Characterization of Unsaturated Polyester Resin Cured with Styrene

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ABSTRACT: In this work, the curing kinetic of an unsaturated polyester resin, mixed with styrene as curing agent, was studied by means of diffential scanning calorimetry (DSC) and infrared (IR) spectroscopy. Investigations were made *in situ* during curing and post-curing periods. The enthalpy (ΔH_{cop}) characterizing the styrene homopolymerization and its copolymerization with the polyester chains was determined from isothermal DSC investigations. The residual enthalpy (ΔH_{res}) was determined from nonisothermal DSC measurements. We find that the quantity ($\Delta H_{res} + \Delta H_{cop}$) depends on the curing temperature (T_{iso}). Styrene homopolymerization and/or copolymerization lead to characteristic bonds modifications. The variations of the most characteristic bonds versus curing duration were studied from Fourier transform IR investigations. The data allow the determination of a relationship between transformation rate and curing duration using a time constant (τ) characteristic of each reaction involved during the liquid to solid-state transformation. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 695–703, 1998

Key words: polyester; styrene; cure; calorimetry; infrared

INTRODUCTION

Unsaturated polyester resins with styrene are widely used in the coating technology area. They are inexpensive and can easily accomodate specific applications by changing either the nature of the unsaturated polyester chain or the ratio of styrene/polyester amounts. The thermal cycles leading to the final products consist generally in curing and post-curing periods, and sometimes a second post curing at high temperature is performed. After the crosslinking reactions, this final products exhibit thermosetting characteristics, as insolubility and infusibility. The knowledge of the conversion rate reached by the resin after the cur-

ing and post-curing periods requires the use of specific technics as dilatometry,[1] infrared (IR) spectroscopy,[2–4] differential scanning calorimetry (DSC),[5,6] or nuclear magnetic resonance (NMR).[7] Inherent to their unsaturated nature, a 100% rate of transformation cannot be reached, and some double bonds will remain in the final product. Moreover, depending on the processing conditions, some residual monomers or other molecular species can remain after the cure. This residual unsaturation could be a source for oxidation and degradation, which can limit the durability of the industrial product. This is the reason why the state of the final product; i.e., the transformation rate has to be controlled.

It is now established that the formation of the three-dimensional network is the result of the competition of complex set of reactions, which includes (1) the copolymerization implying the dou-

Table I   Composition of the Material Used in This Work

Composition (molar ratio)	
Maleic anhydride	1
Isophtalic acid	1
Propylene glycol	2
Styrene monomer	2.5
$\overline{M_n}$ (g/mol)	$\cong 3000$
Unit M_w mol C=C (g/mol)	362
Average number of C=C/polyester molecule	8.3

ble bonds functionalities of the unsaturated polyester and the styrene monomer, and (2) the polymerization of styrene leading to polystyrene formation. From a calorimetric point of view, both reactions are exothermic, and the heat involved can be determined by means of differential scanning calorimetry measurements. In spite of the small difference that exists between the heats of polymerization and copolymerization among styrene derivatives and polyester,[8–10] it was recently shown that these heats of transformation can be obtained, with enough accuracy by coupling isothermal and dynamical DSC experiments.[6] On the other hand, it was also shown that IR spectroscopy was a powerful tool to characterize the nature and the quantities of bonds implied in the formation of the different molecular species obtained during and after the cure.[2–4]

In this work, such DSC and IR investigations are performed on a commercial system. In particular, IR investigations are made *in situ* to characterize the kinetics of local bond modifications, which can appear during curing, post-curing, and second post-curing periods.

EXPERIMENTAL

Materials

The unsaturated polyester resin studied in this work was provided by TECHNIBAT Co (Cravigny, France). This polyester resin consists of maleic anhydride, isophtalic acid, and propylene glycol mixed in a styrene monomer solution. The detailed composition of the material is given in Table I. Both resins and styrene monomer were used as received without removing the inhibitor. The initiator is the methylethylketone peroxide (MEKP, AKZO, Compiégne, France). The promoter is a cobalt octoate (AKZO). To initiate the

reaction 0.2% (w/w) of the promoter solution, which contains 6% of cobalt octoate, was first mixed with the resin. Then 1.5% (w/w) of the initiator solution was added to the mixture (resin + styrene + promoter). In the following, our unsaturated polyester resin will be refered as UPR.

Methods

Fourier Transform Infrared Spectroscopy

The transmission IR spectra of the resin film were obtained with a Nicolet 510M FTIR spectrophotometer by collecting and averaging 30 scans, at a resolution of 4 cm^{-1}. A liquid film of the sample was pasted between two ZnS plates mounted on a specific sample holder located in the FTIR instrument. From this way, the transformations from the liquid to the solid state are analyzed *in situ*. ZnS plates were used because their absorbance is low, between 800 and 4000 cm^{-1}. To remove the substrate contribution, spectra substractions were performed. All the IR spectra presented in the following are shown in absorbance. For these IR measurements, the following thermal cycle was performed: 1440 min at room temperature (curing period); then from 1440 to 1800 min at 80°C (post-curing period); and, finally, from 1800 to 1920 min at 120°C (second post-curing period). This thermal cycle was chosen in agreement with the industrial process.

Differential Scanning Calorimetry

DSC measurements were performed on a Perkin–Elmer DSC4 instrument equipped with a cooling system. Temperature and enthalpy calibrations
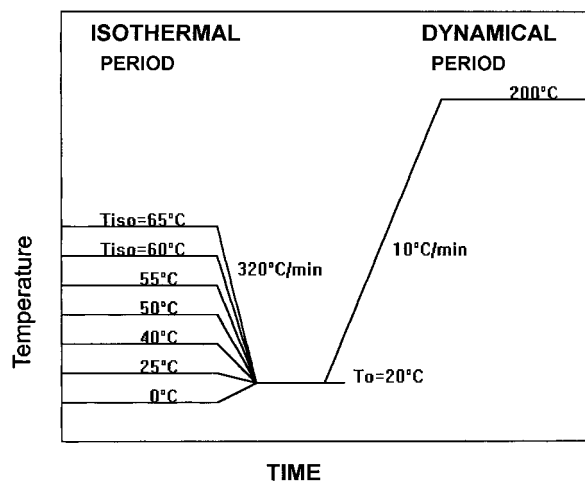

Figure 1   Thermal cycles used for the kinetic studies performed by DSC investigations.
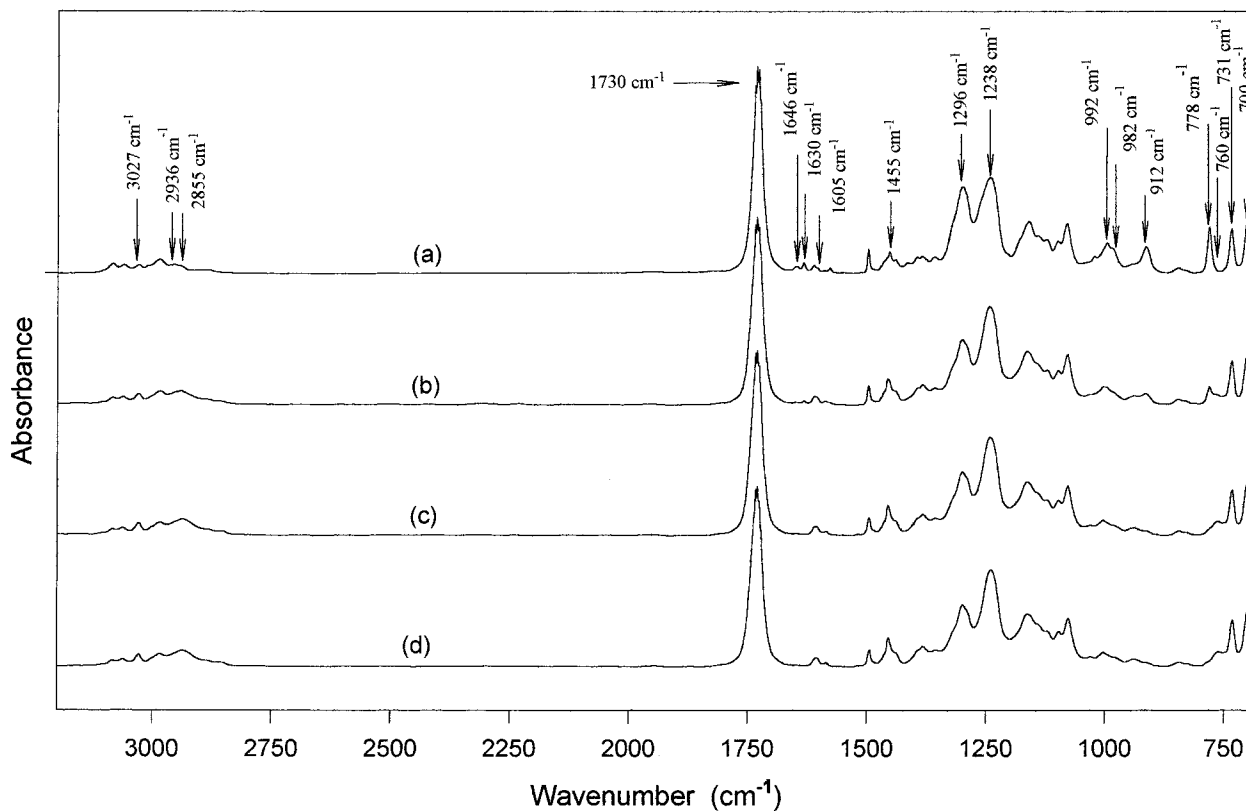
Figure 2 IR spectra obtained on (a) before the curing reaction; (b) after a curing duration of 400 min at 25°C; (c) after a curing duration of 1440 min at 25°C and post-curing duration of 275 min at 80°C; and (d) after a curing duration of 1440 min at 25°C, then a post-curing duration of 360 min at 80°C, and a second post-curing duration of 120 min at 120°C.

were achieved with indium as reference material. Sealed capsules were used. The thermal cycles used for the kinetic studies are displayed in Figure 1. At first, a plateau at different isothermal temperatures, 0, 25, 40, 50, 55, 60, and 65°C was performed to characterize the isothermal transformations. Second, the sample was heated from 20 to 200°C at 10°C/min. This second scan was performed to determine the residual enthalpy characterizing the residual rate of transformation. When isothermal temperatures (T_i) were chosen greater than the load temperature (T_o = 20°C), the sample was first cooled from T_i to T_o at 320°C/min.

RESULTS

Figure 2 shows the whole IR spectra obtained on the same UPR film. Curve (a) shows the IR spectrum before the curing reaction; curve (b), after a curing duration of 400 min at 25°C; curve (c),

after a curing duration of 1440 min at 25°C and a post-curing duration of 275 min at 80°C; and, finally, curve (d), after a curing duration of 1440 min at 25°C, a post-curing duration of 360 min at 80°C, and a second post-curing duration of 120 min at 120°C. On all these curves, we observe characteristic peaks that magnitude increases or decreases as soon as the liquid to solid state reaction occurs.

The expanded views presented in Figure 3(a)–(f) display all the data collected versus the curing and post-curing durations. We observe that the magnitude of the peaks at 778, 912, 982, 994, 1296, 1630, and 1646 cm^{-1} decrease when the curing and post-curing durations increase; while an opposite behavior is observed for the peaks at 762, 1238, 1455, 1605, 2855, 2936, and 3027 cm^{-1}.

Isothermal DSC data recorded for T_{iso} = 50, 55, 60, and 65°C are reported in Figure 4. Except for T_{iso} = 40°C, for which the magnitude of the enthalpic signal was too small to be detected, on all the other curves, an exothermic peak appears. From
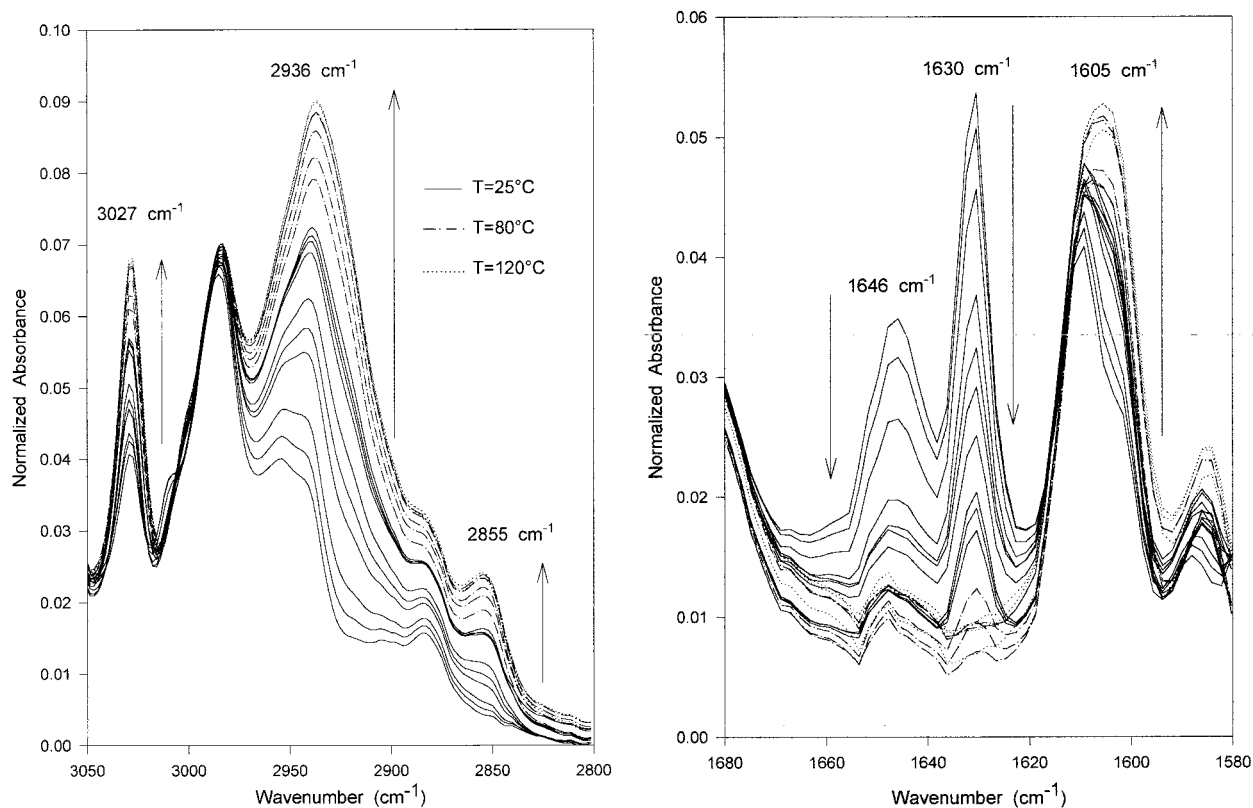
Figure 3 Expended views of IR spectra: (a) $3050 \to 2800$ cm^{-1}, (b) $1680 \to 1580$ cm^{-1}, (c) $1480 \to 1430$ cm^{-1}, (d) $1320 \to 1200$ cm^{-1}, (e) $1050 \to 850$ cm^{-1}, and (f) $800 \to 700$ cm^{-1}. Arrows indicate the evolution of a characteristic peak with time during the curing, the post-curing, and the second post-curing periods.

these experiments, the following different observations can be made:

1. the temperature for which the exothermic peak appears decreases as the curing temperature increases;
2. this peak is more narrow for high curing temperature;
3. the magnitude of this peak increases as the curing temperature increases.

These results are consistent with the observations usually made for the curing reactions of thermosetting resins.

The results obtained during the second set of DSC experiments are reported in Figure 5. Two distinct curves are obtained, depending on the value of the isothermal temperature. When isothermal reactions were performed at T_{iso} lower than 40°C, a very large exothermic phenomenon made of two peaks is observed during the heating period [curves (f) and (g)]. We may also notice that the higher the value of T_{iso}, the lower the

value of T_m (T_m is the temperature of the minimum of the exothermic peaks) and the lower the reaction enthalpy. When isothermal experiments were performed at $T_{\text{iso}} > 40$°C, the enthalpic curves obtained during the second scan exhibit a single exothermic peak. Moreover, for this range of isothermal temperatures, we observe that the higher the value of T_{iso}, the higher the value of T_m and the lower the reaction enthalpy. The isothermal and residual enthalpies determined from these enthalpic curves are reported in Table II.

DISCUSSION

At first, let us discuss the DSC results. Following J. M. Abadie and Sakkas,[6] we may suppose that during the isothermal period, the enthalpy determined on the DSC curve is mainly the result of the styrene homopolymerization and its copolymerization with the C=C double bonds of the unsaturated polyester chains. The variations of this enthalpy (called ΔH_{cop}) with the isothermal
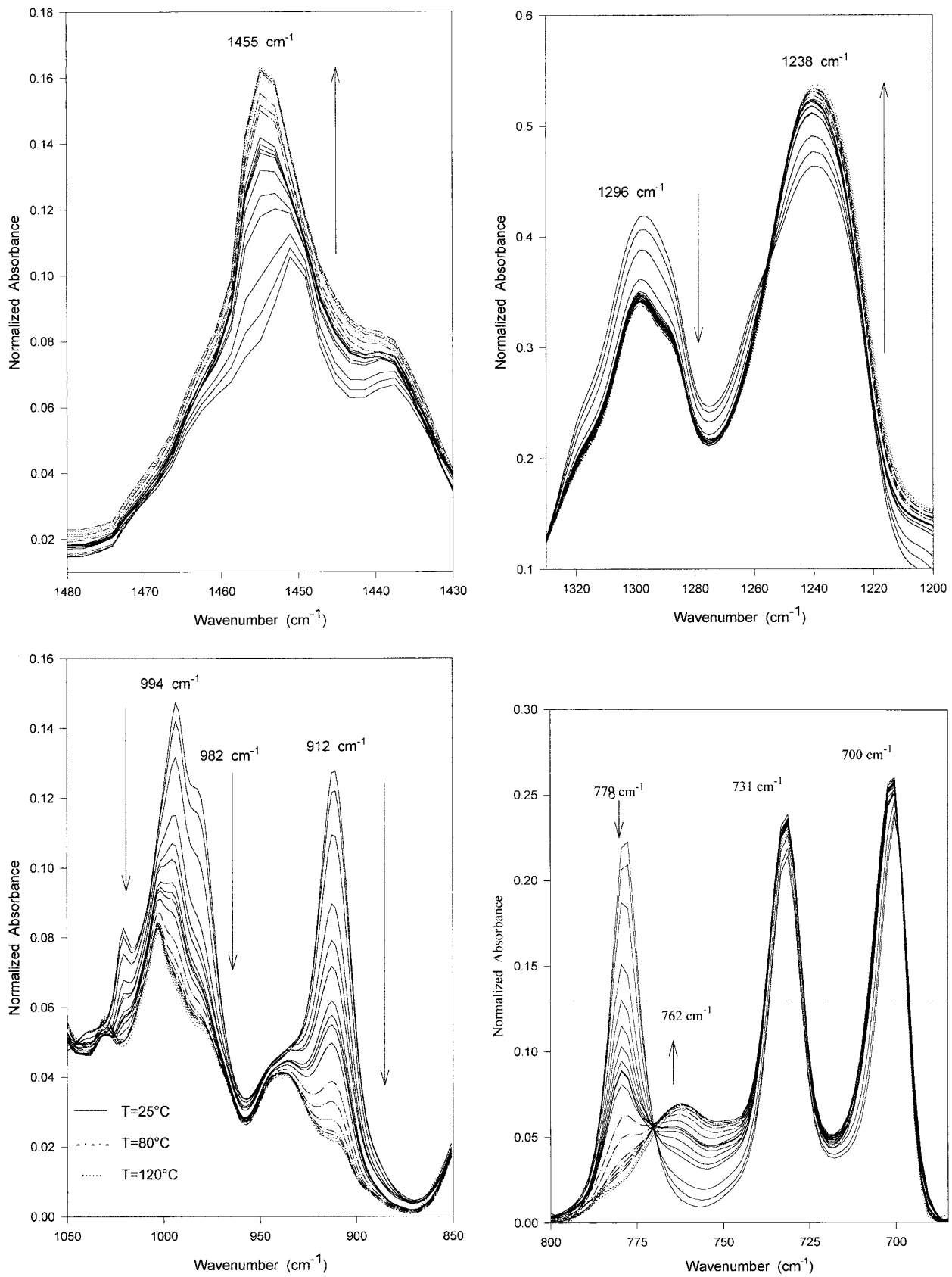
Figure 3 (*Continued from the previous page*)
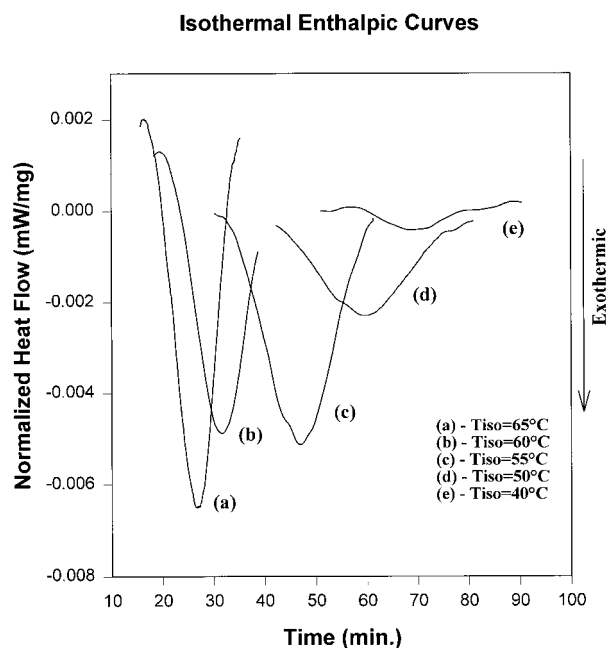
Isothermal Enthalpic Curves

Figure 4 Enthalpic curves obtained during the isothermal curing period, T_{iso} = (a) 65, (b) 60, (c) 55, (d) 50, and (e) 40°C.

curing temperature are reported in Figure 6. We observe that the greater the value of T_{iso}, the greater the value of ΔH_{cop}. This result agrees with those of Abadie and Sakkis,[6] also reported in Figure 6, and obtained on similar UPR materials. For $T_{iso} < 40$°C, no evidence of exothermic reactions
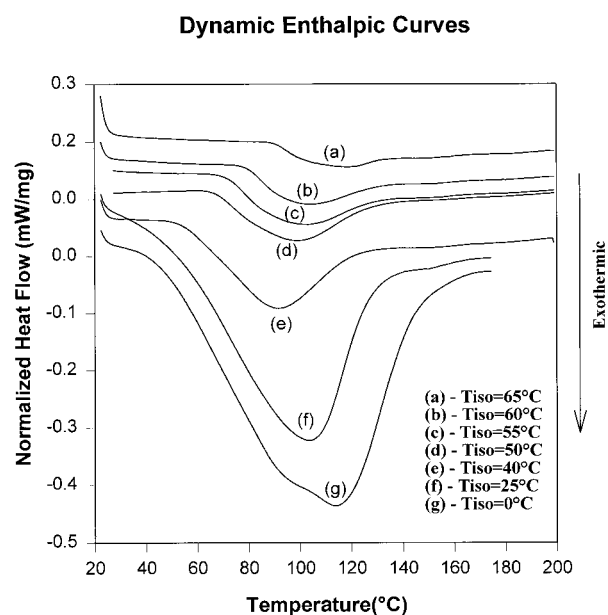
Dynamic Enthalpic Curves

Figure 5 Enthalpic curves obtained after the isothermal curing period at T_{iso} = (a) 65, (b) 60, (c) 55, (d) 50, (e) 40, (f) 25, and (g) 0°C.

Table II The Isothermal and Residual Enthalpy Values Determined from the Curves Presented in Figures 4 and 5

Isothermal Temperature (°C)	Isothermal Enthalpy (J g)	Residual Enthalpy (J g)
0	—	−342
10	—	−262
25	—	−216
40	—	−69
50	−260	−40
55	−270	−34
60	−300	−27
56	−336	−15

is observed on the DSC curve. This observation can be interpreted from two different ways; either no reaction exists, or the reaction is too weak to be detected by means of DSC measurements.

During the dynamic period, the enthalpy determined from the DSC curve is the result of the reactivity of the residual functions that have not reacted during the isothermal period. The variations of this enthalpy (called ΔH_{res}) with Tiso and the results obtained by Abadie and Sakkis[6] are also reported in Figure 6. For both systems, we
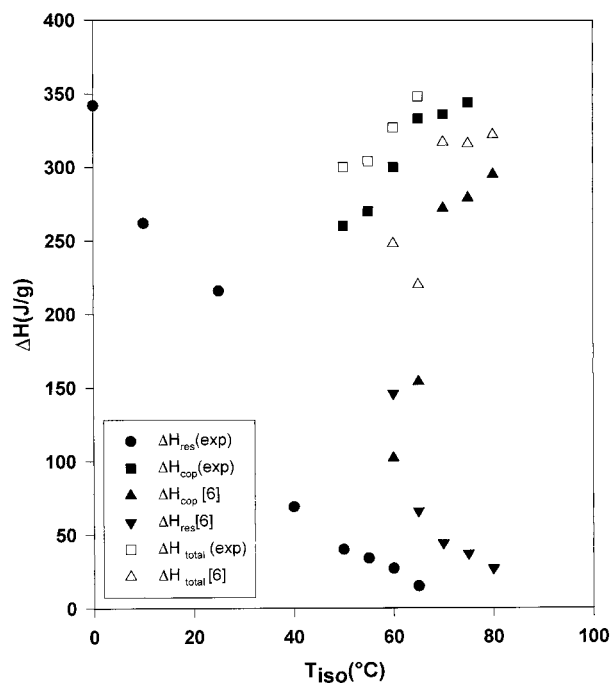

Figure 6 Variations with the isothermal curing temperature of the enthalpy of styrene homopolymerization and its copolymerization with the C=C double bonds of the unsaturated polyester chains.

observe that the greater the value of T_{iso}, the lower the value of ΔH_{res}. Nevertheless, in a range of Tiso (Tiso < 40°C), for which we have no value of ΔH_{cop}, we obtain a value of ΔH_{res}, which decreases when T_{iso} increases. This indicates that during the isothermal periods performed at T_{iso} < 40°C, homopolymerization of styrene and copolymerization or other type of reactions, although not detected by DSC, exist. This is the main difference between our results and those presented by Abadie and Sakkis.[6] On the other hand, Abadie and Sakkis[6] suppose that the quantity (ΔH_{res} + ΔH_{cop}) must remain constant. We do not find this result, except for the greater values of T_{iso}. It is known that evaporation of styrene can appear during the experiments. This leads to experimental errors in the determination of the different enthalpy values. To shake off this difficulty, we have performed thermogravimetry experiments. The results have shown that less than 5% w/w of styrene can be evaporated during the isothermal procedure and that the greater the value of T_{iso}, the lower the mass loss. This indicates that the variations of ΔH_{res} and (ΔH_{res} + ΔH_{cop}) cannot be interpreted only by this mass loss.

To discuss the IR data, we have first to assign at each characteristic absorption band a functional group. The band at 912 cm^{-1} is assigned by Yang and Lee[2] to the C=C bonds of the styrene monomer. For M. C. Mathias et al.,[3] this band appears at 915 cm^{-1} and is supposed to be the most useful band to follow the styrene conversion. Taking into account the IR measurement resolution, we conclude that our band at 912 cm^{-1} characterizes these C=C double bonds. According to Mathias et al.[3] and Yang and Lee,[2] the bands at 992 and 1630 cm^{-1}, also assigned to the styrene vinyl groups, are less useful because they overlap with the bands at 982 and 1646 cm^{-1} assigned to the double bonds of the polyester chains [Fig. 3(a) and (b)]. On the other hand, and from the results presented by Bellamy,[11] the band at 1296 cm^{-1} is also attributed to the C=C styrene; the bands at 982 and 1646 cm^{-1} are assigned to the C=C bonds of the polyester chains; while the bands at 1238, 1455, 1605, and 3027 cm^{-1} are assigned to the polystyrene formation. The bands at 2855 and 2936 cm^{-1} assigned to the —CH$_2$— functional groups come mainly from the polystyrene formation. Finally, according to Urban et al.,[12] three bands at 778, 731, and 700 cm^{-1} are observed. During the reaction, the magnitude of the band at 778 cm^{-1} decreases, while the remaining two bands are practically unaffected. We also observe that, at the same time, a new band at 762 cm^{-1}

appears in the spectrum. This band is attributed to the polystyrene formation. Considering the polystyrene tacticity, different possibilities exist. Urban et al.[12] have shown that the existence of an extended band, located at 762 cm^{-1}, is referred to an atactic configuration. As shown on Figure 3(f), our polystyrene exhibits at 762 cm^{-1} the characteristic of such atactic configuration.

To perform a quantitative analysis of the IR data, we have to normalize the IR absorbance. This normalization must be made because the sample thickness changes during the liquid to solid state transformation. Thus, we have to choose a standard, i.e., a group whose concentration does not change during the reactions. For the same type of resin, Yang and Lee[2] proposed to choose the —CH— peak at 2942 cm^{-1}. For our system, we notice that this peak cannot be used because it overlaps with the peak at 2936 cm^{-1} (peak assigned to the —CH$_2$— formation in polyester chains and polystyrene). On the other hand, Mathias et al.[3] proposed to choose the peak at 1730 cm^{-1} assigned to the carbonyl of the ester group (unchanged during the reactions). Our data show that this peak can be used for the normalization. Thus, using the peak magnitude at 1730 cm^{-1} for normalization and the method proposed by Yang and Lee[2] and Mathias et al.[3] for the calculation of a transformation rate (α) for each functional group, we may define for each IR peak the following relationships:

$$\alpha = 1 - \frac{\overline{A_t - z}}{\overline{A_o - z}}$$

(for the peaks that magnitude decreases)

$$\alpha = 1 - \frac{\overline{A_o - z}}{\overline{A_t - z}}$$

(for the peaks that magnitude increases)

where $\overline{A_o}$ and $\overline{A_t}$ are the normalized absorbances at $t = 0$ and after the polymerization, respectively. The value z is a correction to be made when the styrene is entirely absent, i.e., the peak area corresponding to overlapping with other bands. The variations with time of the rate of transformation (α) for the polystyrene formation (762 cm^{-1}), for the —CH$_2$— formation mainly in polystyrene chains (2936 cm^{-1}), for the double bonds in polyester chains (1646 cm^{-1}), and also for the C=C styrene monomer (778 and 912 cm^{-1}) are displayed in Figure 7 [curves(a)–(e), respectively]. All these curves exhibit the same time dependence behavior. At first, α increases drastically

(at short time) and then reaches a plateau corresponding to the maximal conversion rate (α_{max}). For each functional group, a specific value of α_{max} is obtained. During the first post-curing period, we observe an increase of the α_{max} values (about 5 to 25%), while the second post-curing period leads to a very small change (about 1 to 3%). The analysis of these data leads to the following remarks.

1. For the styrene consumption, a value of $\alpha_{max} \approx 95\%$ (taking into account the styrene evaporation) is obtained after the thermal cycle including post-curing and second post-curing periods, so 5% of styrene monomers do not react.
2. For the polystyrene formation, after the same thermal cycle, a value of α_{max} between 85 and 90% is obtained. Thus, these two first results show that styrene transformation leads mainly to polystyrene formation.
3. For the C=C polyester bonds, the value of α_{max} obtained, is about 87 to 90%. This indicates that $\approx 90\%$ of these double C=C bonds act either to graft polystyrene (copolymerization) or to graft together.
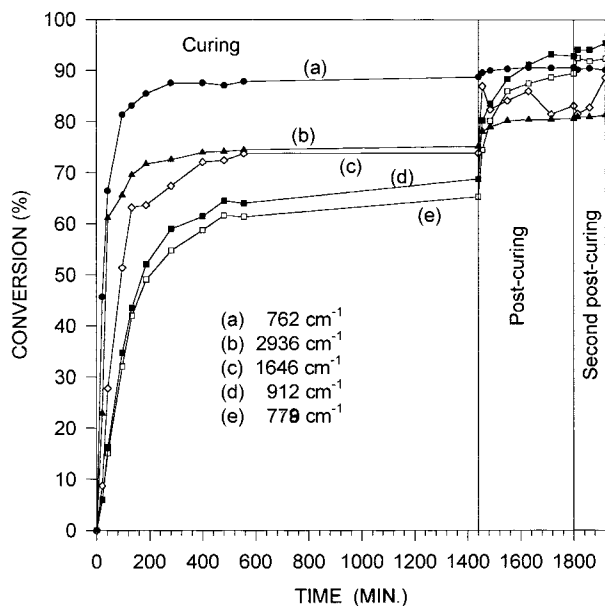4. The first post-curing period (performed at

Figure 8 Kinetics of the different reactions for the first curing period.

80°C) allows an increase of the α value of 5 to 25%, depending on the functionnal group. We may also notice that the shape of the curves obtained during the curing period and the post-curing period is similar: the transformation rate (α) increases at short time and then reaches a plateau. Thus, after 200 min at 80°C, no further chemical transformation appears. This result is in agreement with our previous DSC data.

5. During the second post-curing period performed at 120°C, very small variations of α are observed. Thus, this second post-curing period does not drastically modify the final conversion rate almost obtained at the end of the first post-curing period.

The shape af the (α, t) curves is typical of the behavior of thermosetting resins during the curing period[13] and can be described by the following relationship:

$$\alpha = \alpha_{max}(1 - e^{-t/\tau})$$

where τ is a time constant and α_{max} the rate of transformation reached for $t = t_\infty$. In our case,

Figure 7 Variations with time of the local rate of transformation (α) (a) for the polystyrene formation, (b) for the C=C consumption in polyester chains, (c) for the C=C styrene consumption, and (d) for —CH₂— formation in polyester and polystyrene chains.

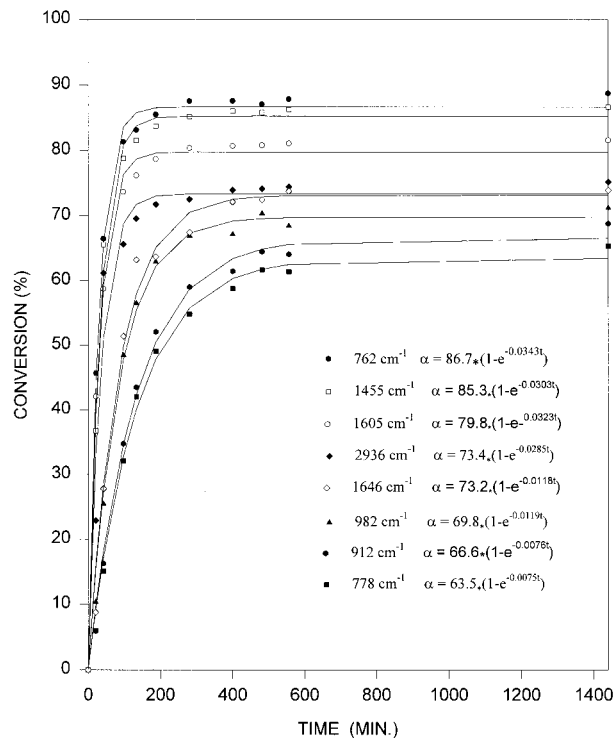**Table III Values of α_{max} and τ for Each Reaction and for the First Curing Period**

λ (cm^{-1})	Function	α_{max} (%)	τ (min)
762	Polystyrene	87	29
1455	Polystyrene	86	33
1605	Polystyrene	80	31
2936	Polystyrene	73	35
982	C=C Polyester	70	84
1646	C=C Polyester	73	85
778	Styrene	64	133
912	Styrene	67	131

α_{max} is experimentally determined, and the value of τ has to be adjusted to fit the data. The experimental data and the calculated curve are reported in Figure 8. The values of α_{max} and τ, obtained for each reaction and for the first curing period, are reported in Table III.

These data show that the time constants characteristic of polystyrene formation are lower than the one characteristic of polyester C=C consumption. The different functional groups characterizing the same transformation exhibit similar values of α_{max} and τ.

These observations show that the velocity of the polystyrene homopolymerization is faster than the velocity of its copolymerization with polyester chains. On the other hand, this indicates that when homopolymerization reaction is achieved, the copolymerization remains active. This result is also consistant with the DSC ones.

CONCLUSION

In this work, the curing kinetic of an unsaturated polyester resin, mixed with styrene as curing agent, was studied by means of DSC and IR spectroscopy. Investigations were made *in situ* during the curing, the post-curing, and second post-curing periods. The variations with the curing temperature (T_{iso}) of the enthalpy (ΔH_{cop}) characterizing the styrene homopolymerization and its copolymerization with the polyester chains were determined from isothermal DSC investigations, while the residual enthalpy (ΔH_{res}) was determined from nonisothermal measurements. We have found that the whole enthalpy ($\Delta H_{res} + \Delta H_{cop}$) depends on the isothermal temperature (T_{iso}). From FTIR investigations, the kinetics of the transformation rate of specific functionnal groups, characterizing the styrene homopolymerization and its copolymerization with the polyester chains, are described from the same mathematical law, which introduces two parameters: α_{max} and τ. We have shown that when the homopolymerization reaction is achieved, the copolymerization remains active (about 5% of the styrene monomers remain in the final solid state), and that a second post-curing period does not drastically modify the final conversion rate.

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