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# Thermodynamic evolution of unsaturated polyester-styrene-hyperbranched polymers

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## Summary

The free energy of mixing during cure has been modeled for different blends of linear unsaturated polyester, styrene and allyl ether functional hyperbranched polymers. The molecular weight of the blend components has been implemented as measured by gel permeation chromatography (GPC) into the Flory-Huggins equation. This approach enables the distinction to be made between the contributions of enthalpy and entropy of mixing, the latter being automatically followed during curing by the development of average molecular weights. The model allows gaining an idea of the factors acting as driving forces for chemically induced phase separation in these blends.

## Introduction

The use of hyperbranched polymers (HBPs) as efficient tougheners in resins based on linear unsaturated polyesters (UP), and/or vinylesters and styrene has been previously reported. In UP, an increase in fracture toughness, expressed by $K_{IC}$, of 30 to 60 % can be obtained by adding only 5 % of a suitable HBP, depending on the final morphology induced, phase separating blends being more efficient for toughening [1,2]. The general experimental picture on phase separation is that systems which are initially fully homogeneous remain homogeneous up to the end of polymerization, whereas if the system is already heterogeneous at the onset of polymerization, its heterogeneity increases with conversion, indicating that compatibility of the blend decreases with the degree of polymerization.

When using HBPs as tougheners, the possibility of altering the solubility of the modifiers is greatly increased, and the conditions for which a chemically induced phase separation becomes possible can therefore be met. However, although extensive theoretical modeling has been done for chemically induced phase separation in epoxy-amine systems modified by rubber, thermoplastic or HBPs [3-6], work in this field is still lacking for systems based on UP resins. In particular the most difficult values to evaluate theoretically are the changes in molecular weights during curing of the resin and modifier respectively, which in the present case are assumed to be UP/styrene and HBP/styrene respectively. The measurement of molecular weight of HBPs is not trivial. Although osmotic pressure can provide the number average

molecular weight, being an equilibrium technique, long times are required for the measurements. If measurement times are reduced, significant errors may be introduced. On the other hand, a correct measurement of HBP molecular weight by GPC would need universal calibration, as shown elsewhere [7,8]. However, it could be argued, if a universal calibration, which involves intrinsic viscosity measurements, would lead to a correct estimation of molecular weight in the case of components with a large quantity of styrene. Thus, this work a standard calibration is used, and the GPC measurements have allowed direct computation of the entropy of mixing in the Flory-Huggins equation. Thus, the modeling of the changing state of the free energy of mixing has been possible during the complex process of polymerization in blends of UP, styrene and HBPs. Although the model is not quantitatively successful, it represents the first attempt to highlight and quantify the entropical driving force to chemically induced phase separation in free radical polymerizing systems. Moreover, the approach is based on an original GPC procedure at different stages of polymerization, which can also be applied to different issues involving the measurement of molecular weights during free-radical polymerization.

## Experimental

### *Materials*

The resin system was constituted, by weight, of 66 % linear unsaturated polyester (Norpol E-2787, Reichhold AS Norway, unsaturated groups content: 3.894 mmole/g), and by 34 % styrene (Fluka, unsaturated group content: 9.601 mmole/g). As an initiator, 2% by weight of MEK-peroxide (Norpol peroxide n° 11, Reichhold AS Norway) was used, and 0.3 % by weight of cobalt solution (Norpol accelerator 9802P, Reichhold AS Norway) was added to the blend in order to accelerate polymerization. P-tert butyl cathechol (Norpol inhibitor 9853, Reichhold AS Norway) was used as an inhibitor to stop the reaction at specific times. The HBP, Boltorn U1™, produced and commercialized by Perstorp AB, was added to the blend, in the amount of 10 per hundred resin (phr). The content of unsaturated groups in the HBP shell was 3.0195 mmole/g. (see Fig. 1). The residual functionality of hydroxyl groups in the HBP shell was as low as 5%, so that, unlike other studies, no effect on the GPC measurements is expected [7].

### *Procedures*

Curing of the compounds in the blended and separate state was performed at 23°C. Samples were allowed to polymerize by the addition of an accelerator and peroxide, and the reaction was then stopped after 0, 5, 10, 17, 27 and 40 minutes respectively by the addition of 1 % by weight of the inhibitor. Immediately after inhibition, the samples were dissolved in tetrahydrofuran (THF) and analyzed by GPC (Marathon, Perkin Elmer Turbochrome). In order to establish the correspondence between molecular weight and GPC column retention time, the GPC column was calibrated with monodisperse polystyrene whose molecular weights ranged between 104 (styrene) and 68000 g/mole. Detection was performed by using a Varian refractive index detector (RI).

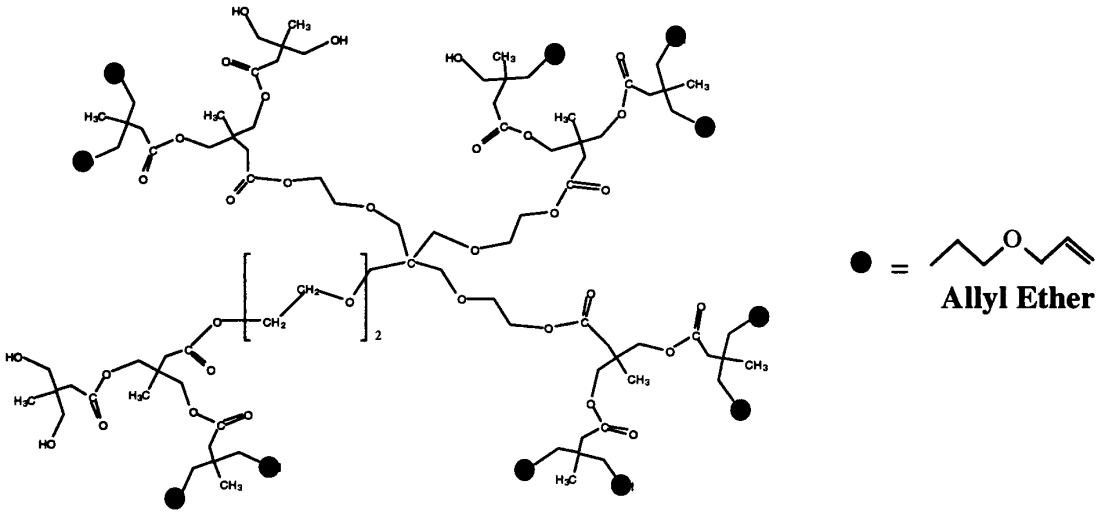


**Fig. 1** Schematic representation of an allyl ether functionalized hyperbranched polyester.

## Results and discussions

According to Flory-Huggins theory [9], the thermodynamic equilibrium of a bi-component system at constant pressure is described by the free energy of mixing which has the following expression [10]:

$$\Delta G_v = RT\left(\frac{\Phi_1}{V_1}\ln\Phi_1 + \frac{\Phi_2}{V_2}\ln\Phi_2 + \Phi_1\Phi_2\chi_{12}\right) \qquad (1)$$

where T is the temperature expressed in Kelvin degrees, R is the perfect gas constant, $\Phi_1$ and $\Phi_2$ are the volume fractions of components 1 and 2 (polymer and modifier), and $V_1$ and $V_2$ are the molar volumes of the two components. The term $\chi_{12}$, which is the direct expression of the enthalpy of mixing, is the ratio between the Flory-Huggins interaction parameter, and $(V_1)_0$ the molar volume of the lattice site. Its value is normally attributed to the molar volume of the solvent molecule, if present. Using a solubility parameter approach, $\chi_{12}$ can be expressed by the following equation [11]:

$$\chi_{12} = \chi_S/(V_1)_0 + [(\delta_{1h}-\delta_{2h})^2 + (\delta_{1p}-\delta_{2p})^2 + (\delta_{1d}-\delta_{2d})^2] / RT \qquad (2)$$

in which the subscripts designate the hydrogen (h), polar (p) and dispersive (d) components of the solubility parameters of components 1 and 2. The term $\chi_s$ has a particular importance for blends in which the polar or hydrogen interactions between molecular segments is so strong to alter the random configurations of coils in the blend. In the present case, since the interactions are mainly of Van der Waals nature, the term $\chi_S$ can be ignored.

In order to express quantitatively the free energy of mixing as a function of time, we assume in this work that the blend UP-styrene-HBP can be divided into two pseudo-components. Following the lines of thought used elsewhere for epoxy systems [12], the first pseudo-component will be formed by UP-styrene in the unsaturation ratio of 1:1 and the HBP and all the remaining styrene in excess will form the second pseudo-

component. The viability of this assumption is supported by the fact that the reaction rate of UP maleate groups with styrene is significantly higher than the rate of homopolymerization of both UP and styrene [13], and also of the copolymerization rate of UP with the allyl ethers grafted into the shell of the HBP [14]. Therefore the network will be built up primarily by the copolymerization of UP-styrene, which thus identifies a component, and secondarily by other reactions (homopolymerization of HBP, homopolymerization of styrene in excess, copolymerization of HBP with styrene, and copolymerization of HBP with UP).
In this way, the solubility parameters of the two pseudo-components can be calculated by using Van Krevelen group contribution theory [15]. Table 1 shows the three components of solubility parameters for each of the two pseudo-components.

**Table 1** Solubility parameter components of the two pseudo-components.

| $(J/cm^3)^{1/2}$ | $*_d$ | $*_p$ | $*_h$ |
|---|---|---|---|
| UP/Styrene | 14.3 | 2.6 | 7.3 |
| HBP/Styrene | 14.9 | 1.6 | 6.3 |

A further assumption in the modeling process relies on the fact that enthalpy is considered to be constant during the whole process, while a small decrease in the dispersive component of the solubility parameters of the pseudo-components occurs during polymerization due to the consumption of unsaturated groups (the groups =CH- turns into -CH- ) [14].

At this point the problem reduces to that of evaluating the volumes $V_1$ and $V_2$ to enter into Equation 1. Since no density changes occur up to gelation (40 min.), the two molar volumes may be calculated starting from the weight average molecular weights $M_w$ and the density $\Delta$:

$$V_i = M_{Wi} / \Delta_i \tag{3}$$

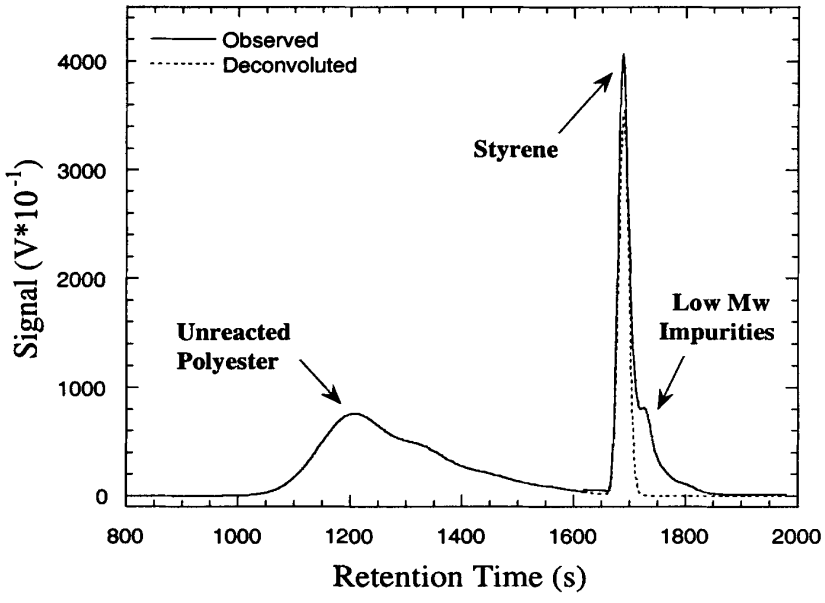


**Fig. 2** GPC signal for the UP/styrene pseudo-component at polymerization onset.

Fig. 2 shows at polymerization onset, the GPC signal for the UP-styrene pseudo-component in a 1:1 ratio of unsaturated bonds.
The peaks of unreacted linear polyester and styrene are easily identifiable, as well as low molecular weight impurities. The presence of impurities in the signal has been treated by deconvoluting the original signal in a new signal formed by the sum of two peaks, that of UP and that of styrene. The ratio of their area was in the proportion 66/34. This was to be expected since the GPC signal is proportional to the weight probability distribution of molecular weights *P*, which is the probability of finding molecules having a mass between *M* and *M+dM* (the signal is directly proportional to the mass of the sample and not to the number of molecules). When polymerization starts, a peak at high molecular weights (low GPC retention times) starts to appear and the area under it increases as curing time passes. This is due to the copolymerization of UP and styrene with a subsequent build up of high molecular weight clusters. Fig. 3 shows the changes in the GPC signal over a period of time. A similar trend has been previously observed by Tanaka [16].

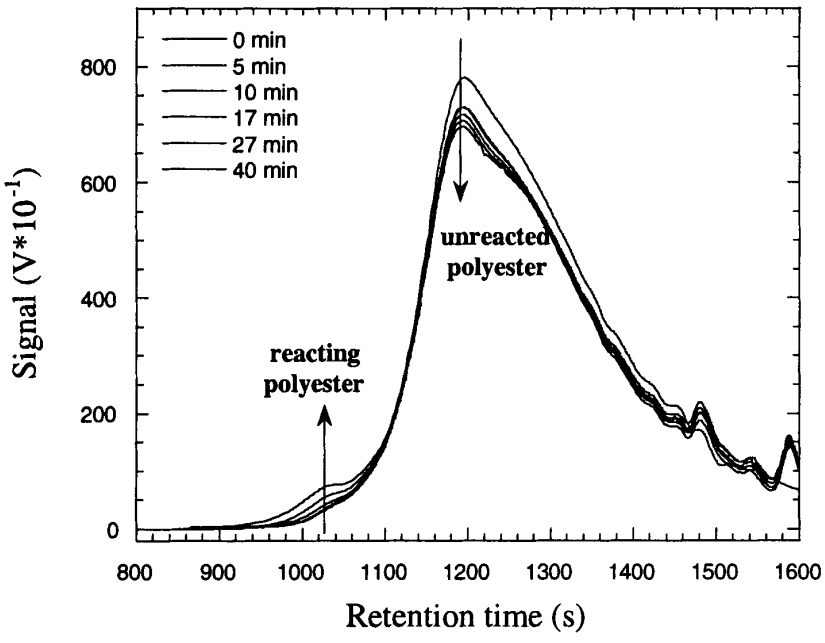


**Fig. 3** Changes during a period of time for the GPC signal for the UP/styrene pseudo-component.

Therefore, since the weight probability distribution P is available at different times, the weight average molecular weight $M_w$ of any of the two pseudo-components at a time *t* can be expressed as:

$$M_W(t) = \left| \int_{104}^{\infty} P * M(t_{retention}) dM \right|_{\text{at time } t} \qquad \textbf{(4)}$$

where the integration starts at 104, i.e. the styrene monomer molecular weight. Equation 4 has been applied to both pseudo-components at the times of 5, 10, 17, 27 and 40 minutes. As can be seen in Fig. 4 the molecular weight of UP-styrene increases rapidly while that of the HBP is quite constant, due to its low reactivity with styrene. It should be also mentioned that the same procedure has been performed on the full blend, with the two pseudo-components mixed together; the GPC signal perfectly

superposes with the sum of the signals of the two pseudo-components run separately. The results of molecular weight measurement can be now implemented into the Flory-Huggins equation. Fig. 5 shows the changes of free energy of mixing as expressed by equation 1, with the $V_1$ and $V_2$ calculated by equations 3 and 4.

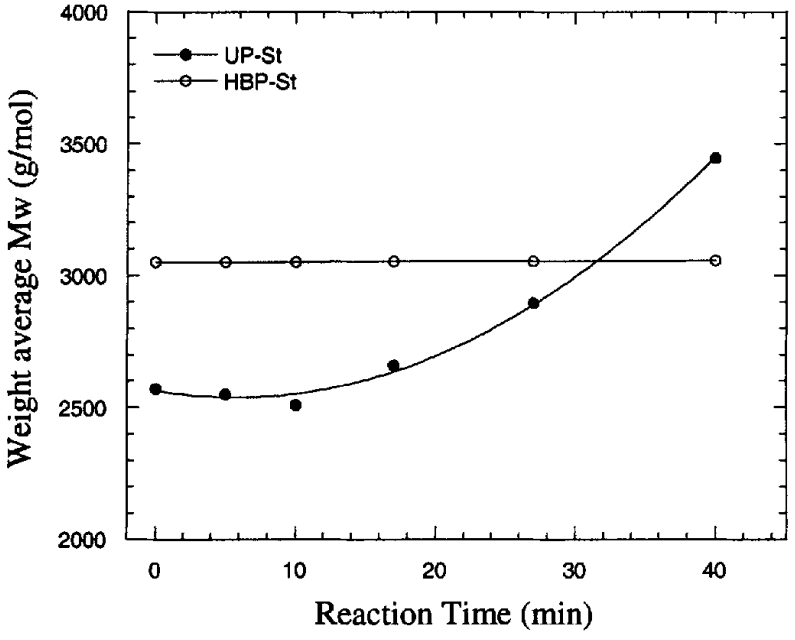


**Fig. 4** Weight average molecular weights increase over a period of time for UP/styrene and HBP/styrene pseudo-components.

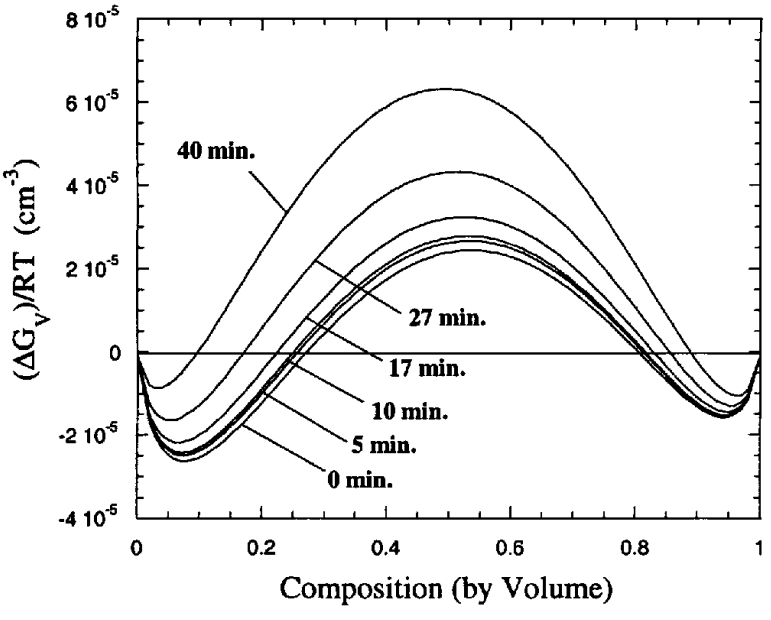


**Fig. 5** Free energy of mixing at different times of polymerization versus blend composition.

Composition is expressed by volume and ranges between 0 (100% HBP-styrene) and 1 (100% UP-styrene). As can be seen, the free energy of mixing becomes more and more positive as the time proceeds, and the inflection points, as well as the two points of equal chemical potential (the two points having a common tangent [17]), shift towards the pure composition of the two pseudo-components. The region in between these two equal chemical potential points corresponds to the conditions of composition for which phase separation is possible.

The evolution of free energy is a consequence of the compatibility decrease of the blend due to the reduction in the entropy of mixing. It should be noted that the composition of 10 phr by weight of Boltorn U1 ™ in a 66/34 UP-styrene mixture, lies in the heterogeneous region at all stages of polymerization, while only a fully homogeneous blend is observed experimentally. The poor agreement with experimental evidence may depend on the GPC calibration procedure, or be a consequence of the assumptions made for the selection of the two highly dispersed pseudo-components, for which a more complex theoretical treatment is needed [18]. However, although the model is not in full agreement with experiments it well highlights the entropic driving force to phase separation in the thermodynamic evolution of blends of UP, styrene and allyl ether functional HBPs.

## Conclusions

In blends of UP, styrene and HBP, the free energy of mixing has been modeled during polymerization by combining Flory-Huggins theory and GPC molecular weight measurements.

The system was divided into two reactive pseudo-components: the UP/styrene, and the HBP/styrene. The enthalpy of mixing, which is a constant during the polymerization process, was evaluated with group contribution theory, while the entropy of mixing, evolving during polymerization, was calculated through weight average molecular weight, as measured by GPC. Although the model failed from a quantitative point of view, it enabled the expression of free energy of mixing up to the gel point of the blend and the decrease in compatibility caused by the reduction of possible configurations of the polymer chains in the blend.

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