

# Theoretical and Experimental Conversion in the Curing of Unsaturated Polyester Resins with Styrene as a Crosslinking Agent

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## SYNOPSIS

The reaction of unsaturated polyester resin is a free radical copolymerization between the styrene monomer and the unsaturated polyester. Depending on the temperature and other processing conditions, some of the reacting molecular species remain, after curing, in the form of residual monomer and soluble polymer that do not contribute to the network structure. By means of DSC and gel permeation chromatography (G.P.C.) techniques, we have investigated the differences between theoretical and experimental reaction heats of unsaturated polyester samples with different styrene/polyester ratios, the residual species formed, and the conversion of reactive groups.

## INTRODUCTION

The curing process of thermoset resins, such as epoxy and unsaturated polyester, is a crosslinking copolymerization, resulting in a macroscopic network formation through the connection of adjacent monomeric molecules. During the polymerization process, the conversion of a double bond to single bond is accompanied by an exothermic heat of polymerization.

Depending on the temperature and other processing conditions, some of the reacting molecular species remains, after curing, in the form of residual monomer and soluble polymer that do not participate in the polymer network.<sup>1</sup>

Isothermal and dynamic reaction heats, obtained by means of DSC techniques, are often used to estimate the degree of conversion and other kinetic parameters of the curing process.<sup>2</sup> Usually, for systems such as thermoset resins, the quantitative dynamic measure by DSC of the exothermic heat reaction is used to quantify the extent to which the complete reaction takes place, or as a reference for

isothermal kinetic studies.<sup>3,4</sup> Because of the possibility that some materials remain unreacted, the above exothermic heat reflects an actual and ultimate cure of the material in the circumstances of the experiment, but it does not always have to be the same as the theoretical heat associated with the total conversion of all the reactant species. In order to avoid this problem, we propose two different methods to achieve theoretical conversion for a thermoset system.

One method uses the chemical composition of the monomeric reacting species. We have applied this method to investigate the differences between theoretical and experimental reaction heats, measured by DSC of unsaturated polyester samples with different styrene/polyester ratios.

The other method, which uses gel permeation chromatography techniques, measures the conversion rate from areas of eluting curves. We have used this method to confirm that in polyester crosslinked with styrene, most of the uncured material is uncured because of the free monomer styrene.

The results presented show that calorimetry and G.P.C. are powerful techniques that permit us to discover the performance of a predetermined formulation according to environmental reaction conditions, and to predict the evolution in their performance according to time.

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## EXPERIMENTAL

Two sets of samples were investigated, one by means of DSC and the other by GPC.

### Materials

Five commercially unsaturated polyester resins were used in this study. Two were supplied by Rio Rodano (Spain), with the commercial names ESTRATIL A-228 and ESTRATIL Al-100, and three by Resisa (Spain), with the commercial names RESIPOL-9298, RESIPOL-9078, and RESIPOL-9028.

These polyesters consisted of maleic anhydride, phthalic anhydride, and propylene glycol with different molar ratios obtained by NMR (Table I). They were supplied with styrene as a crosslinking agent.

### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to monitor the amount of heat generated during the curing reaction of one set of samples.

The calorimetric measurements were performed using a Mettler DSC equipped with a control and programming unit (microprocessor TC10 and calorimetric cell DSC 20 arranged to permit temperature scans from  $-10$  to  $600^{\circ}\text{C}$ ). The dynamic scans were performed from  $0^{\circ}\text{C}$  to  $250^{\circ}\text{C}$  using a programmed heating rate of  $10^{\circ}\text{C}/\text{min}$  and a nitrogen atmosphere. Benzoyl peroxide (BP) was used to initiate the reaction. The concentration of the initiator was 2% by weight of total resin.

### Gel Permeation Chromatography

Gel permeation chromatography was used to determine the amount of soluble materials in the cured resins in the other set of samples investigated.

The resins prepared were cured at  $30^{\circ}\text{C}$  in a constant-temperature water bath for 7 h. After reaction, the pieces were placed in dichloromethane for 20 h

to dissolve the soluble materials. The soluble materials were monitored by G.P.C.

Molecular characterization by G.P.C. was carried out using tetrahydrofuran at  $35^{\circ}\text{C}$  as the eluting solvent. Four Ultrastyrigel columns of  $10^4$ ,  $10^3$ , 500, and  $100 \text{ \AA}$ , were used for this work with a flow rate of  $1 \text{ mL}/\text{min}$ . Calibration curves were established by means of polystyrenes. Benzoyl peroxide (BP) and *N,N*-dimethylaniline (DMA) were used as the initiator and promotor of the reaction. The concentrations were 2% by weight of BP and 0.5% by weight of DMA of the total resin.

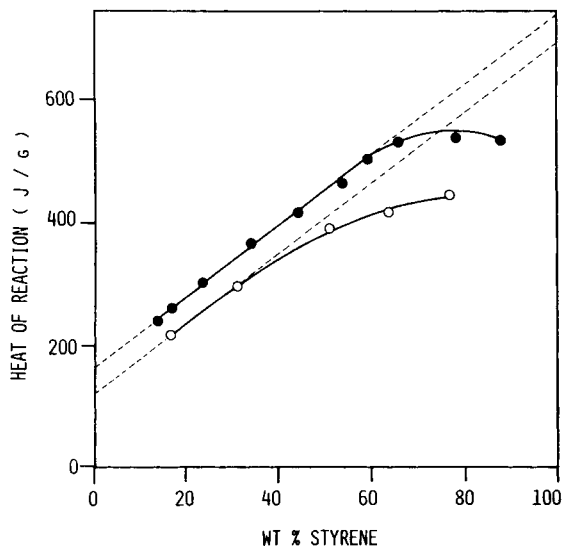
## RESULTS AND DISCUSSION

The curing of a thermoset is complex in that several steps and different reaction processes are involved. As a result of the overall process, heat accompanying the curing is liberated. Assuming the cure reaction is the only thermal event, the reaction advance is directly proportional to the rate of heat generation, and the ultimate extent of conversion is proportional to the total heat that the system is capable of liberating. According to the reaction process, this heat will or will not be the same heat corresponding to total conversion of all reactive groups.

In order to determinate the exothermic heat involved in the total conversion of all reactive groups, we need to associate an exothermic heat per mol of both the polyester  $\text{C}=\text{C}$  double bonds reacted and the styrene  $\text{C}=\text{C}$  double bonds reacted, providing that these two reactive groups are the only ones that contribute to the overall exothermic effect. We calculated these reaction heats per mol of reacting group by extrapolating exothermic heats of reaction obtained by dynamic DSC experiments of different resin formulations with different styrene contents. As can be seen in Figure 1, the extrapolation of experimental results to 100% styrene gives a reaction heat of  $725 \text{ J/g}$  from resin A-228 samples and  $645 \text{ J/g}$  from Al-100 samples. If the extrapolation is correct, this heat can be associated with the con-

**Table I** Unsaturated Polyester Resins Used in this Study

Unsaturated Polyester Resins	A-228	Al-100	RS-9284	RS-9078	RS-9028
Composition (Molar Ratio)					
Maleic Anhydride	2	1	1	3	1
Phthalic Anhydride	3	3	0	2	1
Propylene Glycol	5	4	1	5	2



**Figure 1** Experimental heat of reaction vs. % by weight of styrene: (●) resin A-228; (○) resin Al-100.

version of a C=C double bond of styrene to a C—C single bond of the polystyrene chain. When we extrapolated the experimental results to 0% of styrene, a reaction heat of 170 J/g from resin A-228, and 135 J/g from resin Al-100, is obtained. In this case, it is more difficult to discover the physical meaning of this heat. We have associated this heat to the reaction of polymerization of polyester (maleic) C=C double bonds, assuming that this heat can be attributed to the copolymerization reaction of polyester C=C bonds to styrene, or the polymerization of polyester C=C bonds to polyester C=C bonds. The literature<sup>5,6</sup> says that in the presence of styrene, the maleic autopolymerization reaction will be difficult.

Knowing the polyester resins compositions (see Table I), we estimated for resin A-228 a mass per mol of double bond in the polyester of 465 g/g-mol of double bond and for resin Al-100 of 774 g/g-mol

of double bonds. Assuming that the heat of the reaction per unit mass is proportional to the number of double bonds reacted in that unit mass, we calculated the theoretical heats of polymerization associated with the polyester C=C double bonds and C=C bonds of styrene molecules, and we also compared the values obtained with those reported in the literature (see Table II and Refs. 6-9).

Accepting as correct a heat of polymerization value of 17 Kcal/mol for the C=C double bonds of styrene and 22 Kcal/mol for the polymerization of polyester double bonds, theoretical heats of reaction were calculated, assuming the total conversion of all the reactive groups according to the mol styrene/mol C=C polyester and mol styrene/overall C=C bonds ratios. Figures 2 and 3 show the results obtained for the resin A-228. These representations enable us to see *a priori* the relative importance of styrene and polyester in the total reaction heat.

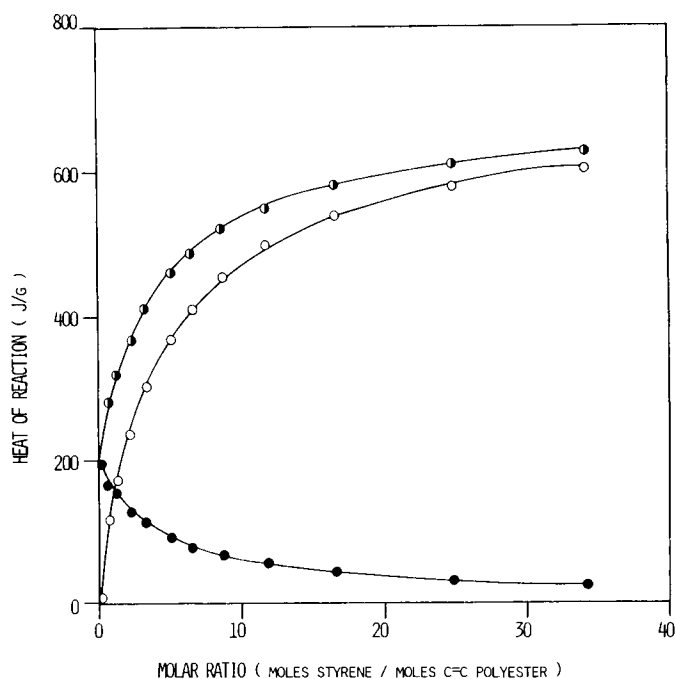
The fraction of double bonds reacted during the curing reaction (conversion) is defined as:

$$\alpha = \frac{\Delta H_r}{\Delta H_{\text{theoretical}}}$$

where  $\Delta H_r$  is the exothermic heat of reaction, obtained by dynamic experimental calorimetric measurements, and  $\Delta H_{\text{theoretical}}$  is the heat corresponding to total conversion of all double bonds. Figures 4-8 show the comparison between the theoretical heats of the reaction calculated and the experimental heat of reaction obtained by DSC. As can be seen, depending on the type of resin and the styrene content, the different samples do not reach 100% conversion. Figures 7 and 8 show that at low styrene/polyester ratios, the theoretical and experimental heats of reaction values of samples A-228 and Al-100 are very close. This is not the case with samples RS-9284, RS-9078, and RS-9028 (Figs. 4-6), where an im-

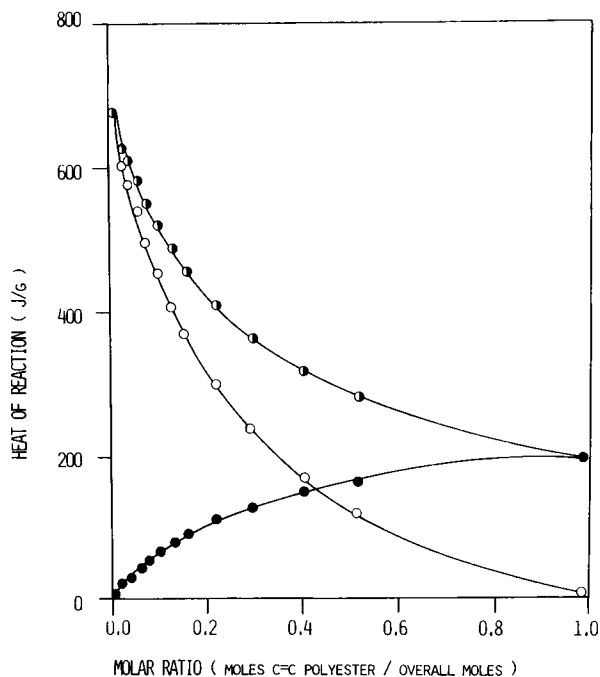
**Table II** Comparison between Heats of Polymerization Obtained in this Study and Reported by Several Investigators

	Kamal and Sourour <sup>7</sup>	Avella et al. <sup>8</sup>	Pusatcioglu et al. <sup>9</sup>	Polymer Handbook <sup>6</sup>	Present Study Resin A-228	Present Study Resin Al-100
Heats of Polymerization of Styrene (Kcal/mol)	17	17	17	16-17	18	16
Heats of Polymerization of Double Bonds in the Polyester (Kcal/mol)	12.8	16.1	22.4	14	18.8	24.8



**Figure 2** Theoretical heats of reaction vs. Molar Ratio (mol/styrene/mol C=C polyester) for the resin A-228: (●) polyester C=C; (○) styrene; (◐) overall.

important gap exists between the theoretical and experimental values in the whole range of styrene/polyester ratios. This fact shows that the conversion

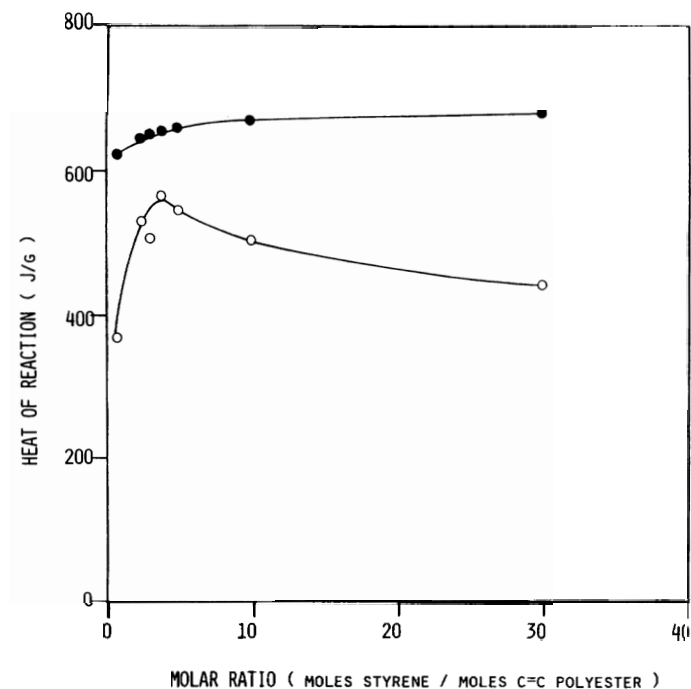


**Figure 3** Theoretical heats of reaction vs. Molar Ratio (mol C=C polyester/overall mol) for the resin A-228: (●) polyester C=C; (○) styrene; (◐) overall.

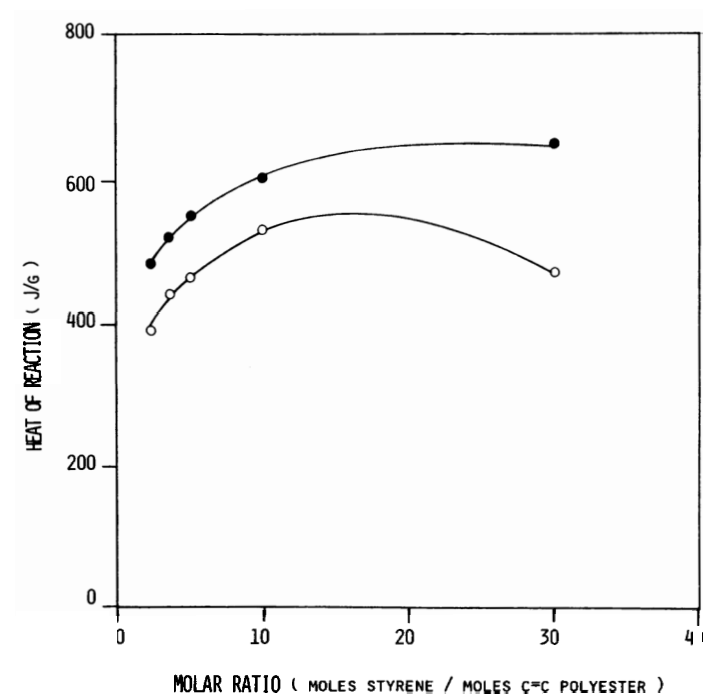
of the reaction depends not only on the styrene/polyester content, but also on the resin composition.

The aromatic ring structure of the phthalic groups makes the polyester molecule more compatible with the styrene monomer through a free-radical mechanism of polymerization. According to Table I, resins A-228 and Al-100 will be more compatible than resins RS-9284, RS-9078, and RS-9028. This fact may explain the different performance of the resins at low styrene/polyester ratios. The differences between theoretical and experimental heats of reaction at large styrene/polyester ratios reflect the fact widely reported in the literature that some styrene remains unreacted.<sup>5,10</sup>

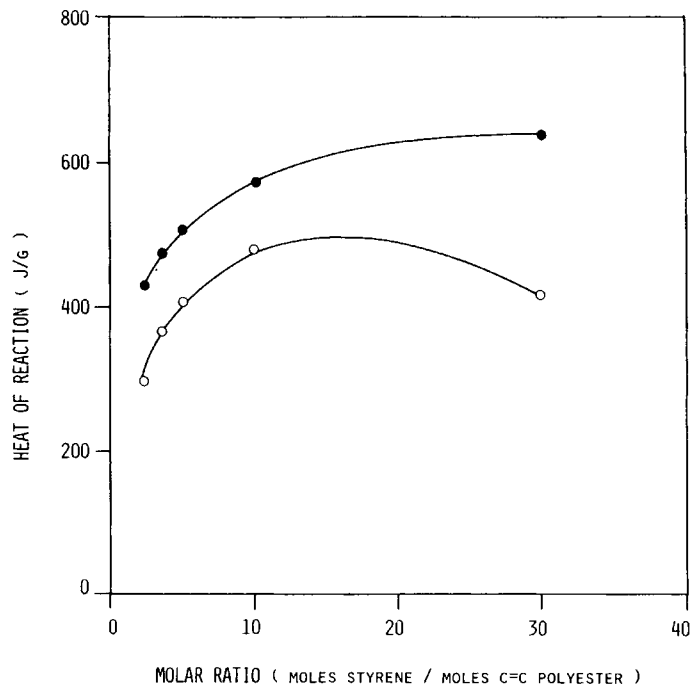
Several authors<sup>2,11</sup> have investigated the reaction mechanism of unsaturated polyester resin, the effect of styrene concentration on the structure of polyester material, and the kinetic changes of polyester reaction. Figure 9 shows that experimental heat of reaction values first increase, reach a maximum and then decrease. Yang and Lee<sup>5</sup> suggested three different structures of polyester resins and it is quite reasonable to explain the maximum as a change in the morphology of the sample when the styrene content increases. The position of the maximum is different for each resin. These results show that the curing of thermosetting resins is complicated by the interaction of the chemical kinetics and the changing physical properties,<sup>12</sup> and, likewise, the morphology



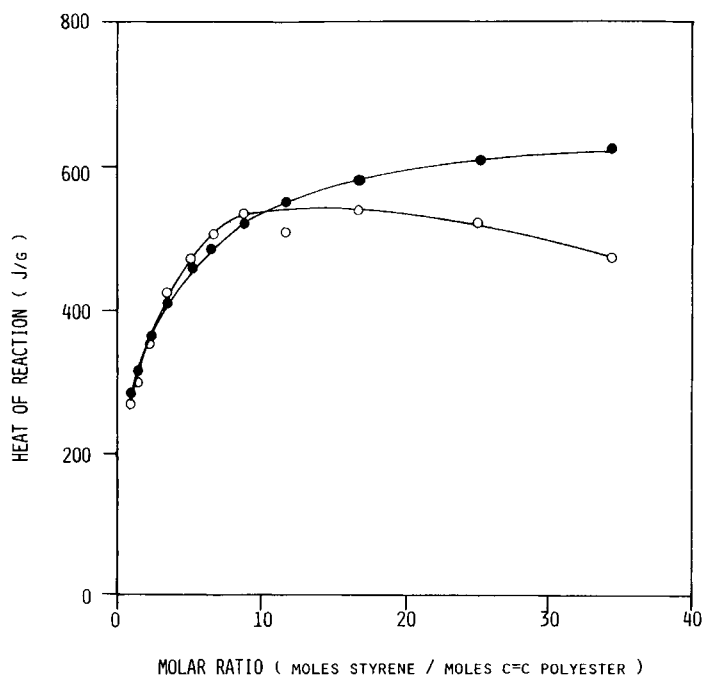
**Figure 4** Comparison between theoretical and experimental heats of reaction vs. Molar Ratio (mol styrene/mol C=C polyester) for the resin RS-9284: (●) theoretical; (○) experimental.



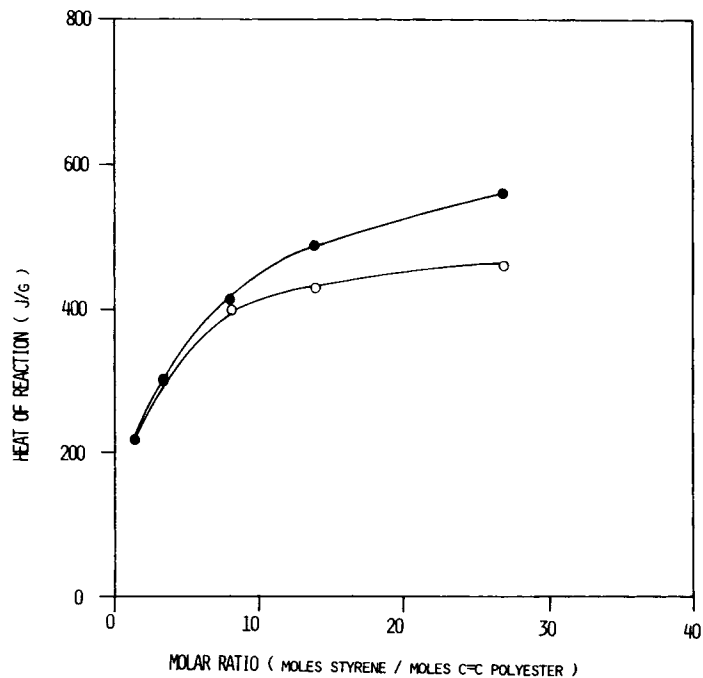
**Figure 5** Comparison between theoretical and experimental heats of reaction vs. Molar Ratio (mol styrene/mol C=C polyester) for the resin RS-9078: (●) theoretical; (○) experimental.



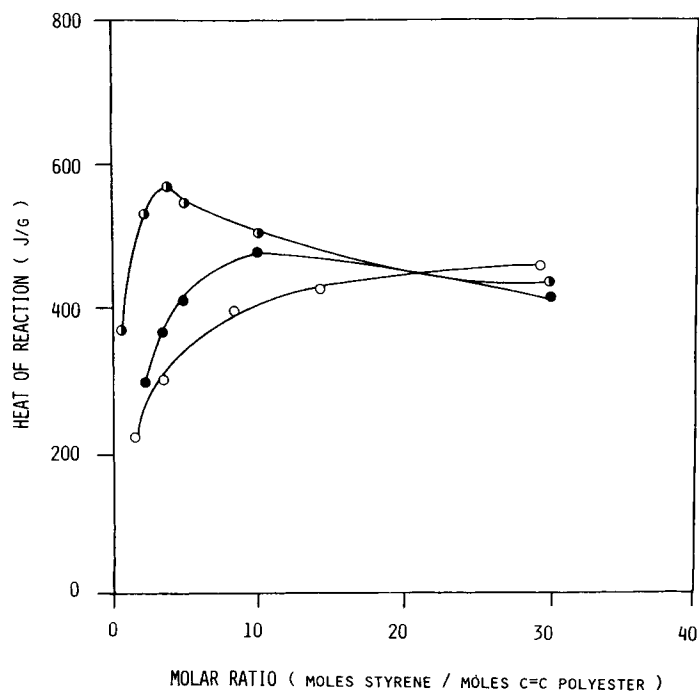
**Figure 6** Comparison between theoretical and experimental heats of reaction vs. Molar Ratio (mol styrene/mol C=C polyester) for the resin RS-9028: (●) theoretical; (○) experimental.



**Figure 7** Comparison between theoretical and experimental heats of reaction vs. Molar Ratio (mol styrene/mol C=C polyester) for the resin A-228: (●) theoretical; (○) experimental.



**Figure 8** Comparison between theoretical and experimental heats of reaction vs. Molar Ratio (mol styrene/mol C=C polyester) for the resin Al-100: (●) theoretical; (○) experimental.



**Figure 9** Comparison between experimental heats of reaction for the resin: (●) RS-9284; (●) RS-9028; (○) Al-100.

of samples.<sup>5</sup> The degree of polyester unsaturation is another important factor to be accounted for. Resin RS-9284 has the highest degree of unsaturation and is the sample that shows the most significant effect when the styrene content is changed.

On the other hand, the maximum in RS-9284 is reached at the lowest styrene/polyester molar ratios. These results suggest that the gap between theoretical conversion and the sharply decreasing conversion, when styrene is added, is due to unreacted molecules trapped in the crosslinked network, caused by the chain segmental immobility.

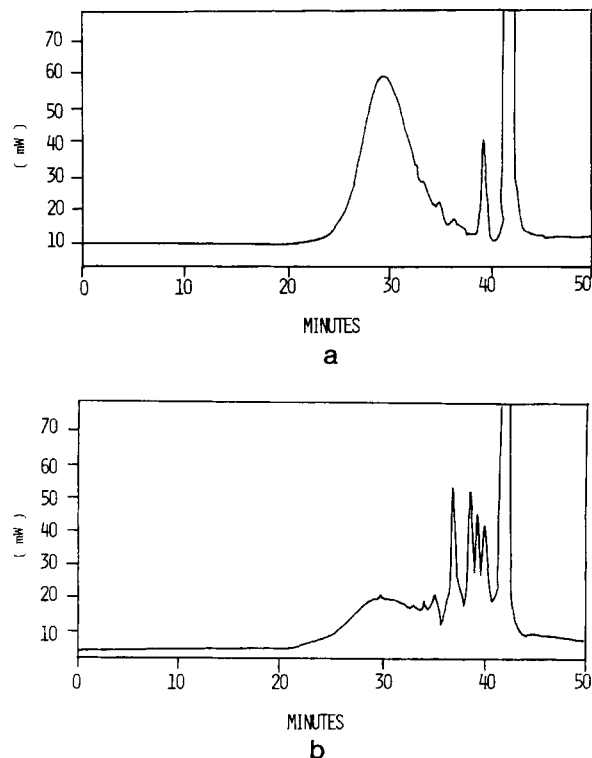
In order to complement the above comments and to verify the assumptions that we have made, we prepared samples with resin A-228 with different ratios of polyester and styrene. We then studied the samples by G.P.C. As we can see in the molecular weight distribution, polyester has retention times of 25 to 39 min and the retention time for styrene is 41.89 min. We can also see that the retention time of 39.56 corresponds to phthalic anhydride that is not prepolymerized in the commercial resin A-228. Integrating different areas, we have constructed a calibration curve for polyester and for styrene. We then used these curves for quantitative determination of polyester and styrene. Figure 10(a) shows the molecular weight distribution for commercial resin A-228 before curing.

Seven samples of resin A-228, with different ratios of styrene, were cured and studied by G.P.C., as we explained in the experimental section. All the samples show an elution curve similar to that in Figure 10(b). Figure 10(b) shows the molecular weight distribution for commercial resin A-228 after curing.

By comparing the retention times in the molecular weight distribution before and after curing, we can clearly see the presence of residual polyester and styrene monomer in the cured samples. It is not unreasonable to assign molecular weights between polyester and styrene to the formation of styrene oligomers of low molecular weight and branch styrene on polyester molecules. All this soluble material probably does not participate in the polymer network.<sup>13</sup> Finally, we calculated the conversion of styrene, polyester C=C bonds, and overall C=C bonds for the seven samples. The conversion calculated by comparing the elution curve before and after curing is defined as:

$$1 - \alpha = \frac{A_{ac}}{A_{bc}}$$

where  $A_{ac}$  is the area associated with the styrene or polyester C=C bond after curing, and is propor-

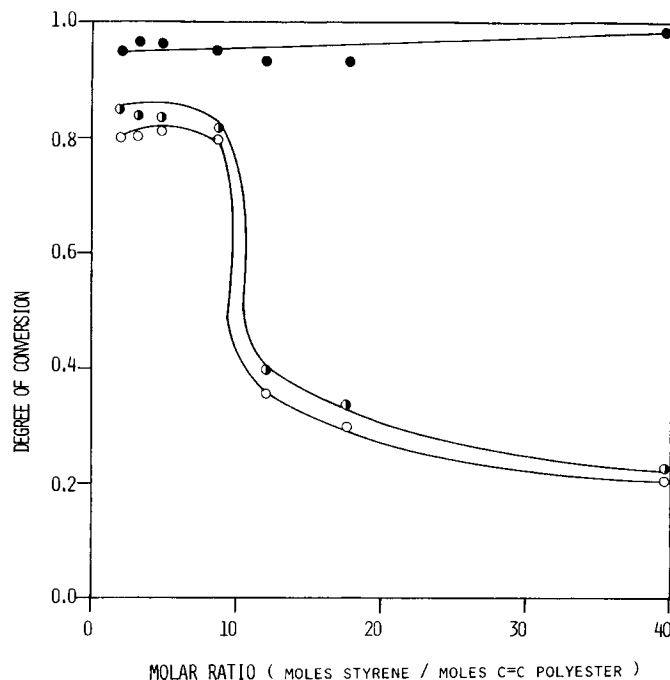


**Figure 10** (a) Molecular Weight Distribution for the resin A-228 before curing. (b) Molecular Weight Distribution for the resin A-228 after curing at 30°C for 7 h.

tional to the double bonds unreacted, and  $A_{bc}$  is the area associated with the styrene or polyester C=C bonds before curing, and is proportional to the conversion of all the double bonds. Table III shows the results. As might be expected, the residual styrene monomer increases according to the styrene/polyester ratio. On the other hand, for this resin, the styrene content has only a slight effect on the polyester C=C conversion, which is very high in all the samples.

The styrene conversion, the polyester C=C bond conversion, and the overall C=C bond conversion obtained as indicated above are plotted in Figure 11 against the styrene/polyester ratio. It can be concluded that for resin A-228, the conversion of the styrene abruptly decreases when the styrene/polyester ratio reaches a value of ten. These results confirm similar results obtained by calorimetric measurements, where the maximum heat of reaction reaches a styrene/polyester ratio close to ten. One explanation of this decrease in the conversion of resin A-228 is a change in the morphology of samples.<sup>5</sup> The conversion of a cured thermoset is the property that ultimately determines the level of all physical properties. Consequently, in order to make





**Figure 11** Degree of conversion vs Molar Ratio (mol styrene/mol C=C polyester) for the resin A-228: (●) overall; (○) styrene; (●) polyester C=C.

optimum use of unsaturated polyester resins, we need accurate knowledge of the conversion according to the styrene/polyester ratio and other processing conditions.

## CONCLUSIONS

The exothermic heat of polymerization, associated with the styrene and polyester double bonds, can be calculated if we know the resin compositions by extrapolating the exothermic heats of reaction, obtained by DSC vs. % of styrene (Fig. 1). Taking a correct heat of polymerization value for the C=C

double bond of styrene, and for polyester double bond, it is possible to estimate a theoretical heat of reaction corresponding to total conversion of all double bonds.

Conversion can be calculated by comparing the theoretical reaction heats with experimental ones obtained by DSC runs (Figs. 4–8). It can be seen that, depending on the type of resin and the percentage of styrene, the material does not reach a total conversion. In all the resins studied, a maximum conversion is observed in correlation with styrene percentage.

The position of the maximum varies according to the type of resin (Fig. 9).

**Table III** Conversion of Styrene and Polyester from G. P. C. Measurements<sup>a</sup>

Sample	Wt % Initial Styrene	Mols Styrene / Mols C=C	Wt % Residual Styrene	$\alpha_p$	$\alpha_s$	$\alpha_t$
1	30.85	2.11	6.08	0.95	0.80	0.85
2	40.96	3.31	8.12	0.97	0.85	0.84
3	51.01	4.99	9.63	0.96	0.81	0.83
4	64.21	8.80	12.85	0.95	0.80	0.81
5	70.99	12.22	45.43	0.94	0.36	0.40
6	77.56	17.73	53.95	0.98	0.30	0.34
7	87.58	40.16	69.19	0.98	0.21	0.22

<sup>a</sup>  $\alpha_p$  = Polyester C=C conversion,  $\alpha_s$  = Styrene conversion,  $\alpha_t$  = Overall C=C conversion.

By comparing the Molecular Weight Distribution obtained by G.P.C., before and after curing (Figs. 10a and b), it is observed that part of the polyester and styrene, as well as low molecular weight oligomers of styrene and branch styrene on polyester molecules, do not participate in the polymer network. From the data obtained by G.P.C., resin, styrene, and total conversion can be determined (Fig. 11 and Table III). Again, a maximum conversion for a given concentration of styrene can be observed.

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Received June 9, 1991

Accepted July 24, 1991