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Analysis of a styrene–divinylester copolymerization: reaction heats, double bond conversions and average sequence lengths

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Abstract

A simple model, based on the free radical copolymerization theory of Mayo and Lewis, is developed to predict reaction heats, calorimetric and molar conversions and average sequence lengths, during the crosslinking reaction between a monounsaturated monomer (M_1) and a multiunsaturated comonomer (M_2). The M_2-double bonds are assumed to react independently with equal initial reactivities. The input variables of the model are the initial reactivity ratios (r_{10}, r_{20}) and their variation with the global molar conversion, the initial composition of the reactive mixture (f_{10}) and the molar heat of formation of the different bonds formed during the copolymerization (ΔH_{11}, ΔH_{22}, ΔH_{12}). The application of this model allows to calculate the overall molar and calorimetric double bond conversions (P_m and P_c), the heat developed during the reaction (ΔH_T), the conversions corresponding to each type of unsaturations (P_{c1}, P_{c2}, P_{m1}, P_{m2}), and the average sequence lengths of the reacted bonds ($\langle N_{11}\rangle$ and $\langle N_{22}\rangle$). Published data of experimental comonomers conversions in the system styrene–divinylester (S–DVER) were satisfactorily reproduced by including a functionality of both reactivity ratios with the overall conversion. Finally, it was shown that the assumption implicitly made in most published kinetic studies from the differential scanning calorimetric (DSC) data, that P_c and P_m are equivalent, is not general and this feature must be investigated in order to perform correct kinetic calculations. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Crosslinking copolymerization; Reactivity ratios; Divinylester resins

1. Introduction

Free radical copolymerization is a usual crosslinking reaction in the synthesis of polymer networks, where a monofunctional monomer (M_1) reacts with a multifunctional comonomer (M_2). The most important commercial systems of this kind, used in the production of composite materials, are the unsaturated polyester resins (UPR) and the divinylester resins (DVER), each one crosslinked with styrene (S) [1,2]. In general, the multifunctional unsaturated resins can be prepared with different chemical compositions and molecular weights, which leads to a large flexibility in the design of the network formulations. Despite their increasingly widespread usage, the relationship between their final properties and the processing conditions are not well understood because of the complexity of the chemistry, kinetics, morphology generated during the reaction and chemorheology.

The curing kinetics is a very important aspect to take into account for modeling thermoset processes. For such a reason, a fairly large number of kinetic studies have been reported using both, mechanistic or phenomenological models [3,4]. A frequently used approach in these kinetic studies is to consider the curing reaction as a simple free radical homopolymerization, that is no differences are made between the reactivities of the double bonds of the styrene and those of the comonomer. Although such a simplifying scheme can be useful to describe empirically the kinetic behavior of the system, it cannot provide a detailed information regarding the reaction mechanism or the different evolution of the conversions of each of the two comonomers during the reaction.

Differential scanning calorimetry (DSC) is a popular method to study the polymerization kinetics of thermosetting resins [5–13] because it does not require a thorough understanding of the curing chemistry. The basic assumption of this method is that the heat evolved during curing is proportional to the extent of the reaction, which means that at a given time, the accumulative heat of copolymerization depends only on the number of bonds formed up to that time. This is equivalent to say that the different bonds

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formed during the copolymerization have the same heat of formation, which is a correct assumption in the special case of a perfectly alternate copolymerization, but it is not valid in general. The curing reaction of a thermoset system, such as styrene (1)/divinylester (2), can be described by the same steps of initiation, propagation and termination as a linear free radical copolymerization. During the propagation step three types of possible bonds, 1–1, 2–2 and 1–2, are formed in different proportions. The instantaneous and the accumulated heat of reaction at a given time depend on the amount of each type of bond created and of its molar heat of formation. Consequently, the calorimetric conversion, calculated as usually from the evolved heat measured with a DSC apparatus, may be different from the molar conversion, which turns the usual kinetic analysis from calorimetric data impossible.

To describe the radical copolymerization of a monounsaturated monomer (S) with a multiunsaturated crosslinker comonomer (DVER), the concept of copolymerization parameters [14–16] must be used, because two different types of molecules having double bond of different reactivities must be considered, along with the fact that the crosslinker molecule has more than one double bond. In the simplest case of DVER, the two double bonds reactivities are virtually identical. However, when one of them has reacted, the reactivity of the remaining one can be markedly diminished due to the reduced mobility of the chain which is bonded to a single molecule, to a microgel particle or to the macrogel network. The effect of a rapid build-up of a 3D network structure, with increasing number of reactive pendant double bonds and radicals, leads to a diffusional control on fundamental reaction steps, in such a way that rate constants become time (conversion) dependant [16]. Diffusion control on the reaction rates can be taken into account by using an overall propagation rate constant that decreases in an empirical way with conversion [6,17,18]. By extension, the reactivity ratios defined in the Lewis–Mayo copolymerization theory, as the quotient of two propagation rates should be conversion dependent too.

The analytical information needed to apply the copolymerization model to this type of systems is usually missing in the published literature. Data reported by Ganem et al. [19] on a S–DVER system show that the reactivity ratios, r_1 and r_2, defined by the simple theory of copolymerization, are not constant throughout the curing reaction. They found that the reactivity of the styrene double bonds increases, while the reactivity of the DVER unsaturations decreases. Similar results had been previously reported for a S–UPR system, showing that the reactivity of styrene also increased with increasing conversion and the reactivity of the multifunctional comonomer decreased [15]. This variation of the reactivity ratios during curing is responsible for the characteristic evolution of the molar conversions of the comonomers S and UPR, whose more interesting feature is to show an up-bending behavior in a P_{m1} vs. P_{m2} plot. This behavior has been described with detail in the literature by different authors [20–26] and in particular by Lee et al. who explained the feature using a model of microgel formation and thus, contributed to the development of this concept.

In this work, a theoretical analysis of the free radical copolymerization of S and DVER unsaturated monomers based on the Lewis–Mayo theory is presented, with the additional complexity of considering the variation of the comonomer reactivities with the conversion. This improved model allows calculate:

1. The total heat of the copolymerization reaction as a function of the initial concentration of comonomers and the molar heats of formation of the different types of bonds created in the reaction.
2. The global calorimetric conversion. The comparison with the global molar conversion will indicate if it is possible to realize a kinetic study based on calorimetric data.
3. The calorimetric and molar conversions of each of the comonomers.
4. The average sequence length of the bonds of each comonomer in the copolymer.

2. Copolymerization model

The common and widespread use of DSC thermograms to calculate conversion vs. time is based on the assumption that the heat evolved during the cure reaction is proportional to the extent of the reaction. This basic assumption is fulfilled if all double bonds and free radicals in the system are identical and there are no diffusional constraints or concentration gradients due to phase separation, thus a global conversion (P_c or P_m) can be calculated.

During the formation of M_1–M_2 copolymer three different kinds of bonds are created during the propagation step: 1–1, 1–2 and 2–2. The instantaneous molar fraction of each one of these bonds in the copolymer are a function of the instantaneous molar fraction of the M_1 and M_2; unsaturations in the feed, f_1 and f_2; and the reactivity ratios, r_1 and r_2. The molar heat of formation of the 1–1 and 2–2 bonds are the molar heats of the homopolymerization ΔH_{11} and ΔH_{22}, respectively, and the molar heat of formation of the 1–2 bond is the hypothetical molar heat of the perfectly alternating copolymerization.

This analysis is supported on three basic assumptions: (1) the Lewis–Mayo copolymerization theory is applicable with the reactivity ratios expressed as functions of the conversion; (2) the unsaturations of the multifunctional monomer M_2 react independently; and (3) there are no concentration gradients due to the phase separation. This analysis cannot predict gelation because the structure being formed by the increasing number of connections is not modeled.

The copolymerization of the M_1 and M_2 monomers was simulated with a total initial number of moles of double bonds, n_{0T}, and molar fractions varying from $f_{10} = 0$ to 1. In each step, Δn moles of M_1 and M_2 unsaturations are reacted and the copolymer formed has an instantaneous molar fraction F_1 of M_1 unsaturated groups.

In a particular step k, the probability that a M_1 radical has reacted with a M_1 unsaturated group, that is of forming a diad M_1M_1 in the copolymer, is:

$$P_{11,k} = \frac{r_1 f_{1,k}}{r_1 f_{1,k} + f_{2,k}} \tag{1}$$

The product $P_{11,k}\, F_{1,k}$ gives the molar fraction of 1–1 bonds incorporated to the copolymer in this step:

$$X_{11,k} = P_{11,k} F_{1,k} = \frac{r_1 f_{1,k}^2}{r_1 f_{1,k}^2 + 2 f_{1,k} f_{2,k} + r_2 f_{2,k}^2} \tag{2}$$

Similarly, the molar fraction of (2–2) bonds is:

$$X_{22,k} = P_{22,k} F_{2,k} = \frac{r_2 f_{2,k}^2}{r_1 f_{1,k}^2 + 2 f_{1,k} f_{2,k} + r_2 f_{2,k}^2} \tag{3}$$

The molar fraction of (1–2) + (2–1) bonds is given by the difference:

$$X_{12,k} = 1 - X_{11,k} - X_{22,k} = \frac{2 f_{1,k} f_{2,k}}{r_1 f_{1,k}^2 + 2 f_{1,k} f_{2,k} + r_2 f_{2,k}^2} \tag{4}$$

The total heat liberated in this particular k step is calculated by adding up the contributions of the different bonds formed in the step:

$$\Delta H_k = \Delta n (X_{11,k} \Delta H_{11} + X_{22,k} \Delta H_{22} + X_{12,k} \Delta H_{12}) \tag{5}$$

The calorimetric conversion calculated up to a particular step, k, is given by the expression:

$$P_{c,k} = \frac{\sum_{i=1}^{k} \Delta H_i}{\Delta H_T} \tag{6}$$

where ΔH_T is the total heat evolved up to complete conversion. Since the number of moles reacted up to the k step is known, thus the molar conversion can also be calculated as:

$$P_{m,k} = \frac{k \Delta n}{n_{0T}} \tag{7}$$

A molar mass balance of the M_1 unsaturations between the steps $(k-1)$ and k, is used in the simulation to obtain the value of the molar fraction of M_1 in the feed at the k step $(f_{1,k})$, as follows:

$$(n_{0T} - k\,\Delta n) f_{1,k} + F_{1,k}\,\Delta n = [n_{0T} - (k-1)\,\Delta n] f_{1,(k-1)} \tag{8}$$

The increment of the conversion of each monomer unsaturations in this step can be calculated from the moles of double bonds of M_1 or M_2 incorporated to the copolymer in the following way:

$$\Delta P_{m1,k} = \frac{F_{1,k}\,\Delta n}{n_{0T} f_{10}} \quad \Delta P_{m2,k} = \frac{(1 - F_{1,k}) \Delta n}{n_{0T}(1 - f_{10})} \tag{9}$$

then conversions are calculated as:

$$P_{m1,k} = \sum_{i=1}^{k} \Delta P_{m1,i} \quad P_{m2,k} = \sum_{i=1}^{k} \Delta P_{m2,i} \tag{10}$$

This monomer unsaturations conversions, $P_{m1,k}$ and $P_{m2,k}$, and the global conversion, $P_{m,k}$, are related by the equation:

$$P_{m,k} = P_{m1,k} f_{10} + P_{m2,k}(1 - f_{10}) \tag{11}$$

The calorimetric conversions of both monomers during the copolymerization can also be simulated. To perform this calculation, it is assumed that half of the alternating copolymerization heat, ΔH_{12}, is due to the reaction of each monomer. Taking into account this assumption, the total heat of reaction of the M_1 unsaturation is:

$$\Delta H_{1T} = \Delta H_{11} \sum_{i=1}^{n_{0T}} \Delta n X_{11,i} + 0.5\,\Delta H_{12} \sum_{i=1}^{n_{0T}} \Delta n X_{12,i} \tag{12}$$

and an analogous equation is valid for reaction heat of the M_2 double bonds.

Then, the calorimetric conversions of both monomer unsaturations in this particular k step are given by the equation

$$P_{c1,k} = \frac{\Delta H_{11} \sum_{i=1}^{k} \Delta n X_{11,i} + 0.5\,\Delta H_{12} \sum_{i=1}^{k} \Delta n X_{12,i}}{\Delta H_{1T}} \tag{13}$$

and an analogous expression gives the value for $P_{c2,k}$

The relation between the monomer calorimetric conversions, $P_{c1,k}$ and $P_{c2,k}$ and the global calorimetric conversion, $P_{c,k}$, is given by the equation:

$$P_{c,k} = P_{c1,k} \frac{\Delta H_{1T}}{\Delta H_T} + P_{c2,k} \frac{\Delta H_{2T}}{\Delta H_T} \tag{14}$$

where $\Delta H_{1T}/\Delta H_T$ and $\Delta H_{2T}/\Delta H_T$ are the fractions of total heat of copolymerization contributed by each monomer unsaturations, their values depend on the initial monomer concentrations, reactivity ratios and heats of bond formation.

The reactivity ratios, r_1 and r_2 are defined in the Lewis–Mayo theory as the quotient of the two propagation rate constants k_{11}/k_{12} and k_{22}/k_{12}, respectively. These rate constants are average values of the propagation reactions that take place at a given conversion. The reactions between radicals and unsaturations, determining each elemental propagation step, are affected by a wide distribution of diffusional and topological restrictions (DTR). This variety of restrictions are originated in the fact that the reactive species (radicals and unsaturations) belong to molecules with a wide distribution of sizes and chemical structures if they form part of the soluble fraction of the copolymer and, if they participate of the gel fraction, these reactive species belong to active or pendant chains inside the macrogel network with different local environments. As a consequence, the rate constants depend on the intrinsic chemical reactivities of the radicals and unsaturations, their number, accessibility, as well as the mobility of the molecules and structures to which they are bonded.

In the simplest case, the two double bonds of the M_2 monomer have a constant reactivity throughout the reaction. In the real more complex case, when one of the double bonds has reacted, the reactivity of the remaining unsaturation can be markedly impaired due to the fact that its mobility and availability is restricted differently if it is attached to a sol molecule or to a chain linked to the macrogel [27,28]. It is expected that for increasing conversions, the reactivity ratio $r_{11} = k_{11}/k_{12}$ will increase continuously because the availability of M_2 unsaturations to react with M_1 radicals decreases drastically in comparison to that of the M_1 unsaturations. For the same reason, the reactivity ratio $r_2 = k_{22}/k_{21}$ decreases continuously with increasing conversion. Kinetic studies carried out on the S–DVER system [18,19] have shown an increment in the reactivity ratio of the styrene and the simultaneous reduction in that of the DVER unsaturations during the curing reaction. This behavior is also found in S–UPR. In this work, empirical functions of the reactivity ratios with the global molar conversion are proposed, in order to simulate the experimental behavior:

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{k_{22}^0}{k_{21}^0} f(P_m) = r_{20}\left(1 - \frac{P_m}{P_{mf}}\right)^S \tag{15}$$

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{k_{11}^0}{k_{12}^0} g(P_m) = \frac{r_{10}}{\left(1 - \frac{P_m}{P_{mf}}\right)^R} \tag{16}$$

where r_{10} and r_{20} are the isothermal reactivity ratios of the monomer unsaturations at zero conversion, P_m and P_{mf} are the global molar conversions at a given time and at the end of the reaction, respectively, and R and S are empirical fitting constants. Similar approaches to take in account the diffusional and topological restrictions on the kinetic propagation constants in the S–UPR system have been proposed by other researchers [3,17,29].

The number-average sequence lengths of M_1 and M_2 unsaturations in the copolymer, $\langle N_{11}\rangle_k$ and $\langle N_{22}\rangle_k$, at a given conversion during the curing reaction are:

$$\langle N_{11}\rangle_k = 1 + r_1\frac{f_1}{f_2} \qquad \langle N_{22}\rangle_k = 1 + r_2\frac{f_2}{f_1} \tag{17}$$

For the simulation runs, the model parameters, n_{0T} and Δn, were fixed in 10 000 and 1 mol, respectively. In the expressions of reactivity ratios (Eqs. (15) and (16)), the R and S exponents were chosen arbitrarily as one for simplicity. To reproduce published experimental results, the final conversion, P_{mf}, was taken as the vitrification conversion, when it was reported, or as the final measured conversion if the vitrification conversion was not reported. The initial reactivity ratios were considered constant for the calculation at different temperatures.

3. Experimental

3.1. Materials

A divinyl ester resin was synthetized by reacting an epoxy resin, diglycidyl ether of bisphenol A (DGEBA MY 790, Ciba Geigy, equivalent weight 176.2 g/eq.) with methacrylic acid (Norent Plast SA, laboratory grade reagent) and triphenylphosfine (Fluka AG, analytical reagent) as the catalyst, in the presence of hydroquinone as stabilizer. The reaction was carried out in a 1 l stainless steel reactor with moderate stirring. The total time of the synthesis was approximately 4.5 h and the temperature was kept at 100°C until the final conversion was reached, usually higher than 93%.

The synthesis of the resin was monitored by titration of the residual acid groups with an alcoholic KOH solution and the final excess of methacrylic acid was washed out from the mixture with distilled water. Finally, the water retained in the mixture was evaporated at 60°C under vacuum, using a rotavapor apparatus (Büchi, R-114). The final product was stored after the addition of 500 ppm of hydroquinone [30]. The DVER molecular weight measured by GPC was 583 g/mol, using polystyrene calibration.

Copolymers of the resin with different proportions of S were obtained by free radical copolymerization. Benzoyl peroxide (BPO) (Lucidol 75%, Akzo Chemicals SA) was used as an nitiator with a concentration of 2% by weight based on the reactive DVER–S mixtures.

3.2. Procedure

Measurements of the heat of reaction were performed using a differential scanning calorimeter (Shimadzu DSC-50), using indium calibration and nitrogen as flushing gas. Different ratios of DVER–S were mixed at room temperature with the BPO initiator and then quickly sampled to carry out the measurements. Aluminum hermetic pans were used to avoid S evaporation. Samples in the range of 5–10 mg were weighed before and after calorimetric runs, finding out that the weight loss was negligible (less than 5%). Dynamic calorimetric scannings were carried out under a constant heating rate of 10°C/min.

4. Results and discussion

As the initial reactivity ratios for the S–DVER vinyl groups, r_{10} and r_{20}, have not been reported in the literature, those of a very similar system, styrene/2-methyl methacrylate of 2-hydroxy-3 phenoxy propane, was adopted [31]. A similar procedure was followed to assign a value to the molar heat of homopolymerization of the DVER vinyl groups, finally taken as equal to that of the 2-methyl methacrylate of 2-hydroxy propane [32]. The molar heat of bond formation of the hypothetic S–DVER perfectly alternating copolymer, was taken as the average of the homopolymerization molar

Table 1
Model parameters

	Monomer	Value
Reactivity ratios	Styrene (r_{10})	0.39
	2-Methylmethacrylate of 2-hydroxy 3-phenoxy propane (r_{20})	0.4
	Bond	Value (kJ/mol)
Molar heat of bond formation	H_{11} styrene/styrene (1–1)	73
	H_{22} 2-methylmethacrylate of 2-hydroxy propane/2-methylmethacrylate of 2-hydroxy propane (2–2)	50.5
	$H_{12} = H_{21}$ styrene/2-methylmethacrylate of 2-hydroxy propane, (1–2 = 2–1)	61.75

heats. The values of these model parameters are given in Table 1.

4.1. Heat of copolymerization

The experimental values of the total reaction heat (ΔH_T), expressed by mol of formed bonds, are plotted in Fig. 1. A linear dependence with the feed composition is observed, as it is predicted from the model. From the linear regression of experimental data, the homopolymerization heat of DVER and S can be calculated as 52.5 and 76 kJ/mol, respectively, which are in reasonable agreement with the most frequently reported values of 50.5 and 73 kJ/mol. As the model calculations were performed using the homopolymerization heats reported in the published literature, the model predicts values lower than the experimental ones. The plot includes also the reaction heat calculated if the system cannot reach complete conversion ($P_{mf} = 0.96$).

Fig. 2(a) and (b) shows the instantaneous molar heat of reaction as a function of the conversion for the S–DVER system with different initial compositions, for the simplest case (a) where the DTR are neglected ($R = S = 0$) and for the actual case (b) where the DTR are considered ($R = S = 1$). In Fig. 2(a) the three horizontal lines in the plot are predicted for the two homopolymerizations and for the system with classical azeotropic behavior, with the corresponding molar heats of reaction being: $\Delta H_{11} = 73$ kJ/mol, $\Delta H_{22} = 50.5$ kJ/mol and $\Delta H_{22} = 61.75$ kJ/mol.

If no DTR effects are considered, then the heat of reaction of the reactive mixtures with an initial composition $f_{10} > 0.4958$ increases slowly first and steeply at the end of the reaction to reach the homopolymerization value of styrene, 73 kJ/mol. Analogously, if $f_{10} < 0.4958$ the heat decreases reaching the homopolymerization value of the DVER, 50.5 kJ/mol, at the end of the reaction. However, if the effect of the restrictions is included in the model, no classical azeotropic behavior is predicted. The instantaneous heat of reaction increases slowly at the beginning of the copolymerization, but then drops abruptly toward the end of the reaction to finally reach the value of the DVER homopolymerization heat, and this is true for all the initial compositions showed. This is a consequence of the larger reactivity of the S unsaturations ($r_1 > r_2$) which are consumed faster while the residual DVER unsaturations react at the end of

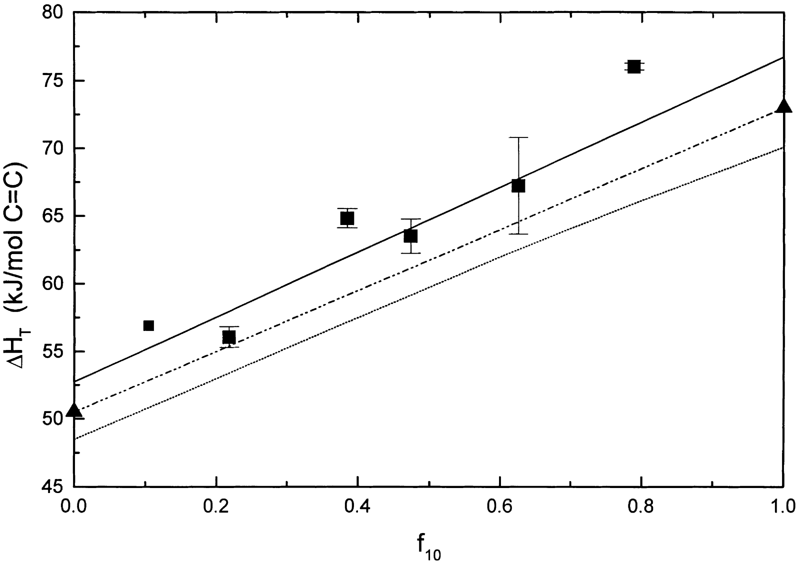

Fig. 1. Total heat of reaction as a function of the initial molar fraction of styrene in the reactive mixture: ▲, literature data; ■, experimental data; —, linear regression of experimental data; –··–, reaction heat calculated for complete conversion; …, reaction heat calculated for a final conversion of 0.96.

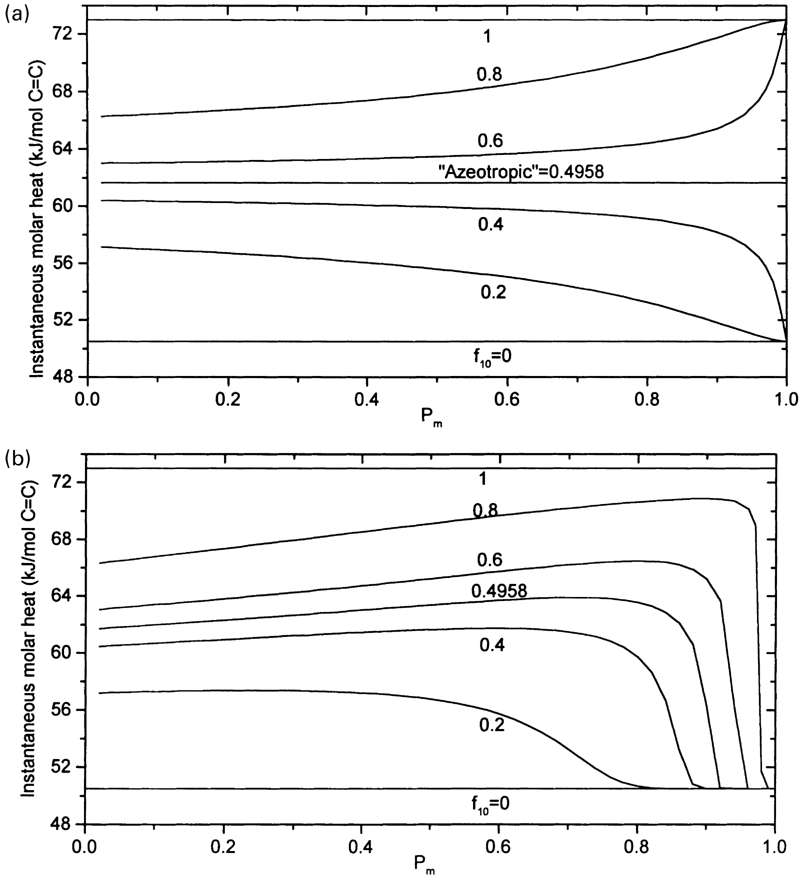

Fig. 2. Instantaneous molar heat of reaction as a function of the conversion of the S–DVER system with different initial compositions: (a) DTR effects are not considered; (b) DTR effects are considered.

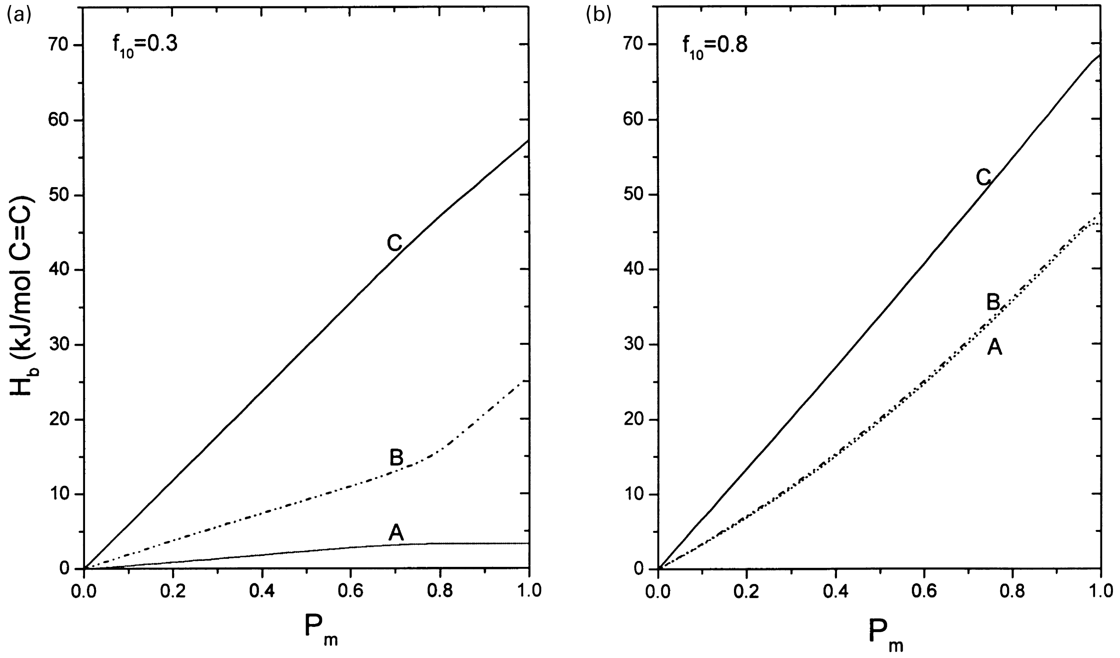

Fig. 3. Contributions of 1–1, 2–2, 1–2 bond formation to the instantaneous molar heat of reaction, H_b, as a function of the global conversion, P_m, if the feed has an initial concentration of: (a) $f_{10} = 0.3$; (b) $f_{10} = 0.8$. (A) ···, Contribution of the 1–1 bonds, H_{11}; (B)–··–, contribution of the 1–1 and 2–2 bonds, $H_{11} + H_{22}$; —, contribution of the 1–1, 2–2 and 1–2 bonds, $H_{11} + H_{22} + H_{12}$.

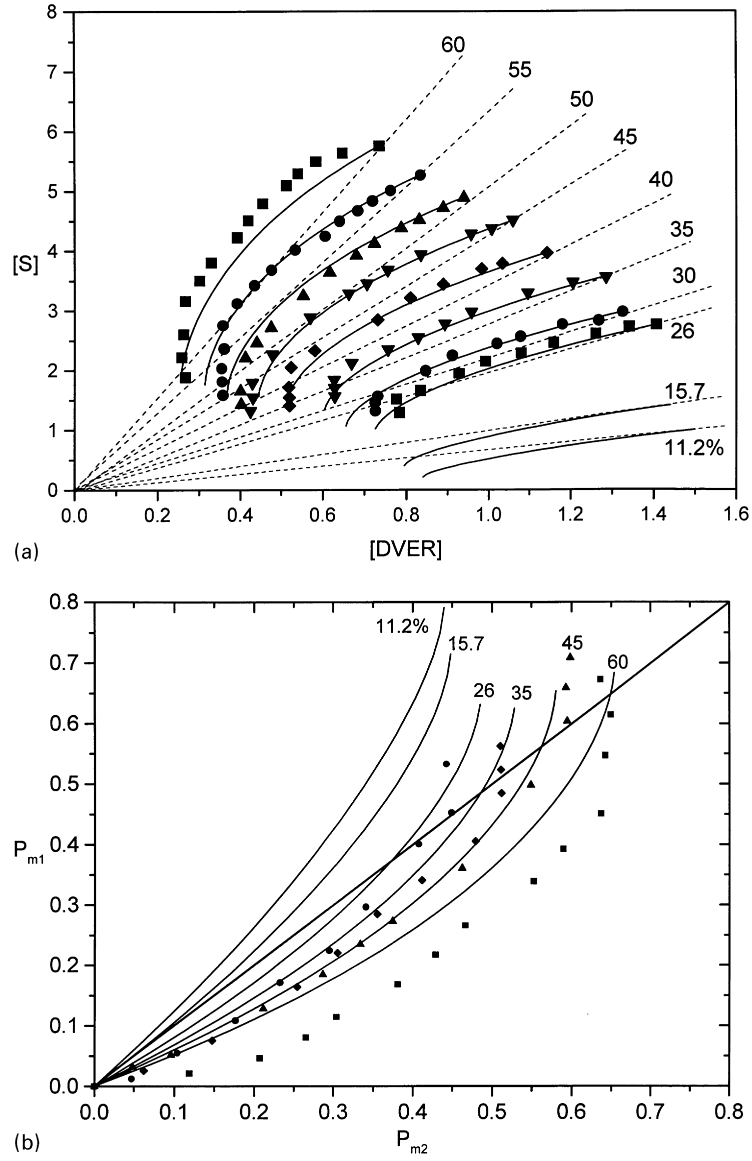

Fig. 4. (a) Experimental results reported by Ganem et al. [19] (filled points) and model predictions (continuous curved lines) for the S–DVER system expressed as molar concentration of styrene, [S], vs. molar concentration of DVER double bonds, [DVER]. 15.7%: azeotropic composition. (b) Styrene conversion, P_{m1}, vs. DVER conversion, P_{m2}, for different feed compositions (wt% of S). Filled points, experimental data reported by Ganem et al. [19]; —, prediction of the model; straight line, classical azeotropic behavior, $f_{10} = 0.4958$.

the copolymerization. There is a strong effect of the initial composition on the heat of reaction, at higher styrene initial concentrations the heat is higher and the steep drop in its value occurs at higher conversions.

The contributions of the 1–1, 1–2, and 2–2 bonds to the instantaneous molar heat of reaction as a function of the global conversion are shown in Fig. 3(a) and (b) for the initial compositions $f_{10} = 0.3$ and 0.8, respectively. In both plots, curve (A) represent the heat contribution of the formation of 1–1 bonds, H_{11}; curve (B) is the sum of 1–1 and 2–2 contributions, $H_{11} + H_{22}$; and curve (C) shows the three contributions, $H_{11} + H_{22} + H_{12}$. It can be seen that for an initial composition of $f_{10} = 0.3$ that the main contribution to the total heat of reaction is due to the formation of the 1–2 bond formation, and in decreasing order the formation of the 2–2 and 1–1 bonds. If the feed has an initial concentration of $f_{10} = 0.8$, the main contribution is due to the 1–1 bonds, and following a decreasing order the contribution of the 1–2 bonds, and finally the contribution of the 2–2 bond formation, which is almost negligible in this case. These differences are due to the larger consumption of DVER unsaturations in the formation of 1–2 alternating bonds at increasing styrene concentrations of the initial feed.

4.2. The global and particular conversions

Ganem et al. [19] have reported experimental results of

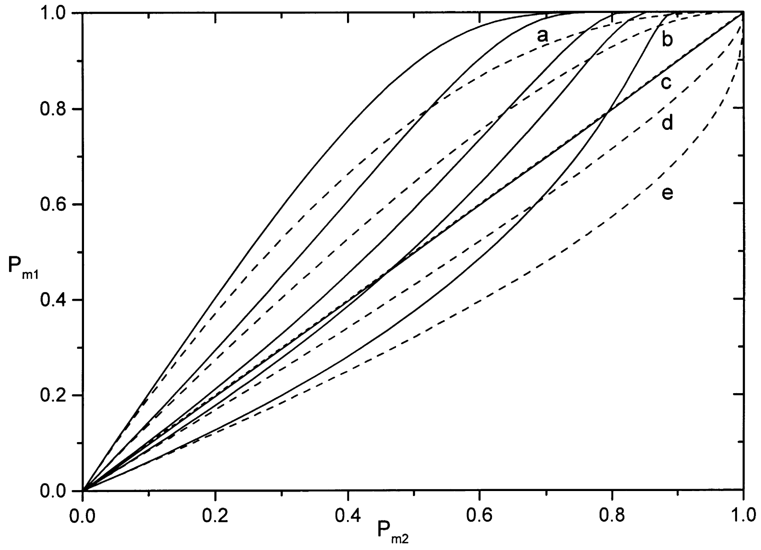

Fig. 5. Evolution of the conversion of styrene unsaturations, P_{m1} as a function of that of DVER, P_{m2}, for reactive mixtures of different initial molar compositions: (a) 0.2; (b) 0.4; (c) 0.4958; (d) 0.6; and (e) 0.8. - - - - -, Prediction not affected by DTR ($R = S = 0$). —, Prediction affected by DTR ($R = S = 1$).

the molar concentrations of S and DVER ($M_n = 1100$) for systems with initial feed concentrations in the range of 26–60% by weight of styrene and cured at 25°C. It must be remarked here that in these experimental conditions the reaction is stopped due to vitrification and the model must take this fact into account to make sound predictions. This problem can be solved if the final conversion reached by the system is included in the model calculations. Fig. 4(a) includes those experimental results and the predictions of the present model marked as continuous curved lines. The straight dashed lines in the plot indicate the expected azeotropic behavior with no DTR. The curved lines were calculated using the same initial reactivity ratios for all the compositions, $r_{10} = 0.39$ and $r_{20} = 0.4$, and the final conversions used in Eqs. (15) and (16) were slightly higher than the last experimental conversion measured for the system. This was a fitting parameter in the calculations and resulted in values such as 0.7 for the $f_{10} = 60\%$ mixture (last measured conversion: 0.67) and 0.6 for the $f_{10} = 26\%$ mixture (last measured conversion: 0.51). While these input values of the model respond primarily to a better fitting of the experimental values, they may be showing the real experimental impossibility of measuring the final conversion of the system at reasonable time. The runs are stopped when the rate of reaction becomes very small, but not necessarily zero, thus, the final conversion reached by the system is higher than the last measured value.

Fig. 4(b) shows these same results in the form of styrene conversion vs. conversion of DVER-unsaturations. This type of plot is very common in the studies of S–UPR systems and it is presented here to stress the similitude of the behavior of the two systems. As it has been observed in S–UPR systems, in all mixtures of S–DVER with initial concentrations $f_{10} > 0.4958$, ($f_{10} = 0.4959$ is the azeotropic composition for null conversion), the curves intersect the $P_{m1} = P_{m2}$ line showing the characteristic up-bending behavior caused by effects of the DTR on the reactivity ratios. On the contrary, for the systems with $f_{10} < 0.4958$ the curves begin above the diagonal line taking monotonously increasing values.

In Fig. 4(b) is also shown clearly that the $f_{10} = 60\%$ mixture shows DVER double bond conversions markedly advanced if compared with the other systems with lower initial concentration of styrene. This behavior has also been seen in the S–UPR systems cured at low temperatures with large styrene concentrations [20,23,24,33] and it is probably originated in the two-phase morphology of these reactive mixtures [34,35], where there is a phase rich in styrene occluded in a matrix rich in DVER partially reacted. Simultaneously to this phase separation, preferential segregation of low molecular weight species initiators, inhibitors and catalysts also takes place. Consequently, the reactive mixture is not chemically homogeneous and the conversions of the styrene and DVER unsaturations do not evolve at the same rate in both phases. The overall effect is to increase significantly the conversion of the DVER unsaturations with respect to those of the styrene.

A high temperature cure was simulated, which means that the reaction does not stop due to vitrification and the final conversion is $P_{mf} = 1$. Fig. 5 shows the evolution of the conversion of styrene unsaturations, P_{m1}, as a function of that of DVER, P_{m2}, for different initial compositions. The dashed lines represent the results obtained if the reactivity ratios were not affected by diffusional and topological restrictions during reaction, that means that $R = S = 0$ in Eqs. (15) and (16), which would predict a classical azeotropic behavior ($P_{m1} = P_{m2}$) at a composition $f_{1z} = 0.4958$. These curves show that for

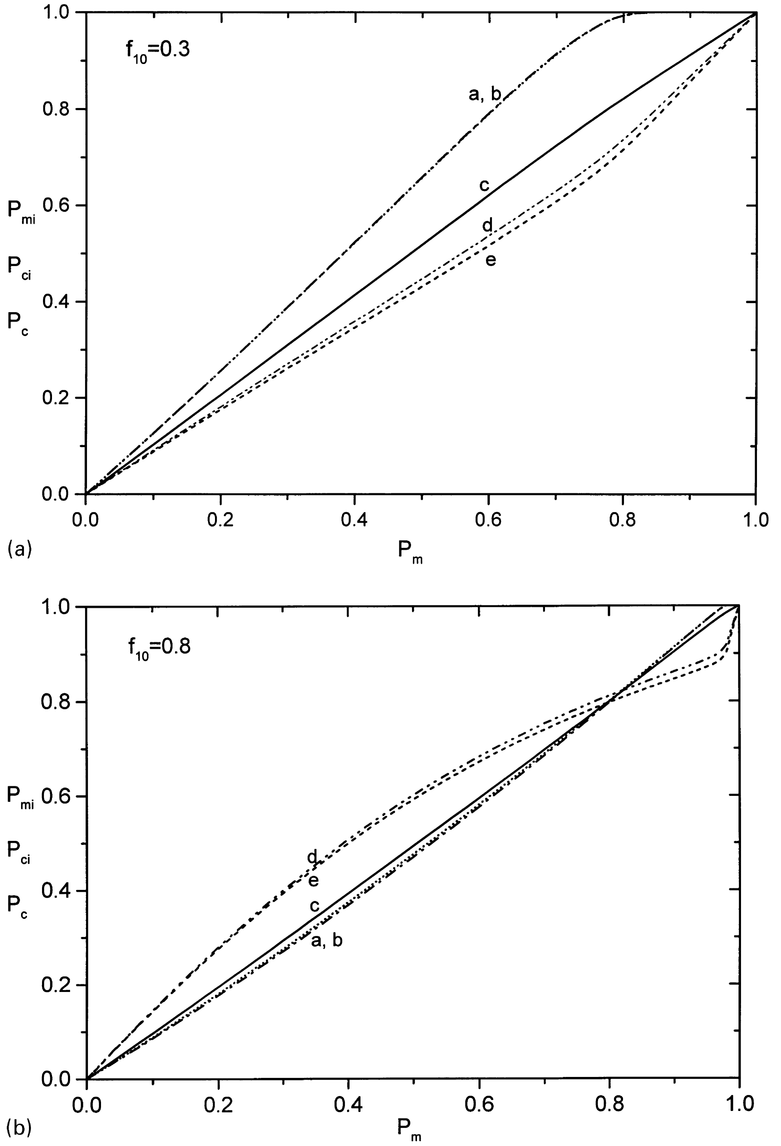

Fig. 6. Evolution of the calorimetric and molar conversions of each type of unsaturations, for initial compositions: (a) $f_{10} = 0.3$; (b) $f_{10} = 0.8$. (a) –·–, P_{c1}; (b) ···, P_{m1}; (c) —, P_c; (d)–··–,P_{c2}; (e) - - - -, P_{m2}.

initial compositions $f_{10} < f_{1z}$, the conversion of the styrene unsaturations is always lower than the conversion of the DVER double bonds and the reverse is true if the initial composition $f_{10} > f_{1z}$, as it has been described by the Lewis–Mayo copolymerization theory. Continuous lines show the effect of the DTR on the S and DVER conversions with $R = S = 1$, for the same conditions as above. The S–DVER copolymerization behavior at high temperatures can be summarized as follows:

1. At low conversions, the predictions of the model considering DTR are coincident with those of the unmodified model, since topological and diffusional restrictions are negligible in those conditions.
2. The conversion of styrene, P_{m1}, calculated considering DTR is always higher than the value calculated with the simpler model without DTR, that is with constant reactivity ratios (r_{10}, r_{20}).
3. At the end of the copolymerization, homo reaction occurs between the less reactive unsaturations of the DVER, which are less reactive than S and were more affected by the DTR. They remained in the mixture in large excess with respect to the styrene.
4. The diffusional and topological restrictions are responsible for the absence of a classical azeotropic behavior in the sense of the Lewis–Mayo theory (straight line in Fig. 1) that is predicted only if DTR are absent.
5. Systems with initial composition $f_{10} > 0.4958$ produced P_{m1} vs. P_{m2} curves that intersect the straight line. The point of intersection is $P_{m2} = 0$ for $f_{10} = 0.4958$ and takes increasing values for higher S initial concentrations. This up-bending behavior,

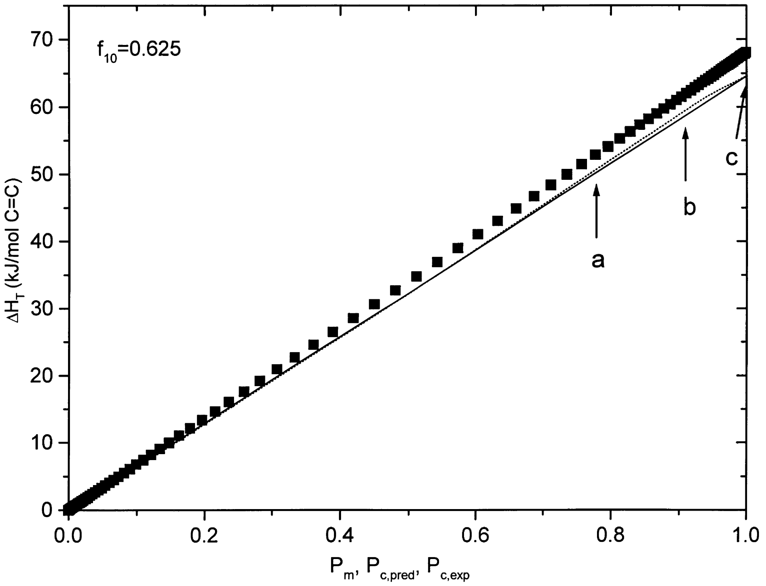

Fig. 7. Filled squares, experimental heat of reaction, $\Delta H_{T,exp}$, vs. experimental conversion, P_{exp} ··· Predicted heat of reaction, $\Delta H_{T,pred}$, vs. calorimetric conversion, P_c.—, $\Delta H_{T,pred}$ vs. molar conversion, P_m., for an initial composition $f_{10} = 0.625$. Final conversion reached at: (a) 90°C; (b) 100°C; and (c) 110°C.

with respect to the line $P_{m1} = P_{m2}$, has been reported by several researchers [20–26] working with different S–UPR systems.

4.3. The molar and calorimetric conversions

As mentioned before, the use of calorimetric techniques for determining the global conversion of the system is based on the assumption that the heat of reaction is proportional to the extent of reaction, so that $P_c = P_m$. This assumption must be verified by using other analytical techniques that measure the actual molar conversion.

The analysis of the S–DVER system shows that the molar heat of formation of the 1–1, 1–2 and 2–2 bonds are very different and that the number of each type of bond formed at each time step is a function of the instantaneous reactivities of the M_1 and M_2 unsaturations and the initial composition of the feed. These characteristics of the S–DVER reactive mixtures indicate that there may be differences between the global conversions, P_c and P_m, as well as between the particular conversions of each type of unsaturations, P_{ci} and P_{mi} $(i = 1, 2)$.

Fig. 6(a) and (b) shows the evolution of the global calorimetric and molar conversions and those for each type of unsaturations, for initial compositions $f_{10} = 0.3$ and $f_{10} = 0.8$, respectively. The agreement between molar and calorimetric conversions is reasonably good in all cases. It must be remarked that for the P_c calculation, the total heat of reaction predicted for each particular composition of the system was considered, that is, the theoretical prediction corresponding to complete final conversion as shown in Fig. 1.

The use of calorimetry for kinetic studies was already addressed and the need to assure that P_c and P_m be equal was remarked. This must be hold true, even if the cure temperatures are varied in wide ranges, and thus the effect of the DTR changed. Moreover, the initial feed composition and the glass transition temperature of the system affects the DTR, which together with the temperature of the curing reaction will determine the final conversion of the system. Fig. 7 shows the experimental results for an initial composition $f_{10} = 0.625$ of the accumulative total heat of reaction, $\Delta H_{T,exp}$, as a function of the experimental calorimetric conversion, $P_{c,exp}$, measured by DSC. In the same plot, the total heat predicted by the model, $\Delta H_{T,pred}$ vs. $P_{c,pred}$ and $\Delta H_{T,pred}$ vs. $P_{m,pred}$, are included. Differences between the experimental and model results for the calorimetric data are only due to the values used as total heats of reactions. The experimental conversions, $P_{c,exp}$, were calculated using the total heat interpolated from the straight line that better fits the experimental results, which lays above the ΔH_T results calculated from the literature values, as it was discussed previously in Fig. 1. The predicted and experimental global calorimetric conversions, $P_{c,pred}$ and $P_{c,exp}$, would be exactly coincident if only the same total heats of reactions were used in the calculations. Thus, it is concluded that for the particular system studied S–DVER it is possible to realize kinetic studies based on calorimetric measurements.

Fig. 1 shows very clearly that the total heat of reaction is a function of the initial composition of the system and that calorimetric studies should take this fact into account for the calculation of the global conversions. It is evident that taking a single average total heat of reaction valid for all compositions will lead to wrong conversion values.

The good agreement between the calculated and the experimental results, is very encouraging because there were no fitting parameters in this part of the calculation. Note also, the good agreement between the experimental

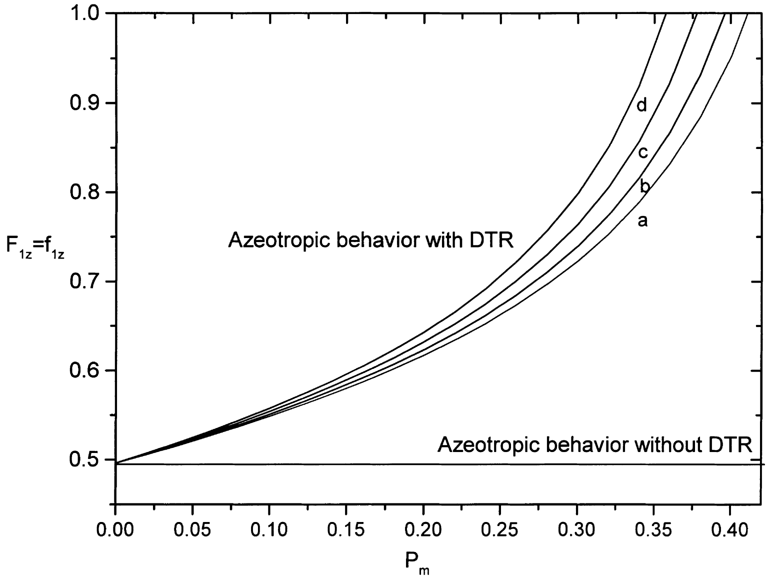

Fig. 8. Predictions of $F_{1z} = f_{1z}$ vs. conversion, P_m, for different initial composition: (a) 55%; (b) 45%; (c) 35%; and (d) 15.7%. Azeotropic behavior: straight line obtained with the simple Lewis–Mayo model ($F_1 = f_1 = 0.4958$).

P_c and calculated P_c and P_m, which is only valid for this particular system. For the S–DVER mixtures studied, it was observed that this agreement was equally good for all the initial compositions considered, being the differences smaller than the experimental error inherent to the calorimetric measurements.

4.4. The azeotropic behavior

It is also noteworthy that a S–DVER mixture with feed composition $f_{10} = f_{1z} = 0.4958$, the azeotropic composition to null conversion, does not follow the diagonal line $P_{m1} = P_{m2}$. Fig. 4(b) includes this curve for $f_{1z} = 0.4958$, which corresponds to 15.7% by weight of styrene. This mixture also shows the up-bending behavior due to the change in the reactivity ratios by the DTR effects, which lead to increased S double bond conversions with respect to the DVER ones.

From the equation that determines the azeotropic composition in the theory of Lewis–Mayo

$$F_{1z} = f_{1z} = \frac{1 - r_2}{2 - r_1 - r_2} \tag{18}$$

is obtained the relation between the values of the reactivity ratios that keep the composition of the feed and the copolymer constant and equal to the initial value of $F_{1z} = f_{1z} = 0.4958$. This relation are given by the equation:

$$r_1 = r_2 1.0169 - 0.0169 \tag{19}$$

This equation is satisfied if the instantaneous r_1 and r_2 pairs are simultaneously increasing or decreasing, leading to $P_{m1} = P_{m2}$ in the whole the conversion range. This requirement is in contradiction with that observed during cure in S–DVER mixtures, in which r_1 increases but r_2 decreases due to the DTR effects.

For every S–DVER reactive mixture with reactivity ratios that vary with conversion in the range $0.39 \le r_1 \le 1$ and $r_2 \le 0.40$, an “azeotropic” composition can be calculated. However, depending on the initial concentration of the styrene in the system, the calculated values of $F_{1z} = f_{1z}$ will increase, and they will be affected by the conversion. This is understandable because, as it has been discussed before, each initial composition leads to networks with different density of crosslinks and different vitrification or ultimate conversions, that is different weight of the contributions of the DTR to the overall system behavior. Predictions of $F_{1z} = f_{1z}$ vs. P_m, for different initial compositions, are shown in Fig. 8 illustrating the above discussion. The horizontal line represents the classical azeotropic behavior without DTR effects. The curves labeled from a to d show the effect of increasing amount of M_2 crosslinker that causes, proportionally, a more intense effect on DTR for the same global conversion.

This analysis shows that it is impossible to find a “classical azeotropic” behavior during cure of S–DVER mixtures and, even with the initial azeotropic feed composition $F_{1z} = f_{1z} = 0.4958$, the P_{m1} vs. P_{m2} curve shows the characteristic up-bending behavior as it is shown in Figs. 4(b) and 5.

The behavior of this particular “azeotropic” feed for the S–UPR was experimentally studied by many authors [20–26]. The reported results show coincidence with the line $P_{m1} = P_{m2}$ at low conversions but, as the conversion increases, P_{m1} deviates upward.

4.5. The average sequence lengths

The model predictions for the average sequence lengths of 1–1 and 2–2 bonds, $\langle N_{11} \rangle$ and $\langle N_{22} \rangle$, as function of the global conversion at high temperature curing, are shown in

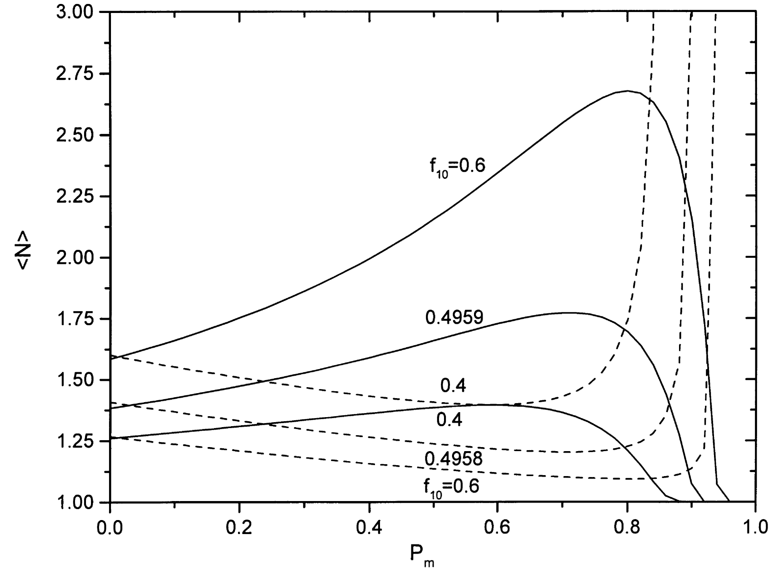

Fig. 9. Predictions of the model for the average sequence lengths (high cure temperature) of 1–1 and 2–2 bonds as functions of the global conversion, P_m, for different initial compositions. —, Sequence length of 1–1 bonds $\langle N_{11} \rangle$; - - - -, Sequence length of 2–2 bonds, $\langle N_{22} \rangle$.

Fig. 9. The values shown in the figure correspond to three different compositions of the initial feed, assuming that the copolymerization reaction could achieve complete conversion at a high cure temperature. The sequence length of 1–1 bonds increases with increasing f_{10}, passing through a maximum value because of the increasing reactivity ratio of the styrene and then, decreases because the feed becomes poor in styrene unsaturations. The opposite behavior is observed for the sequence length of the 2–2 bonds, which takes very large values at the end of the copolymerization because of the reaction between 2–2 residual pendant double bonds.

Fig. 10 shows the instantaneous average sequence lengths, $\langle N_{11} \rangle$ and $\langle N_{22} \rangle$, for S–DVER mixtures with different initial compositions cured isothermally at low temperature. The final conversions, calculated from Ganem's report and discussed before, are used also here. The styrene sequence length, $\langle N_{11} \rangle$, is initially larger and increases even more for higher initial concentrations of this comonomer. Simultaneously, $\langle N_{22} \rangle$ decreases slowly down to the final value of 1. At low temperatures, the high r_1 values reached at low or medium conversions cause larger $\langle N_{11} \rangle$ sequence lengths than at high cure temperature for mixtures with the same initial composition. This effect is more marked at the end of the reaction, where very large styrene chains are interrupted by an isolated DVER reacted double

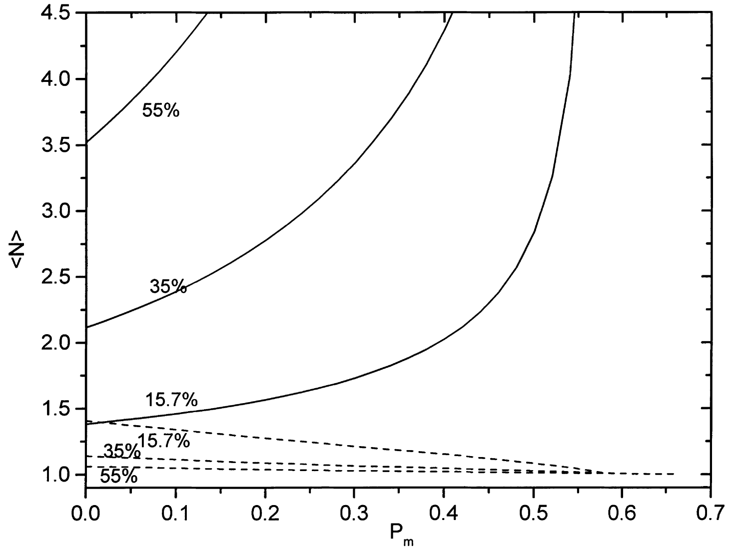

Fig. 10. Instantaneous average sequence lengths (low cure temperature), $\langle N_{11} \rangle$ and $\langle N_{22} \rangle$, for systems S–DVER with different initial compositions and final conversions calculated from Ganem's experimental data: —$\langle N_{11} \rangle$; - - - - $\langle N_{22} \rangle$.

bond. The differences between these results and those of Fig. 9 is that in this last case it was assumed that the cure temperature was higher than the final glass transition temperature and thus, vitrification did not stop the reaction and the system reached complete conversion. In the case illustrated by Fig. 10, the styrene achieves higher final conversions than the DVER due to its higher mobility, and the effect of the DTR is that the DVER unreacted unsaturations remain attached to the network and thus, they are topologically inhibited to react with each other. However, important amounts of styrene and DVER double bonds remain unreacted resulting in an incomplete final global conversion.

5. Summary and conclusions

A modified Lewis–Mayo model has been applied to predict the reaction behavior of the S–DVER system with good results. It was assumed that the two unsaturations of the DVER reacted independently and that the changes caused by the DTR on the reactivity ratios during the copolymerization are a function of the global conversion.

The total heat of copolymerization and the particular heat of each monomer reaction can be calculated after assigning a value to the formation of 1–1, 2–2 and 1–2 bonds in the copolymer. Experimental and predicted values for the total copolymerization heats show a good agreement.

Calorimetric and molar conversion are essentially equal if experimental errors are considered, which would allow the use of calorimetry for kinetic studies and calculation of global conversion. This conclusion is valid for this particular system and should not be generalized without verification.

The proposed dependence of the reactivity ratios with conversion allows to reproduce the experimental up-bending behavior in the plots of the unsaturations conversions of S vs. DVER.

The change of the reactivity ratios by the diffusional and topological restrictions is the cause of the impossibility to achieve a classical azeotropic behavior in the sense of the Lewis–Mayo copolymerization theory.

The average sequence lengths are affected by the DTR. Styrene–styrene sequence lengths increases with conversion, while that for the DVER double bonds diminishes, in agreement with the effect of the DTR on the consumption of each comonomer.

This simple model is able to simulate the S–DVER behavior without vitrification constrains at high temperatures and also the behavior if DTR are present at low cure temperatures.

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