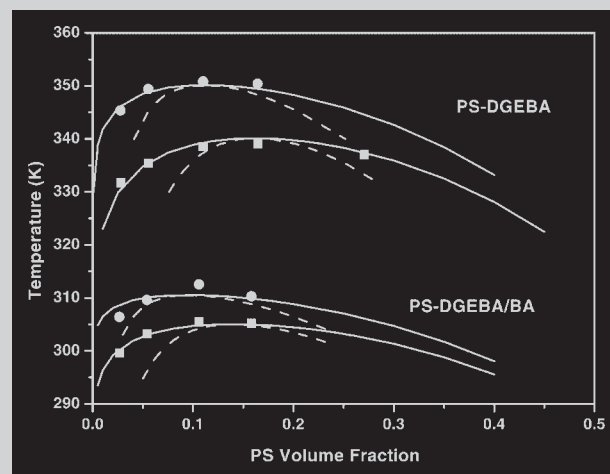
Cloud-point curves for PS-DGEBA binary solutions.

A Model System for the Thermodynamic Analysis of Reaction-Induced Phase Separation: Solutions of Polystyrene in Bifunctional Epoxy/Amine Monomers

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Introduction

The thermodynamic analysis of the polymerization-induced phase separation in a modified thermoset is usually performed using the Flory-Huggins (FH) model.[1−3] A qualitative explanation of observed trends may be performed by characterizing the thermoset as a pseudo-component with an average size that increases with conversion, following a particular statistical model.[4−10] However, quantitative fittings of cloud-point temperatures and cloud-point conversions could only be obtained when molar mass

distributions of both the thermoset and the modifier were taken into account in the model.[11−20] The fitting required the consideration of the continuous variation of the chemical composition, through the use of an interaction parameter varying with conversion.[9,13,15,17,18,20,21]

The mathematical modeling of the reaction-induced phase separation in modified thermosetting polymers encounters a major difficulty when conversion approaches gelation. At this point, a significant increase in the number of species representing the molar mass distribution of the thermoset is required.[17,18] In the post-gel stage, the

contribution of the elastic free energy has to be incorporated into the model, a fact that leads to additional difficulties, such as the need to calculate the evolution of the concentration of elastic chains and the arbitrary selection of a model accounting for their contribution to the free energy.[17,18]

A good test of the applicability of the FH equation to modeling a polymerization-induced phase separation occurs when gelation can be excluded by selecting a monomer and a co-monomer undergoing a linear polymerization. The system composed of stoichiometric amounts of the diglycidyl ether of bisphenol A (DGEBA) and benzylamine (BA) is particularly useful because the stepwise polymerization follows an ideal path.[22] We have recently analyzed the polymerization-induced phase separation in solutions of a carboxyl-terminated poly(butadiene-co-acrylonitrile) rubber (CTBN), dissolved in a stoichiometric DGEBA/BA solution.[23] Initial solutions were homogeneous but phase separation occurred over the course of polymerization. The FH model provided a reasonable fitting of experimental cloud-point conversions using an interaction parameter depending exclusively on temperature.[23]

The aim of the present study is to extend the analysis to a system where the initial cloud-point curve (CPC) can be determined. An almost monodisperse polystyrene (PS) was selected as a modifier, because the location of the CPC in a temperature vs. composition diagram can be shifted by varying its molar mass. The way in which the function describing the interaction parameter changes with the initial solvent (DGEBA compared to DGEBA/BA) and with increasing conversion in the epoxy/amine reaction will be described and compared to trends predicted using group-contribution methods.[21,24,25] Limitations of the FH model to describe the reaction-induced phase separation will be analyzed and possible ways of improving the thermodynamic description will be discussed.

Theoretical Analysis

Size Distribution of the Epoxy/amine Linear Polymer

The molar mass distribution of the DGEBA/BA linear polymer may be calculated from the Stockmayer equation applied to a stoichiometric $A_2 + B_2$ polymerization, up to a conversion p of functional groups.[26] The number of moles of a generic species, $E_{m,n}$, containing m BA units and n DGEBA units, is given by:

$$E_{m,n} = 2(BA)_0(1-p)^2 p^{m+n-1} \quad (m = n) \tag{1}$$

$$E_{m,n} = (BA)_0(1-p)^2 p^{m+n-1} \quad (m = n+1 \text{ or } n = m+1) \tag{2}$$

where $(BA)_0 = (DGEBA)_0$, is the initial number of moles of BA. The volume fraction of $E_{m,n}$ in the reaction mixture, is

obtained from:

$$\phi_{m,n} = E_{m,n}(m V_{BA} + n V_{DGEBA})\phi_1/[BA]_0 V_{BA} + (DGEBA)_0 V_{DGEBA}] \tag{3}$$

where $\phi_1 = 1 - \phi_2$ is the volume fraction of the epoxy/amine component in the blend and $V_{BA} = 109.2 \text{ cm}^3 \cdot \text{mol}^{-1}$, $V_{DGEBA} = 297.9 \text{ cm}^3 \cdot \text{mol}^{-1}$, which are the molar volumes of both monomers.

A pseudo-component with a generic degree of polymerization, $y = m + n$, may be defined. The number of moles (E_y), molar volume (V_y), and volume fraction (ϕ_y), are given by:

$$E_y = 2(BA)_0(1-p)^2 p^{y-1} \tag{4}$$

$$V_y = (y/2)(V_{BA} + V_{DGEBA}) \tag{5}$$

$$\phi_y = y(1-p)^2 p^{y-1}\phi_1 \tag{6}$$

Thermodynamic Model

For solutions of an almost monodisperse PS in DGEBA or in DGEBA/BA, before polymerization, the Flory-Huggins equation may be written as:

$$(V_r/RT)\Delta G = (\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2 + g(T,\phi_2)\phi_1\phi_2 \tag{7}$$

where ΔG is the free energy per unit volume, R is the gas constant, T is temperature, V_r is the reference volume taken as the one of the constitutional repeating units of PS ($V_r = 99.05 \text{ cm}^3 \cdot \text{mol}^{-1}$), ϕ is the volume fraction (1: solvent, 2: PS) and r represents the ratio of the molar volume of a particular component with respect to the reference volume. $r_1 = 3.01$ for DGEBA and 2.06 for DGEBA/BA. $r_2 = 798.1$ for the (almost) monodisperse PS of molar mass equal to 83 000 and 2 086.0 for a molar mass of 217 000.

The following functionality of the interaction parameter, defined by Prausnitz and co-workers,[27] was used to fit experimental results:

$$g(T,\phi_2) = (a + b/T)[1/c(1-\phi_2)]\ln[(1-c\phi_2)/(1-c)] \tag{8}$$

where a, b and c are adjustable parameters. This interaction parameter is related to the chi-parameter defined in the expression of chemical potentials, by:[27,28]

$$\chi(T,\phi_2) = g(T,\phi_2) - \phi_1 g'(T,\phi_2) = (a + b/T)/(1-c\phi_2) \tag{9}$$

where the prime denotes the first derivative with respect to the volume fraction of component 2.

The analysis of phase separation in the course of polymerization required solving the FH equation for a particular conversion, p. In this case, the first term of the

right-hand side of Equation (7) was replaced by $(1/r_1)\Sigma(\phi_y/y)\ln\phi_1$. The distribution was truncated for a y_{max} such that the difference of mass-average molar masses of the truncated distribution and the exact distribution was negligible. A value of $y_{max} = 30$ was appropriate to cover the experimental values of cloud-point conversions.

Cloud-point and spinodal curves were obtained using standard procedures, including the introduction of two separation factors.[12,27,29,30] The numerical solution was obtained using Mathcad 8 and a Levemberg-Marquardt program to obtain the best set of adjustable parameters.

Experimental Part

Materials

The diepoxide monomer was based on the diglycidyl ether of bisphenol A (DGEBA, Der 332, Dow). It was characterized by a mass per mole of epoxy groups equal to $174.3 \text{ g} \cdot \text{mol}^{-1}$, with a molar ratio of secondary hydroxyls with respect to epoxy groups equal to 0.015 and a mass density of $1.17 \text{ g} \cdot \text{cm}^{-3}$. Benzylamine (BA, Riedel-De Haën, mass density $= 0.981 \text{ g} \cdot \text{cm}^{-3}$), was used in a stoichiometric ratio with respect to DGEBA.

Two different (almost) monodisperse polystyrenes (PS, Polymer Source), were used. Values of molar masses and polydispersity indices were: $\bar{M}_n = 83\,000 \text{ g} \cdot \text{mol}^{-1}$ (IP $= 1.045$) and $217\,000 \text{ g} \cdot \text{mol}^{-1}$ (IP $= 1.05$). The mass density was $1.05 \text{ g} \cdot \text{cm}^{-3}$.

Homogeneous solutions were obtained by dissolving the desired amount of PS in DGEBA at about $85-90\,°C$. Solutions were cooled to room temperature and the stoichiometric amount of BA was added. Homogeneous solutions resulted when temperature was increased above the cloud-point curve. In particular, at the selected polymerization temperatures of 70 and $80\,°C$, initial solutions were homogeneous but phase-separated in the course of polymerization.

Techniques

Transmission optical microscopy (TOM) was employed to determine cloud-point temperatures and cloud-point times during polymerization at constant temperature. A Leica DMLB microscope equipped with a video camera (Leica DC 100) and a hot stage (Linkam THMS 600), was used for these purposes. Samples were placed between two glasses using a 0.5 mm stainless-steel spacer. The cloud point was neat, even for PS contents as low as 2.5 wt.-%.

The polymerization kinetics of the neat DGEBA/BA system and of PS-modified DGEBA/BA solutions were measured using size exclusion chromatography (SEC) and near-infrared spectroscopy (NIR).

The kinetics obtained from SEC were based on the determination of the DGEBA concentration as a function of polymerization time at constant temperature. Glass tubes containing known masses of the reacting mixture, in the range of $8-25$ mg, were placed in a thermostat held at either 70 or $80\,°C$. Tubes were removed at pre-specified times, their

contents dissolved in 5 mL tetrahydrofuran (THF) and 25 μL of the resulting solution injected into the size exclusion chromatograph (SEC, Waters 510 with HR 0.5, 1 and 3 ultrastyragel columns, a UV detector at 254 nm and a THF flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$). The height of the peak corresponding to the DGEBA monomer was measured and expressed per unit mass of the initial mixture. Assuming that both epoxy groups have equal reactivity and that there are no substitution effects, the fraction of unreacted DGEBA at a particular epoxy conversion, p, is given by the simultaneous probability that both epoxy groups remain unreacted:[31]

$$c/c_0 = h/h_0 = (1 - p)^2 \qquad (10)$$

where h/h_0 is the ratio of the actual height of the peak with respect to the initial one (both expressed per unit mass of sample). The conversion was calculated as:

$$p = 1 - (h/h_0)^{1/2} \qquad (11)$$

Near-infrared spectroscopy (NIR) was the second technique used to determine the polymerization kinetics at 70 and $80\,°C$. An FT-IR (Genesis II, Mattson) equipped with a heated transmission cell (HT-32, Spectra Tech) with quartz windows (32 mm diameter, 0.5 mm lead spacer) and a programmable temperature controller (Omega, Spectra Tech, $\Delta T = \pm 1\,°C$) was employed. Conversions of epoxy and primary amine groups were respectively followed by measuring the height of absorption bands at $4\,530 \text{ cm}^{-1}$ and $4\,940 \text{ cm}^{-1}$, with respect to the height of a reference band at $4\,620 \text{ cm}^{-1}$.[32,33] A small band was found in the NIR spectrum of BA at $4\,530 \text{ cm}^{-1}$. As no residual band was present at this wavelength in the fully polymerized DGEBA/BA system, this band was ascribed to primary amine groups.[32] Therefore, the band at $4\,530 \text{ cm}^{-1}$ included both epoxy and primary amine groups. The contribution of the primary amine to the intensity of this band was estimated from the ratios of absorptions of primary amine bands at $4\,940 \text{ cm}^{-1}$ and at $4\,530 \text{ cm}^{-1}$ in pure BA. Then, using the experimental value of the absorption of the primary amine at $4\,940 \text{ cm}^{-1}$ in a partially polymerized DGEBA/BA system, the expected intensity of the contribution of the primary amine at $4\,530 \text{ cm}^{-1}$ was estimated and subtracted for the observed intensity at this wavelength. This correction was found to be practically insignificant in the resulting value of epoxy conversion.

Results and Discussion

PS-DGEBA Solutions

Cloud-point curves for both PS-DGEBA binary solutions are shown in Figure 1, indicating an upper critical solution temperature (UCST) behavior. Both sets of experimental results were fitted with the following functionality of the chi-parameter:

$$\chi = (0.087 + 29.03/T)/(1 - 0.62\phi_2) \qquad (12)$$

where T is expressed in K.

In order to analyze the applicability of Equation (12) to polystyrenes covering a different range of molar masses,

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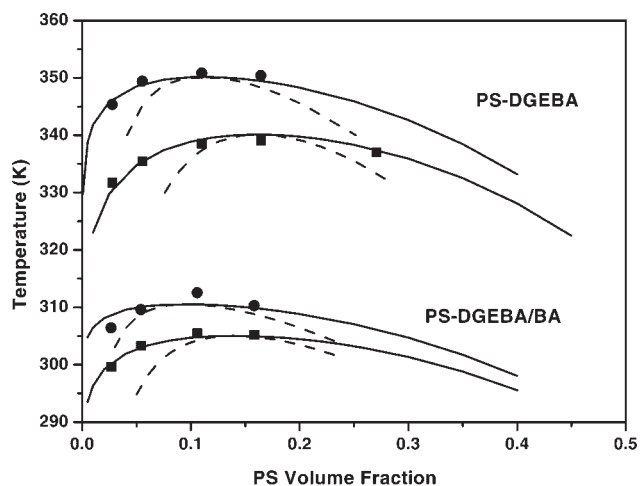**Chemistry and Physics** 679

Figure 1. Comparison of CPCs obtained for PS-DGEBA and PS-DGEBA/BA solutions at $p = 0$. Solid lines indicate the CPCs fitted with the thermodynamic model (dashed lines are the corresponding spinodals). The upper curve of both sets corresponds to the PS with $\bar{M}_n = 217\,000$ and the lower curve to the PS with $\bar{M}_n = 83\,000$.

CPCs of PS-DGEBA solutions reported in the literature were employed,[34] together with another CPC obtained in our laboratory for a PS with $\bar{M}_n = 28\,400$. The fitting shown in Figure 2 shows that the interaction parameter does not depend on the molar mass of PS.

It is interesting to compare the enthalpic contribution of the interaction parameter, $b = 29.03$ K, obtained from the experimental fitting of cloud-point curves, with the value arising from a combination of empirical equations with group-contribution calculations. According to Van Kreve-
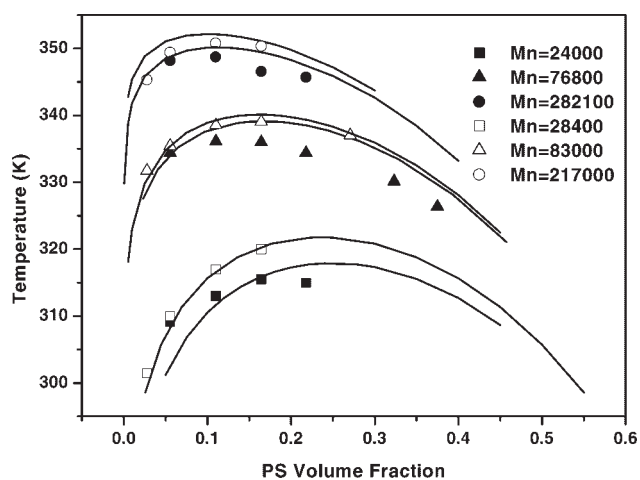

Figure 2. Fitting of experimental cloud-point curves of (almost) monodisperse PSs dissolved in DGEBA (open symbols: CPCs determined in our laboratory; filled symbols: CPCs reported in the literature[34]).

len,[25] polystyrene is soluble in solvents for which

$$\Delta^2 (J \cdot cm^{-3}) = (\delta_v - 18)^2 + (\delta_h - 5)^2 \qquad (13)$$

is the smallest possible value ($\Delta^2 < 25$ is a suggested boundary); $\delta_v = (\delta_d^2 + \delta_p^2)^{1/2}$, where δ_d, δ_p and δ_h are the contribution of dispersion forces, polar forces and hydrogen bonding to the solubility parameter, respectively.

The enthalpic contribution to the interaction parameter may be defined by:

$$b = \Delta^2 V_r / R \qquad (14)$$

The different contributions to the solubility parameter of DGEBA may be obtained using the method of Hoftyzer and Van Krevelen.[25] The following values were obtained: $\delta_d = 18.34$ $(J \cdot cm^{-3})^{1/2}$, $\delta_p = 1.40$ $(J \cdot cm^{-3})^{1/2}$ and $\delta_h = 6.43$ $(J \cdot cm^{-3})^{1/2}$, leading to $b = 26.1$ K, which is surprisingly close to the experimental value. The matching of both values would not have been possible if the calculated contributions to the solubility parameter of PS had been used instead of the empirical Equation (13).

PS-DGEBA/BA Solutions at $p = 0$

CPCs resulting from the addition of a stoichiometric amount of BA are also shown in Figure 1. Both curves are shifted to lower temperatures indicating that the systems became more miscible with the addition of BA. Resulting CPCs could be fitted using the following function of the chi-parameter for both PSs:

$$\chi = (0.087 + 49.85/T)/(1 - 0.62\phi_2) \qquad (15)$$

The addition of BA produced an increase in the b parameter from 29.03 K to 49.85 K, leading to a corresponding increase in the interaction parameter. From the point of view of the enthalpic contribution to the free energy, the presence of BA should have led to a decrease in miscibility. However, miscibility increased as revealed by the shift of the CPCs to lower temperatures. This is the result of the decrease in the average size of the solvent molecules, from $r_1 = 3.01$ for DGEBA to $r_1 = 2.06$ for DGEBA/BA.

The significance of the entropic contribution to the miscibility of a polymer in a particular solvent is clearly evidenced in this example. The increase in the average size of the solvent over the course of the reaction is the main cause of the polymerization-induced phase separation.[4]

The different contributions of the DGEBA/BA pseudo-component to the solubility parameter may be also obtained using the method of Hoftyzer and Van Krevelen.[25] The following values were obtained: $\delta_d = 18.28$ $(J \cdot cm^{-3})^{1/2}$, $\delta_p = 2.06$ $(J \cdot cm^{-3})^{1/2}$ and $\delta_h = 7.14$ $(J \cdot cm^{-3})^{1/2}$, leading to $b = 56.6$ K, which is again close to the experimental value. The group-contribution method explains the higher value of the interaction parameter found when DGEBA/BA is used instead of DGEBA, as a result of the higher value of the hydrogen bonding contribution.
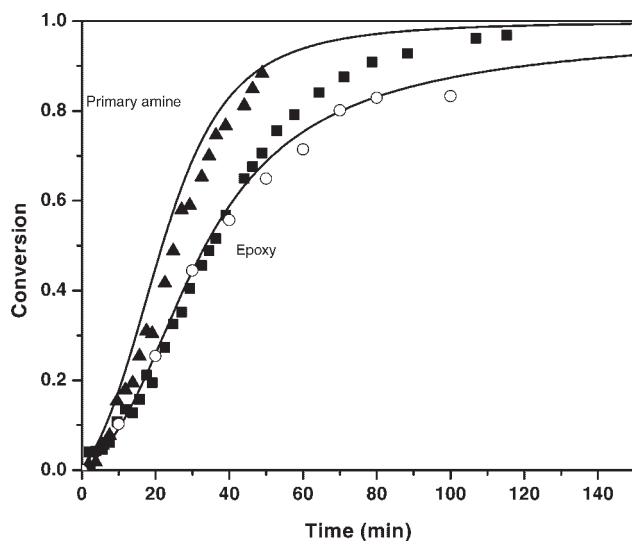
Figure 3. Conversion of primary amines (upper curve) and epoxy groups (lower curve), as a function of time, at 70 °C. Full symbols represent values determined by NIR and open symbols are SEC determinations. The curves represent the fitting with the proposed kinetic model.
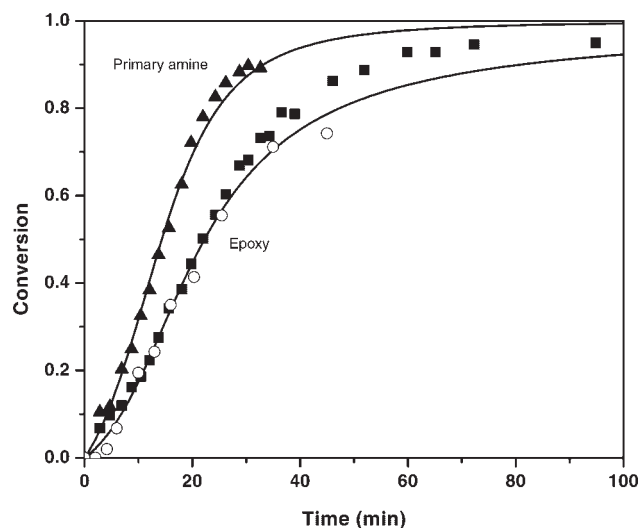

Figure 4. Conversion of primary amines (upper curve) and epoxy groups (lower curve), as a function of time, at 80 °C. Full symbols represent values determined by NIR and open symbols are SEC determinations. The curves represent the fitting with the proposed kinetic model.

PS-DGEBA/BA Solutions in the Course of Polymerization

The polymerization kinetics will be analyzed first. Figure 3 and 4 show conversion vs. time curves of primary amine and epoxy groups, at 70 and 80 °C, respectively. Epoxy conversions determined by SEC and NIR were practically the same within the experimental error of both techniques (due to the dependence of the square root of the signal; the use of SEC in the range of conversions beyond 0.8 incorporates a high experimental error).

The simplest mechanistic kinetic model that can be used to fit the experimental curves assumes: a) two reaction paths: a second-order path catalyzed by impurities present in the sample and a third-order path catalyzed by hydroxyls initially present and generated in the course of reaction and b) equal reactivity of primary and secondary amine hydrogens. The corresponding rate equation may be written as:[3]

$$\mathrm{d}p/\mathrm{d}t = [K' + K([OH]_0/e_0 + p)](1 - p)^2 \quad (16)$$

$$P_{A1} = 1 - (1 - p)^2 \quad (17)$$

where p and p_{A1} are, respectively, the conversion of epoxy and primary amine groups and $[OH]_0/e_0 = 0.015$ for the DGEBA used in the present study. Constants K' and K in time^{-1} units are defined by:

$$K' = k'e_0; K = ke_0^2 \quad (18)$$

where k' and k represent specific rate constants and e_0 is the initial concentration of epoxy groups.

A reasonable fitting of both epoxy and primary amine conversions, up to conversions in the range of 0.7–0.8, was

obtained using the following functions for the rate constants:

$$K'(\mathrm{min}^{-1}) = 2.578 \times 10^5 \exp[-6\ 156/T(K)] \quad (19)$$

$$K(\mathrm{min}^{-1}) = 7.168 \times 10^4 \exp[-4\ 592/T(K)] \quad (20)$$

The kinetic model must be adapted for the case of DGEBA/BA solutions containing an initial amount of PS. The most simple assumption is to invoke the presence of a dilution effect, at least up to the cloud-point conversion (which was observed at values lower than 0.20 for the range of temperatures and initial concentrations explored). In this case, the pre-exponential factors in K' and K vary with the initial epoxy concentration as indicated by Equation (18). Experimental conversions were determined by NIR for PS ($\overline{M}_n = 83\ 000$)-DGEBA/BA solutions containing 5 and 15 wt.-% PS, polymerized at 80 °C. A good agreement was found between experimental and predicted conversions, considering only the presence of a dilution effect.

Phase separation in the course of polymerization was analyzed for solutions containing 2.5–15 wt.-% PS (83 000), dissolved in DGEBA/BA. Cloud-point times recorded by TOM at 70 and 80 °C were expressed as cloud-point conversions using the kinetic model incorporating the dilution effect. Values of cloud-point conversions were located in the range 0.13–0.19, indicating that a very small increase in the average size of the solvent gave rise to phase separation.

The fitting of experimental cloud-point conversions with the FH model is shown in Figure 5. The best fit was obtained

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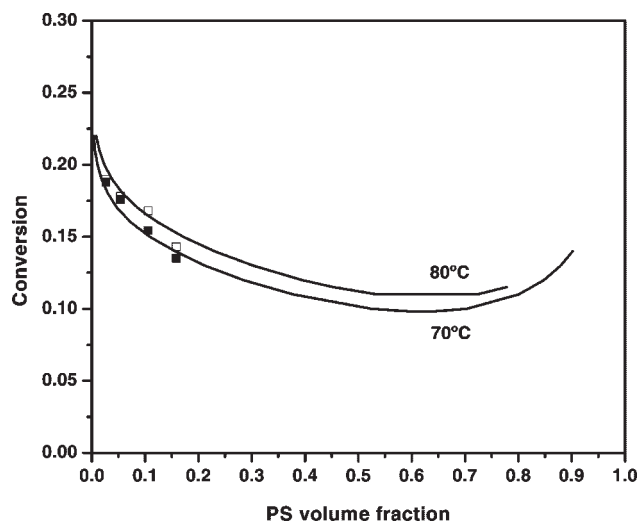**Macromolecular Chemistry and Physics** 681

Figure 5. Fitting of experimental cloud-point conversions determined at 70 °C (open symbols) and 80 °C (full symbols), for a PS (83 000)-DGEBA/BA system, using the FH equation with an interaction parameter depending on composition, temperature and conversion.
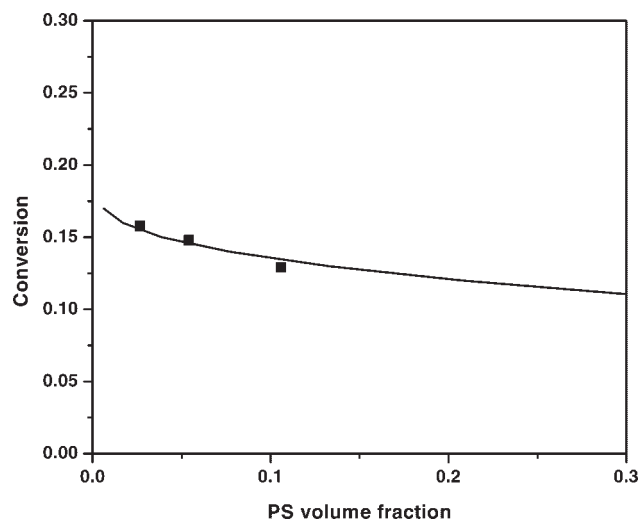

Figure 6. Fitting of experimental cloud-point conversions determined at 70 °C, for a PS (217 000)-DGEBA/BA system, using the FH model with the interaction parameter obtained for a PS of different molar mass.

with the following functionality of the chi-parameter:

$$\chi = (0.087 + [24.80 + 25.05 \exp(-7.273p)]/T)/(1 - 0.70\phi_2) \quad (21)$$

Compared to the expression obtained for the initial solution ($p = 0$), it was necessary to introduce a decreasing functionality of b with conversion and to change slightly the value of c. The $b(p)$ functionality is such that it fits the initial value at $p = 0$ and decreases sharply at low conversions, tending to an almost constant value at intermediate and high conversions (although the reliability of the proposed equation is limited to a maximum conversion close to $p = 0.2$, which is the range covered by the experimental information).

The question may be asked regarding the possibility of using the function obtained for the interaction parameter during polymerization to predict cloud-point conversions for a PS of different molar mass. Figure 6 shows the excellent agreement of experimental values with predicted cloud-point conversions for a PS (217 000)-DGEBA/BA solution, using the FH model with the interaction parameter given by Equation (21). Therefore, at least in the explored range of PS molar masses, the predictive capability of the FH model has been confirmed.

Although a decrease of the interaction parameter with conversion has been found for several modifier-thermoset blends,[15,17,18] this was not the result expected for the PS-DGEBA/BA system. The group-contribution method may be applied to the average species formed at different conversions. For example, for $p = 0.15$, 15% of epoxy groups were transformed into secondary hydroxyls, 25.5% of

primary amines were transformed into secondary amines and 2.25% into tertiary amines, according to the statistics of an ideal polymerization. The following contributions to the solubility parameters were determined: $\delta_d = 18.13$ $(\text{J} \cdot \text{cm}^{-3})^{1/2}$, $\delta_p = 1.97$ $(\text{J} \cdot \text{cm}^{-3})^{1/2}$ and $\delta_h = 7.76$ $(\text{J} \cdot \text{cm}^{-3})^{1/2}$, leading to $b = 91.4$ K. The value required for the fitting of cloud-point conversions is $b = 33.2$ K, which is lower than the initial value ($b = 49.85$ K). Therefore, the association of the FH model with the solubility parameter approach cannot be used even to provide a qualitative description of the observed trends (the opposite effect was predicted).

On the Use of Advanced Thermodynamic Models

A significant failure of the classic Flory-Huggins model is its inability to describe phase behavior of compressible solutions. Several equation-of-state models that take into account compressibility effects have been developed and applied to polymer solutions and blends.[35] However, it has been proven that the FH potential arises independently of any lattice description, with the assumption of simple volume additivity on mixing.[35] In this derivation, volume fractions and interaction parameters should be considered as temperature and pressure dependent. This means that the same formal FH equation may be used to take into account compressibility effects. Therefore, the question is how to develop a more rigorous description of the polymerization-induced phase separation process by taking into account compressibility effects (using any of the equation-of-state models proposed in the literature or the FH model with variables depending on both temperature and pressure).

For a particular conversion in the polymerization reaction, the mixture is composed of a linear polymer (PS in the present case) and a distribution of reactive polymer y-mers (epoxy/amine species for the selected system). The main problem for the application of equation-of-state models is the need to obtain the characteristic parameters experimentally (P^*, T^*, V^*), for every one of the y-mers present in the distribution. Only for the case of distributions placed in the region of large molar masses may a single set of characteristic parameters be used for every y-mer, making the thermodynamic analysis in terms of equation-of-state models possible.[36–40] Characteristic parameters of oligomers are a function of their size, making it necessary to obtain experimental correlations in terms of molar mass.[41] For the present system, it would be necessary to obtain characteristic parameters for the diepoxide (monomer), the amine (co-monomer), both trimers (1 epoxy + 2 amines, 1 amine + 2 epoxies), both pentamers, etc., to generate a correlation between characteristic parameters, chemical structure and molar mass. Every one of these particular y-mers has to be synthesized and purified. The series of y-mers with $y =$ an even number cannot be used because they will polymerize because of the presence of two different reactive groups at both ends. For the usual case of polymerizations leading to a polymer network, this experimental study cannot be performed due to the reactivity of most of the multifunctional oligomeric species (they contain functional groups that react among themselves). Any approach requiring the fitting of arbitrary parameters cannot compete with the simplicity of the FH model, which only requires describing the interaction parameter as a function of conversion to fit experimental cloud-point curves. This explains why the FH model has survived for twenty years in the analysis of polymerization-induced phase separation processes.

However, there are some improvements in the thermodynamic analysis that may worth consideration in future works. The idea is based on the fact that for different polymerization chemistries it has been necessary to use a decreasing function of the interaction parameter with conversion to fit experimental cloud-point curves. This was also the case in the present study. Estimations using group contribution methods to account for variations in the chemical structure predict either an increase of the interaction parameter with conversion (as in the present case), or its decrease with conversion. The classic FH model leads to the use of an interaction parameter lower than the one predicted from the value fitted to the initial solution. A possible explanation of this trend may be related to an increase in the contribution of configurational entropy, arising from an increase in the fraction of vacancies with conversion. On the one hand, the contribution of terminal groups to the specific volume should be differentiated from the contribution of the rest of the structure of the y-mer species. This can account for the increase in specific density with conversion. On the

other hand, mixing of the particular oligomer produced at a given conversion level with the linear polymer (PS) generates a fraction of free volume that increases with conversion. An extended FH model can be used to take into account the contribution of vacancies to the configurational entropy, a possibility that will be explored in the future.

Conclusions

The study of the reaction-induced phase separation in a model system consisting of an almost monodisperse PS dissolved in bifunctional epoxy/amine monomers undergoing an ideal linear stepwise polymerization, permitted the analysis of the applicability of the Flory-Huggins model in the absence of the usual assumptions present in the case of modified thermosetting polymers. The model revealed its versatility to fit CPCs for the initial solutions, through the use of an interaction parameter depending on temperature and composition but independent of the molar mass. The enthalpic contribution to the interaction parameter could be roughly estimated through the use of a group-contribution method and an empiric equation that had been proposed to determine the solubility of PS in different solvents. Cloud-point conversions in the course of polymerization could be fitted using an interaction parameter depending on temperature, composition and conversion, but independent of the molar mass of PS. However, it was not possible to predict the decrease of the interaction parameter with conversion using the group-contribution approach. This indicates an intrinsic limitation of the classic FH model to predict cloud-point conversions using the interaction parameter fitted for the initial solution. The thermodynamic analysis should be improved by including compressibility effects. Although the theory is available (equation-of-state models), there is a major limitation related to the experimental determination of characteristic parameters for reactive oligomers. An extension of the FH model including the contribution of vacancies to the configurational entropy is suggested as a possible way to improve the thermodynamic description.

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