

# Monitoring the Cure of Unsaturated Polyester Resins by Pressure DSC and FTIR-PLC

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## Synopsis

A high pressure differential scanning calorimeter (DSC) and a Fourier transform infrared (FTIR) spectrometer with a prism liquid cell (PLC) were used to monitor the reaction kinetics of styrene-unsaturated polyester resins at elevated curing temperatures and pressures. The thermal method is easy to perform but provides only an overall reaction exotherm. The spectroscopic method can detect the detailed reaction mechanism of copolymerizations. It is, however, less quantitative and the calculation is much more time-consuming compared to the thermal analysis. Reactions of two unsaturated polyester resins with different molecular structure were measured by these two methods. Results showed that applying cure pressure on unsaturated polyester resins reduced the reaction rate but increased the final conversion. The styrene reaction was enhanced more than the polyester reaction at high curing temperatures.

## INTRODUCTION

Performing kinetic measurements during the reaction of thermoset polymers is inherently difficult since resin solidification due to chemical crosslinking obviates most solution techniques such as titration or standard size exclusion chromatography. Differential scanning calorimetry (DSC) is by far the most widely used experimental technique for measuring the reaction kinetics of thermoset polymers.<sup>1-5</sup> It has the advantages of simplicity, few limitations, and the capacity to yield simultaneous information regarding kinetics, energetics and thermal properties. However, DSC only measures the overall heat release during the reaction and cannot differentiate between chemical reactions in copolymerizations.

Spectroscopic methods like infrared, ultraviolet, or nuclear magnetic resonance can be much more specific to particular bond formation. The recent development of computer-assisted FTIR spectroscopy has enabled accurate monitoring of fast and complex polymerizations.<sup>6-10</sup> The disadvantages of spectroscopic methods are that the equipment is often more expensive, and data analysis is more time-consuming and less quantitative compared to differential scanning calorimetry. Although both thermal and spectroscopic methods have been used in the analysis of polymerizations, the measurements are often limited to slow reactions at atmospheric conditions. They are seldom

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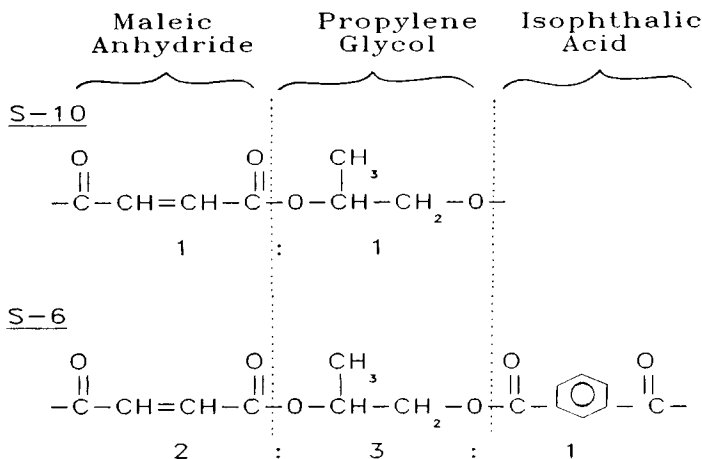


Fig. 1. Chemical structures and molar ratios of unsaturated polyester resins used in this study.

used at high pressures and high temperatures. Such reactions are, however, the ones which occur in most manufacturing processes and yet are less understood.

In this work, the curing of two unsaturated polyester resins was studied using a pressure DSC and a FTIR with a prism liquid cell. Unsaturated polyester resins are widely used in polymeric composites. With the aid of fillers, reinforcements, and additives, they are usually available in the form of compounds for compression molding (i.e., sheet molding compound, SMC), injection molding (i.e., bulk molding compound, BMC), resin transfer molding (RTM), and pultrusion. The objective of this study is to investigate the effect of molding pressure and temperature on the copolymerization of unsaturated polyester resins and styrene.

## EXPERIMENTAL

### Materials

Two unsaturated polyester resins were provided by the Ashland Chemical Co. These polyesters consist of maleic anhydride, isophthalic acid, and propylene glycol with differing molar ratios. Maleic anhydride provides  $\text{C}=\text{C}$  double bonds to the polyester resin, while propylene glycol and isophthalic acid serve as chain extenders. The aromatic ring structure of isophthalic acid makes the chain more rigid and more compatible with styrene monomer. The chemical structures of these resins are shown in Figure 1, and their compositions are listed in Table I. The number average molecular weights of these two resins are very close, 1580 g/mol for resin S-10 and 1700 g/mol for resin S-6, but the degree of unsaturation varies. The average number of  $\text{C}=\text{C}$  bonds per molecule is 10.13 for S-10 and 6.56 for S-6. Because of different chemical structure, the S-10 resin has a higher degree of unsaturation and a more flexible chain. On the other hand, the S-6 resin has a lower degree of unsaturation, has more rigid chain, and is more compatible with styrene monomer.

TABLE I  
Unsaturated Polyester Resins Used in This Work

	Unsaturated polyester resins	
	S-10	S-6
Composition (molar ratio)		
Maleic anhydride	1	2
Isophthalic acid	0	1
Propylene glycol	1	3
$\bar{M}_n$ (g/mol)	1580	1700
Unit MW/mol C=C(g/mol)	156	259
Avg. no. of C=C/polyester molecules	10.13	5.56
$\bar{r}$ (Å) <sup>a</sup>	18.70	20.99

<sup>a</sup> Root mean square end-to-end distance.<sup>17,18</sup>

Both polyester resins and styrene monomer were used as received without removing the inhibitor. *t*-Butyl perbenzoate (TBP) was used to initiate the reaction. The concentration of initiator was 1% by weight of total resin for all samples. Before the experiment, polyester resin was weighed and mixed with styrene monomer at a molar ratio of styrene/polyester C=C bonds = 2/1. To start the measurement, the solution was mixed with the initiator at room temperature, and was quickly sampled and loaded for kinetic measurements.

### Instrumentation and Procedures

A differential scanning calorimeter (DuPont 9900 DSC with a high-pressure cell) was used to measure the exotherm rate during the polymerization. All reactions were conducted in volatile aluminum sample pans. Sample weight was 2–3 mg with an empty pan as reference. Isothermal reactions at 120°C were ended when there was no further exotherm. Samples were then reheated from room temperature to 235°C in the scanning mode with a heating rate of 10°C/min to detect the residual reactivity left in the isothermally reacted samples. DSC cure was also carried out in the scanning mode from room temperature to 235°C at a heating rate of 10°C/min. The total heat of reaction for sample S-10 is 505 J/gm and that for sample S-6 is 395 J/gm, as determined in a previous work.<sup>11</sup> Both isothermal and scanning reactions were carried out at atmospheric pressure (0 psig), 2.07 MPa (300 psig), 3.45 MPa (500 psig), and 6.21 MPa (900 psig).

The exotherm data measured during the reaction can be converted into the reaction rate and conversion as a function of time based on the following calculations:

$$\frac{d\alpha}{dt} = \left( \frac{d\Delta H_t}{dt} \right) \left( \frac{1}{\Delta H_T} \right) \quad (1)$$

$$\alpha = \frac{\Delta H_t}{\Delta H_T} \quad (2)$$

where  $d\alpha/dt$  and  $\alpha$  are the reaction rate and conversion at a given time,  $\Delta H_t$  is the accumulated exotherm from  $t = 0$  to the given time, and  $\Delta H_T$  is the total reaction exotherm.

Several assumptions are made for the above calculation. First, thermophysical properties such as heat capacity, density, and heat of reaction are assumed unchanged during the reaction. This has been found acceptable for thermosetting and amorphous polymers.<sup>12-14</sup> Second, heat of reaction is the same for all reactions if there is more than one reaction taking place at the same time, which may be inappropriate for unsaturated polyester resins. For pressure DSC, the pressure may affect the measured reaction exotherm. This was calibrated by measuring the heat of fusion of a standard material, indium, at different pressures.

An FTIR spectrometer (Nicolet 20DX) was also used for kinetic measurements. A prism liquid cell (PLC) with an IR beam condenser (Harrick Scientific) was installed in the sample compartment of the FTIR spectrometer. This cell can be used at high temperatures (up to 200°C) and high pressures (up to 500 psig). An Irtran 2 (ZnS) miniprism with 45°-45°-90° angles and 36 mm<sup>2</sup> of sample surface was used for single bounce internal reflection measurement. The liquid cell consists of a sample mounting stage (lower plate) and a sample holding stage (upper plate). A heater (15 W, 120 V) was embedded in the sample mounting stage with a type K (nickel-chromium

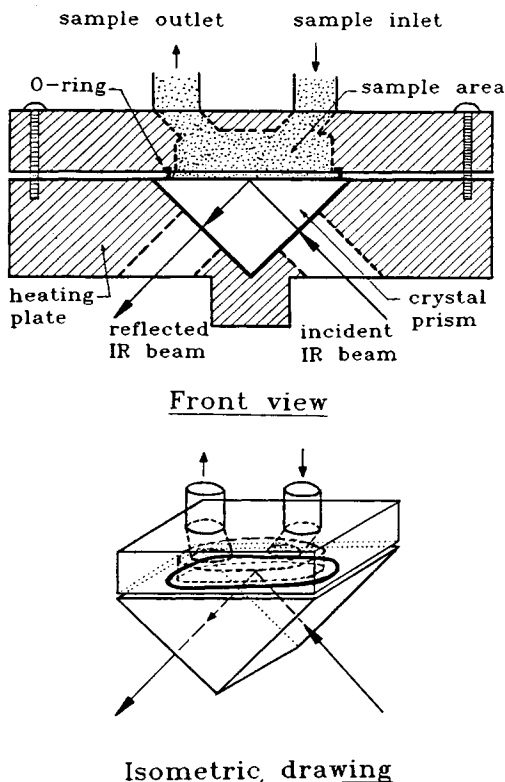


Fig. 2. Schematic drawing of prism liquid cell (PLC) used in FTIR measurements.

vs. nickel–aluminum silicon) thermocouple inserted in the upper plate for temperature control. Two 4.8 mm stainless steel tubes were connected to the upper plate for sample loading and pressurization. Pressure was provided by a nitrogen gas cylinder through the control of a pressure regulator. The whole setup was aligned for IR beam reflection by adjusting five mirrors on the beam condenser, after the setup was installed in the FTIR sample compartment. A schematic of the PLC is shown in Figure 2.

The liquid cell was first heated to the desired temperature before any measurements. A liquid sample was injected in the sample inlet tube and pushed into the liquid cell by applying a low nitrogen pressure. The pressure was then raised to the preset level and stayed there until the end of reaction. Two pressures (atmospheric pressure and 300 psig) were chosen in this study. Measurement was ended at a preset time. A MACRO program was written to control the action of the spectrometer. Scanning and sampling were started before the sample injection. Seven consecutive 1-s scans with a resolution of 4  $\text{cm}^{-1}$  and a gain of 16 were taken at each sampling time, and their interferogram average was stored in floppy disks for later data transform and analysis. The sampling interval was 20 s during the reaction.

Infrared analysis is based on the fact that each chemical group in a sample absorbs infrared radiation of some characteristic frequencies. During the reaction period, peaks of functional groups or characteristic linkages in the spectrum will change, which provides a means to measure the reaction kinetics. In the reflection mode, the IR absorption is limited to the sample near the prism surface. Therefore, the measured data represent the reaction profile of resins near the mold surface. To compensate for the change of optical contact between the sample and the prism surface during the polymerization, a ratio was taken between the absorbance of the group of interest and that of an internal standard, i.e., a chemical group whose concentration does not change during the reaction. In this study, the C—H peak around 2942  $\text{cm}^{-1}$  was chosen as the internal standard, and the peak area was used to calculate the absorbance. Reaction conversion can be determined from the change of the normalized absorbance,

$$\alpha = 1 - \bar{A}_t / \bar{A}_0 \quad (3)$$

where  $\bar{A}_0$  and  $\bar{A}_t$  are the normalized absorbances of the monomer functional group before the reaction and after a reaction time  $t$ . All IR spectra in this study were expressed in absorbance.

## RESULTS AND DISCUSSION

Figures 3 and 4 show the isothermal reaction rate profiles and conversion profiles of sample S-10 measured by DSC at different pressures. Increasing cure pressure reduced the reaction rate, which is indicated by the increase of the onset time and peak time listed in Table II. As shown in Table II and Figure 4, there was a significant increase of final conversion when pressure was applied to the reaction system [i.e., 45% at 0 psig, 69.5% at 300 psig (2.07 MPa)]. These results agreed well with a similar work carried out by Lee and Han.<sup>15</sup> For sample S-10, the level of pressure seemed to have a very minor

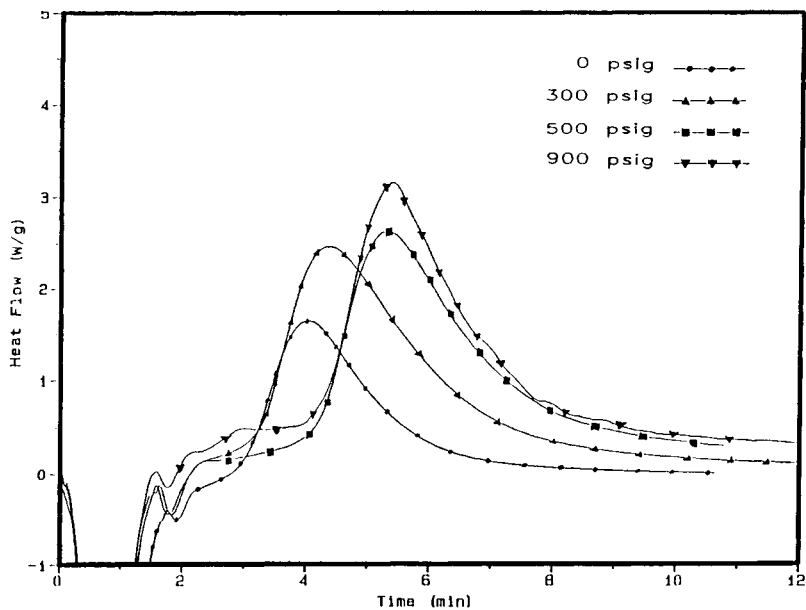


Fig. 3. Reaction rate profiles of sample S-10 at 120°C by isothermal DSC measurements: (●) 0 psig; (▲) 300 psig; (■) 500 psig; (▼) 900 psig.

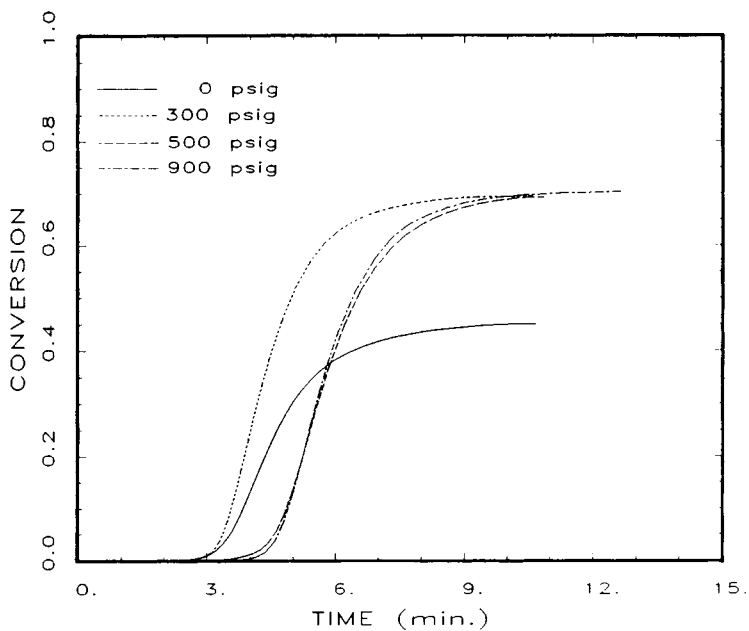


Fig. 4. Conversion profiles for sample S-10 at 120°C by isothermal DSC measurements: (—) 0 psig; (···) 300 psig; (---) 500 psig; (-·-·) 900 psig.

TABLE II  
Isothermal Cure of Samples S-10 and S-6 at 120°C

Sample	Pressure (psig)	Onset time (min)	Peak time (min)	Isothermal		Isothermal + scan	
				$\Delta H$ (J/g)	Conversion (%)	$\Delta H$ (J/g)	Conversion (%)
S-10	0	2.30	3.71	227	45.0	323	64.0
	300	2.50	4.33	351	69.5	424	84.0
	500	3.00	5.28	350	69.3	427	84.6
	900	3.50	5.40	355	70.3	419	83.0
S-6	0	1.50	2.24	227	70.1	341	86.3
	300	1.80	2.57	291	73.7	360	91.1
	500	1.80	2.74	355	89.9	405	100.0
	900	2.00	3.02	349	88.4	403	100.0

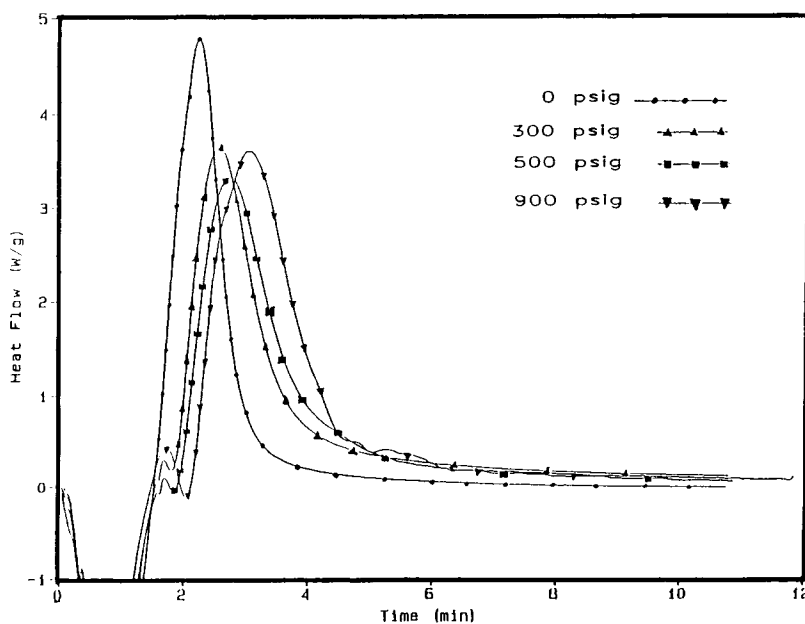


Fig. 5. Reaction rate profiles of sample S-6 at 120°C by isothermal DSC measurements: (●) 0 psig; (▲) 300 psig; (■) 500 psig; (▼) 900 psig.

effect on the final conversion when the pressure was higher than 300 psig (2.07 MPa). When the isothermally reacted samples were reheated from room temperature to 235°C, the final conversions of all samples increased (64% at 0 psig, around 84% at high pressures) as shown in Table II. Figures 5 and 6 show the isothermal reaction rate profiles and conversion profiles of sample S-6 measured by DSC at different pressures. Compared to Figures 3 and 4, sample S-6 had a higher reaction rate and a higher conversion than sample S-10 at all pressures. Again, increasing cure pressure reduced the reaction rate but increased the final conversion. Unlike sample S-10, the level of pressure had a strong effect on the final conversion of sample S-6. At 0 and 300 psig (2.07

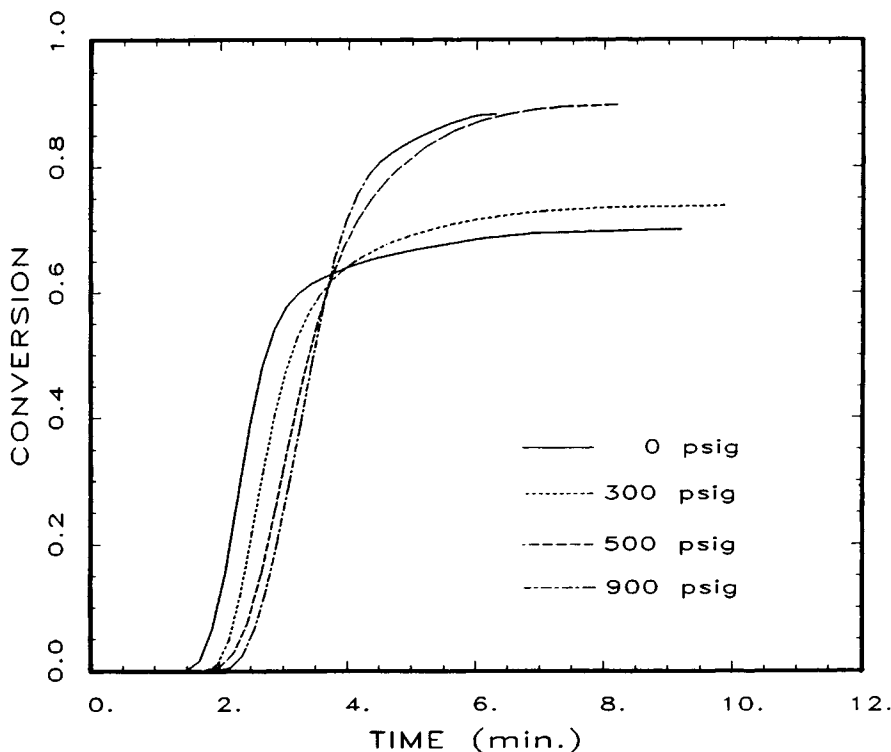


Fig. 6. Conversion profiles of sample S-6 at 120°C by isothermal DSC measurements: (—) 0 psig; (···) 300 psig; (---) 500 psig; (-·-·) 900 psig.

MPa), the final conversions were 70.1 and 73.7%. This value increased to 89.9% at 500 psig (3.45 MPa) and 88.4% at 900 psig (6.21 MPa).

The reaction rate profiles for samples S-10 and S-6 from DSC scanning (nonisothermal) runs are shown in Figures 7 and 8, respectively. The results show that the reaction rate, indicated by the onset temperature and the peak temperature (listed in Table III), seems to be relatively independent of the molding pressure for both samples in the nonisothermal condition. The conversion profiles for both samples, shown in Figures 9 and 10, are, however, pressure-dependent. Applying pressure increased the resin conversion. At the given scanning rate (i.e., 10°C/min), both samples showed a low conversion at atmospheric pressure. Adding pressure to the reaction system increased the final conversion greatly. The final conversion went through a maximum at 300 psig (2.07 MPa) for sample S-10 as the pressure was increased from atmospheric pressure to 900 psig (6.21 MPa). Such a maximum, however, was not found for sample S-6 in the same pressure range. It was interpreted by Lee and Han<sup>15</sup> that adding pressure has two competing effects on the curing behavior of unsaturated polyester resins. The decrease of the free volume due to pressure hinders the curing reaction, while the thermodynamic effect favors the reaction with increasing pressure since the curing reaction of unsaturated polyester resins is accompanied by a decrease in volume. When the pressure is higher than a certain level, the free volume effect may become predominant



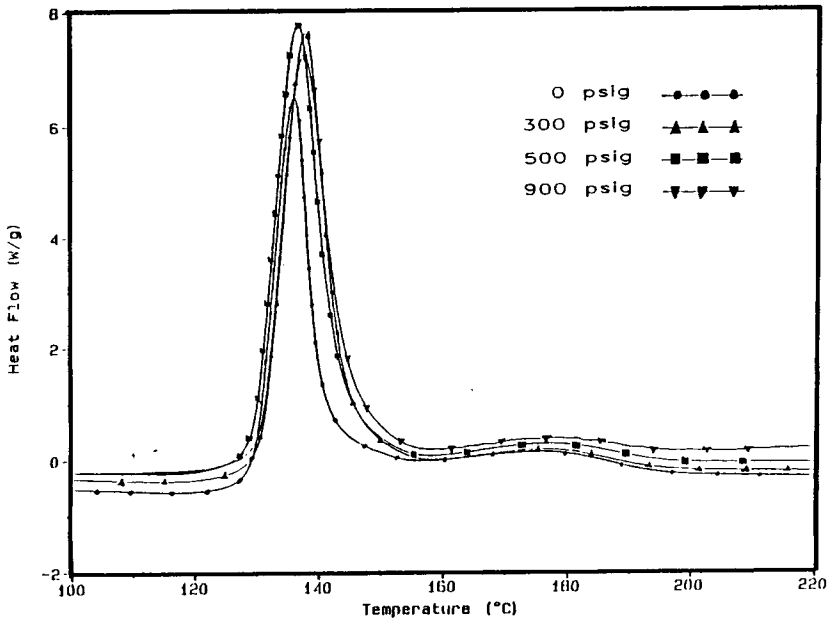


Fig. 7. Reaction rate profiles of sample S-10 by scanning DSC measurements: (●) 0 psig; (▲) 300 psig; (■) 500 psig; (▼) 900 psig.

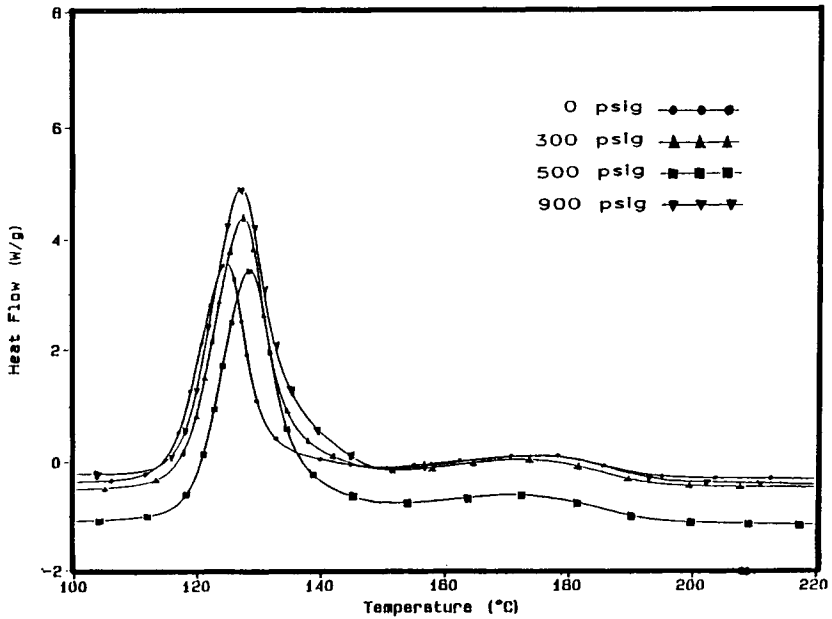


Fig. 8. Reaction rate profiles of sample S-6 by scanning DSC measurements: (●) 0 psig; (▲) 300 psig; (■) 500 psig; (▼) 900 psig.

TABLE III  
Nonisothermal Cure of Samples S-10 and S-6 at 120°C

Sample	Pressure (psig)	Onset temp (°C)	Peak temp (°C)	Conversion (%)
S-10	0	121	136	90.5
	300	120	138	100.0
	500	120	136	100.0
	900	118	137	94.9
S-6	0	105	125	92.0
	300	102	127	100.0
	500	104	128	100.0
	900	106	127	100.0

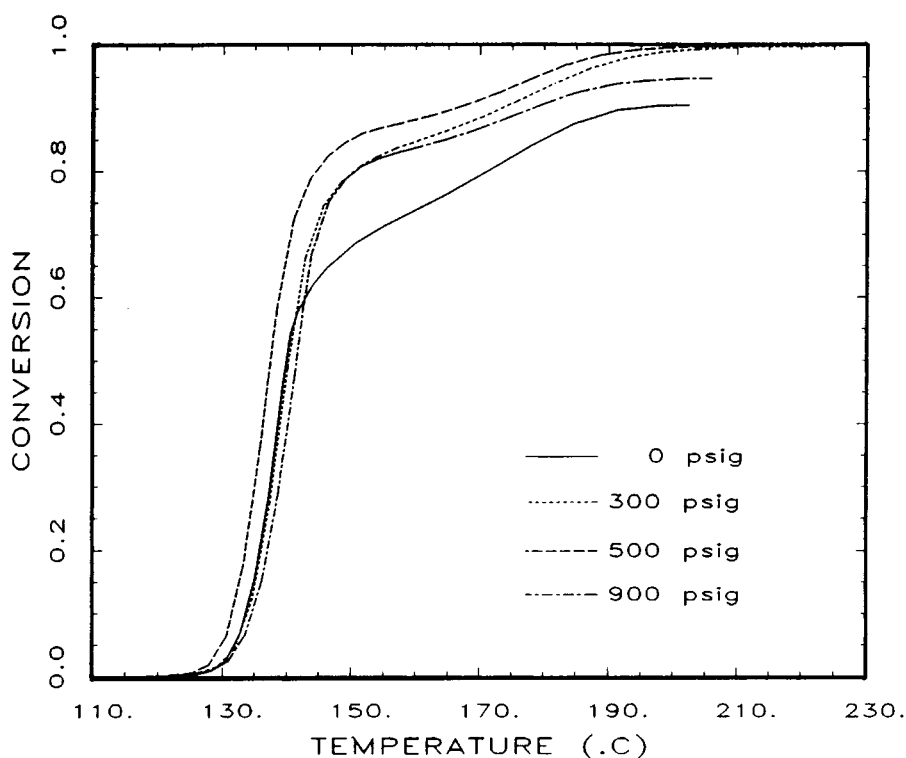


Fig. 9. Conversion profiles of sample S-10 by scanning DSC measurement. (—) 0 psig; (···) 300 psig; (---) 500 psig; (-·-·) 900 psig.

over the thermodynamic effect. Our results imply that different polyester resins may have different responses to these two effects.

Figure 11 shows the treated FTIR spectra from 850 to 1050  $\text{cm}^{-1}$  for the reaction of sample S-10 at 120°C and 300 psig (2.07 MPa) at three different reaction times. The raw spectra were covered by a great deal of noises because the IR beam throughput has been reduced to about 10% of the original value due to the use of PLC setup in the internal reflection mode. One way to

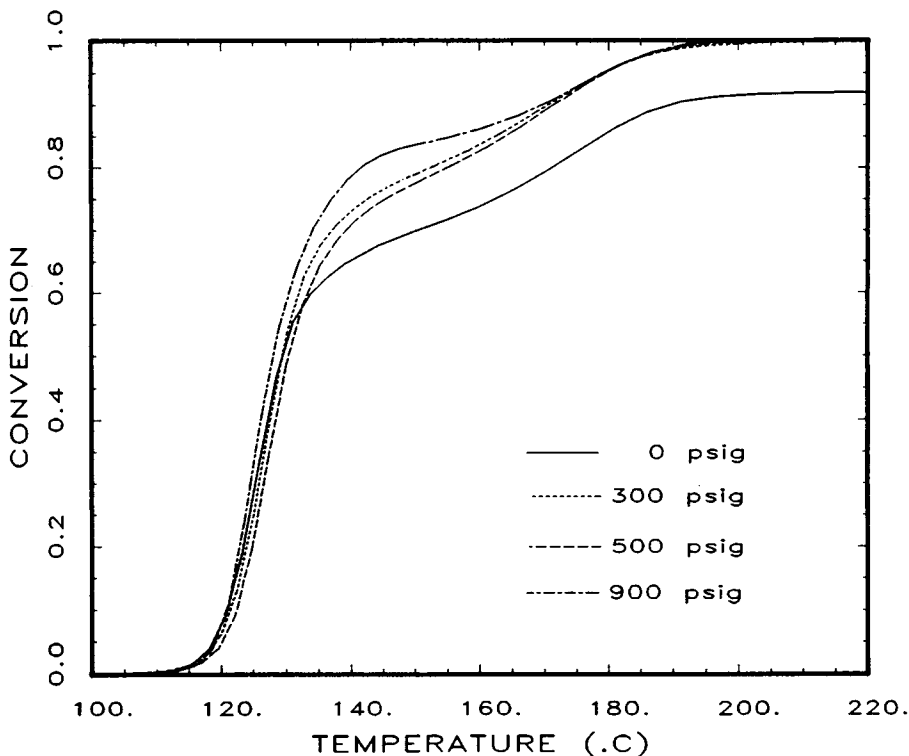


Fig. 10. Conversion profiles of sample S-6 by scanning DSC measurements. (—) 0 psig; (···) 300 psig; (---) 500 psig; (-·-) 900 psig.

increase the signal-to-noise ( $S/N$ ) ratio is to increase the number of scanning for each spectrum. This is, however, not possible for a fast reaction system such as styrene-unsaturated polyester resins at high temperatures. A spectra-smoothing method provided by Nicolet was used to solve the noise problem by averaging the values of every nine consecutive points for the center point of the selected nine points. The spectra shown in Figure 11 are the ones after applying the nine-point smoothing method three times on the raw spectra. This method is able to provide smooth spectra, but the accuracy and resolution of the data are reduced.

The characteristic peaks of styrene monomer and polyester vinyls in the internal reflection mode are different from those in the transmission mode,<sup>10,11,16,17</sup> and they tend to shift slightly during the reaction. The styrene's C—C deformation peaks are located around 900–910  $\text{cm}^{-1}$  (styrene-I) and 987–992  $\text{cm}^{-1}$  (styrene-II) in the internal reflection mode instead of 912 and 992  $\text{cm}^{-1}$  in the transmission mode. The deformation peak of the C=C bonds of unsaturated polyester resins (PES C=C) is around 974–978  $\text{cm}^{-1}$  in the internal reflection mode instead of 982  $\text{cm}^{-1}$  in the transmission mode. Because the absorbance spectra in the internal reflection mode are somewhat different from those in the transmission mode, the calibration curves from the transmission measurements<sup>11,17</sup> cannot be applied for the reflection results. A new set of calibration curves for styrene and unsaturated polyesters in the

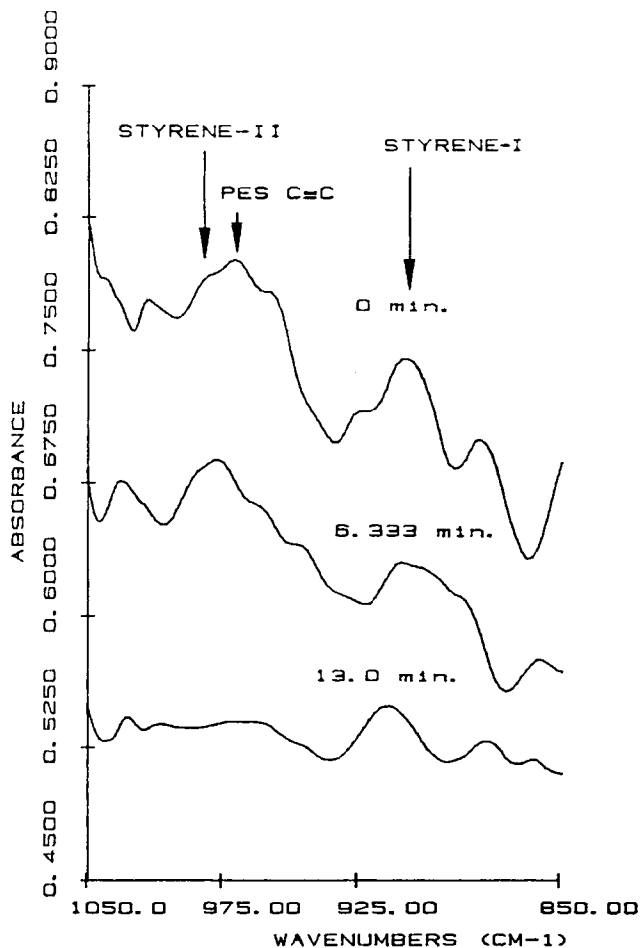


Fig. 11. Treated FTIR-PLC spectra for sample S-10 reacted at 120°C and 300 psig (2.07 MPa).

internal reflection mode were established by preparing a set of monomer-dichloro-methane solutions of known concentrations. The calibration curves for styrene-I, styrene-II, and PES C=C based on the change of peak area are shown in Figure 12. A linear relationship between peak area and monomer concentration was obtained for all three peaks, which was used to calculate the conversions during the polymerization. A subtraction method<sup>10</sup> was applied for solving the overlapping peaks of styrene-II and PES C=C.

Figures 13 and 14 show the conversion for each individual reaction in sample S-10 at 120°C and two different pressures [0 and 300 psig (2.07 MPa)] by FTIR-PLC measurements. In both cases, the styrene conversion was higher than the conversion of polyester C=C bonds. Similar results were found for sample S-6 at 120°C and 300 psig (2.07 MPa) as shown in Figure 15. Compared with Figure 6, the overall conversions resulted from pressure DSC and FTIR-PLC agree with each other fairly well as shown in Figure 16 for the reaction of sample S-10 at 120°C and 300 psig (2.07 MPa). Similar to the DSC results, FTIR measurements in Figures 13, 14, and 15 also show that the S-6

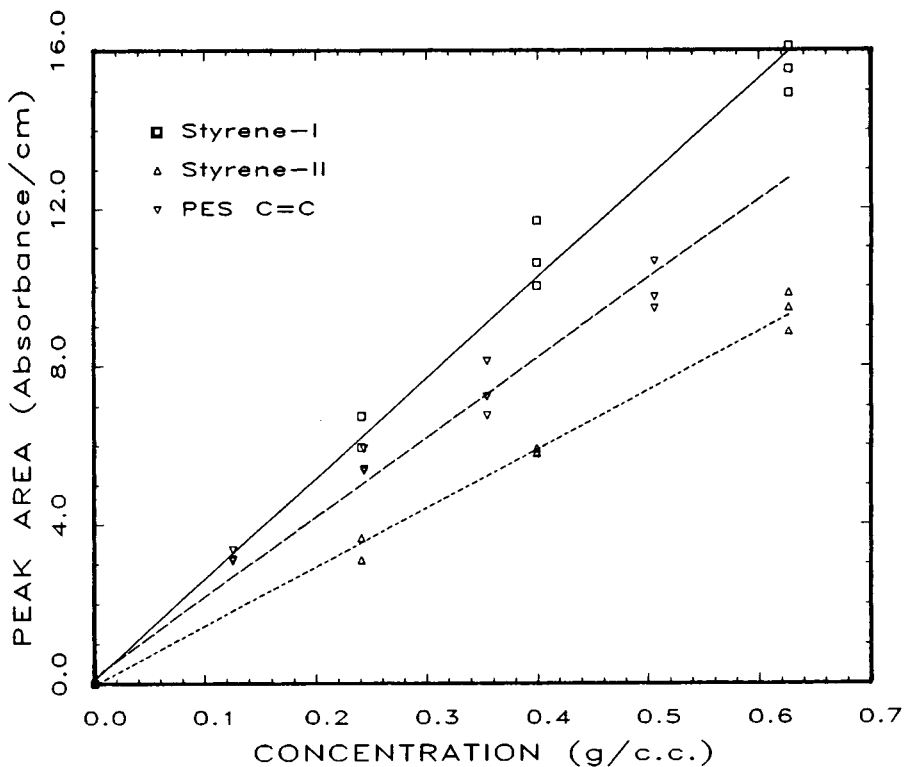


Fig. 12. FTIR-PLC calibration curves for peaks styrene-I (□), styrene-II (Δ), and PES C=C (▽) bonds at 120°C.

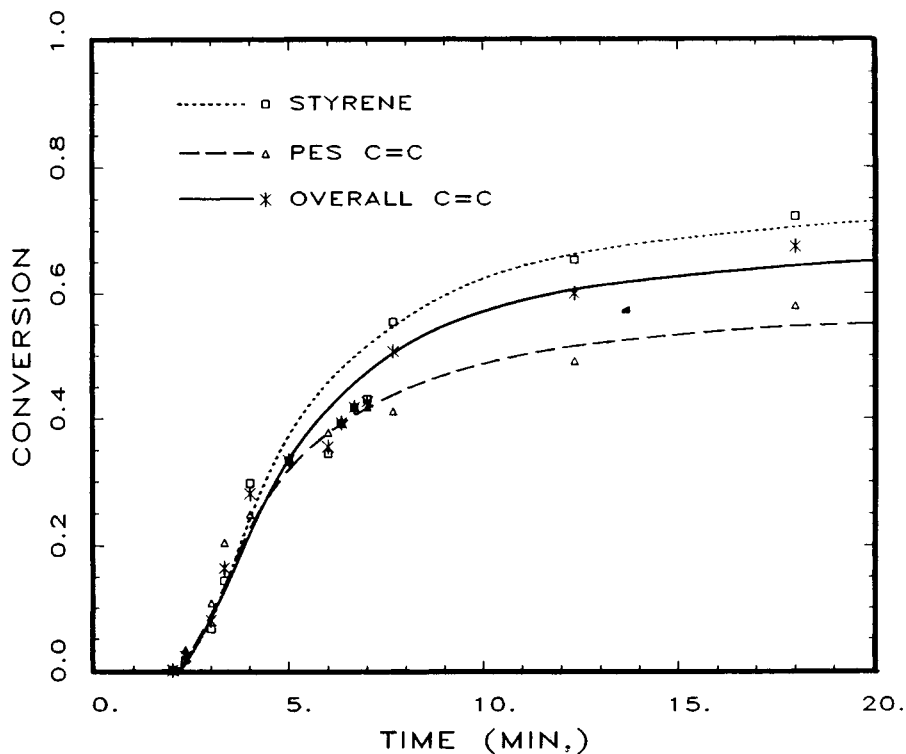


Fig. 13. Conversion profiles of sample S-10 at 120°C and 0 psig by FTIR-PLC measurements: (---□) styrene; (---Δ) PES C=C; (---\*) overall C=C.

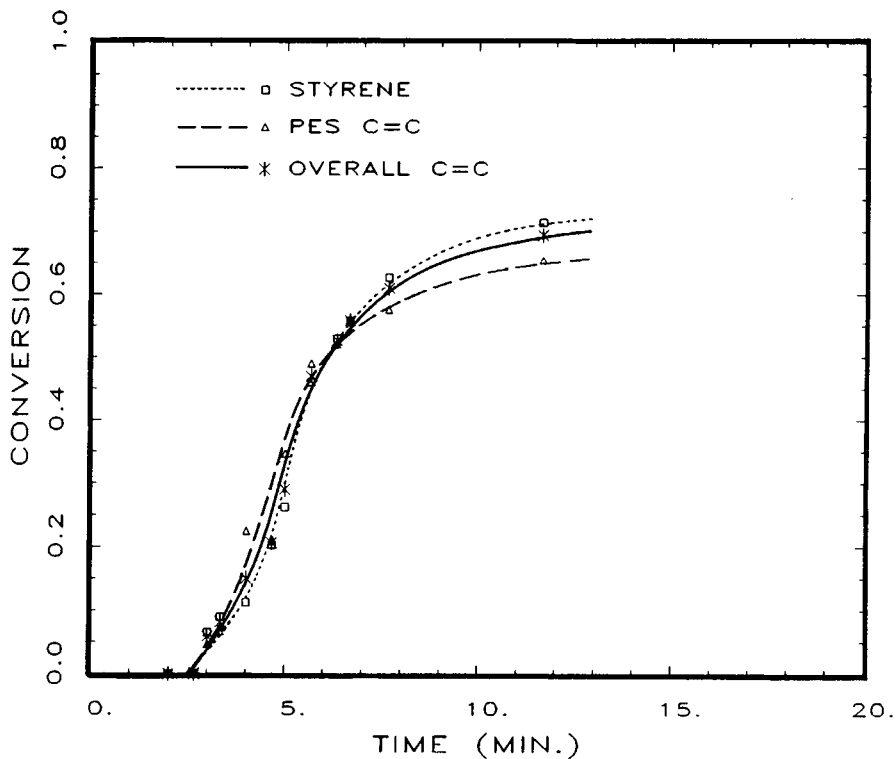


Fig. 14. Conversion profiles of sample S-10 at 120°C and 300 psig (2.07 MPa) by FTIR-PLC measurements: (---□) styrene; (---Δ) PES C=C; (—\*) overall C=C.

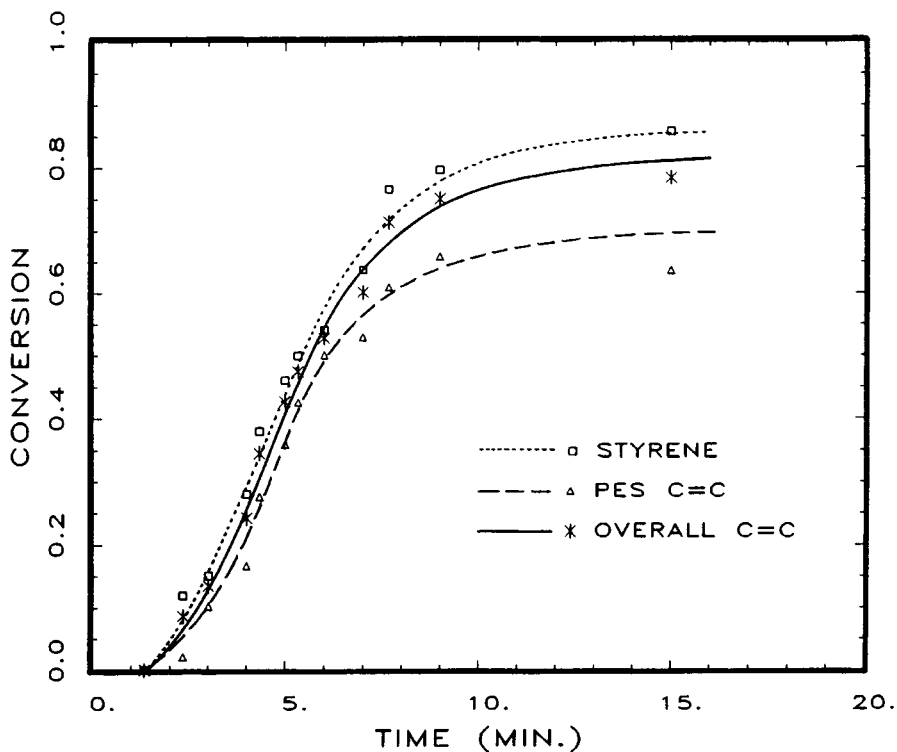


Fig. 15. Conversion profiles of sample S-6 at 120°C and 0 psig by FTIR-PLC measurements: (---□) styrene; (---Δ) PES C=C; (—\*) overall C=C.

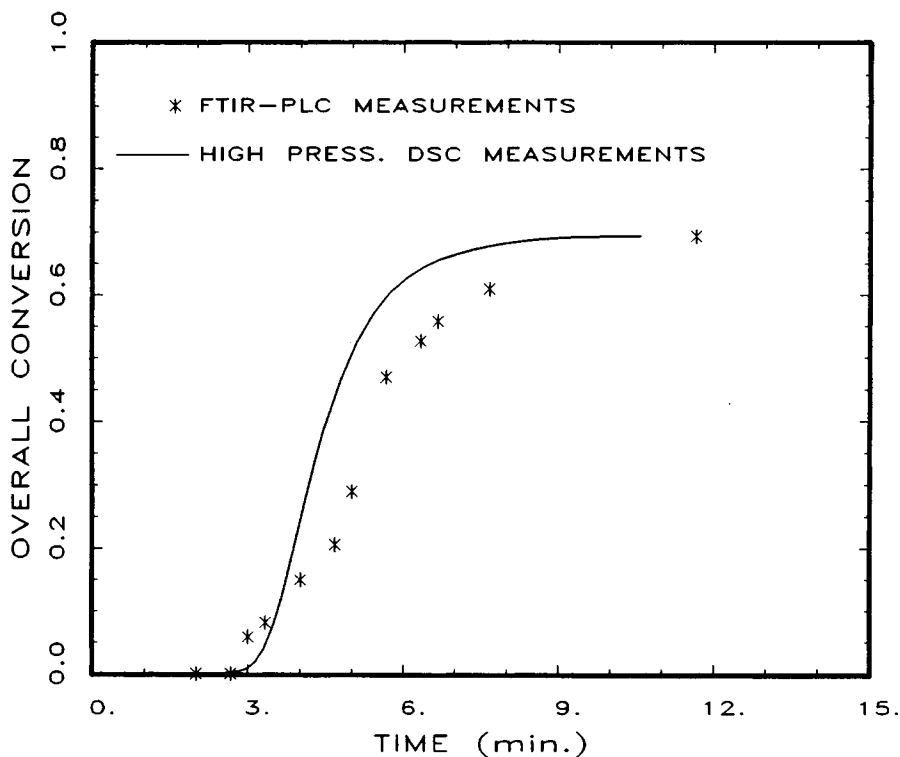


Fig. 16. Comparison of conversion vs. time measured by high pressure DSC (—) and FTIR-PLC (\*) for sample S-10 reacted at 120°C and 300 psig (2.07 MPa).

resin reacts faster than the S-10 resin, and pressure tends to slow down the initial reaction rate of unsaturated polyester resins but allows the reaction to reach a higher level of final conversion.

The reaction of unsaturated polyester resins is a free radical chain growth crosslinking copolymerization between the styrene monomer and the unsaturated polyester molecule. Polyester molecules form the backbone of the polymer network, while styrene monomers serve as chainlinking agent to link the adjacent polyester molecules. Since the network structure of polyester resins depends strongly on the copolymerization mechanism, information regarding the relative conversion of styrene vs. polyester C=C bonds is of great interest. Figures 17 and 18 reveal such plots, where the diagonal dashed line represents the azeotropic reaction and the lower dashed line represents an alternating copolymerization.<sup>10,16</sup> For sample S-10, results shown in Figure 17 reveal that the curing of unsaturated polyester resins at 120°C has a copolymerization route located between the azeotropic and the alternating copolymerization lines in the early stage of reaction. The copolymerization gradually shifts above the azeotropic line. At low conversions, the polyester C=C bond reaction is more favorable than the styrene reaction due to the intramolecular cyclization of polyester chains.<sup>16-18</sup> At high conversions, the styrene reaction becomes predominant as indicated by the up-bending curve. This is because polyester molecules are much more immobile than styrene monomers at high

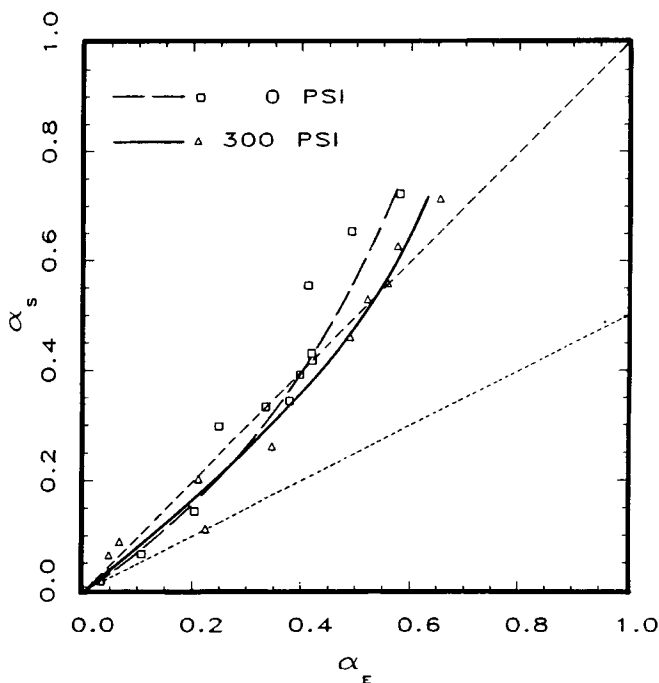


Fig. 17. Relative conversion of styrene ( $\alpha_S$ ) vs. polyester C=C bonds ( $\alpha_E$ ) for sample S-10 at 120°C and two pressures: (—□) 0 psig; (—△) 300 psig (2.07 MPa).

conversions. Adding pressure seems to slightly increase the polyester C=C bond conversion at high conversions as shown in Figure 17. Figure 18 compares styrene conversion vs. polyester C=C bond conversion at 120°C and 300 psig for samples S-10 and S-6. At the given conditions, the styrene conversion of S-6 was higher than that of S-10 at a constant polyester C=C bond conversion through the entire reaction course.

The effect of temperature on the curing of styrene-unsaturated polyester resin was also studied in this work. In addition to the 120°C cure, samples S-10 and S-6 were also cured at 30 and 60°C. One percent methyl ethyl ketone peroxide (MEKP) with 0.25% cobalt naphthenate was used as the initiator for the reactions at 30 and 60°C, while 1% TBP was used for the 120°C cure. The curing results at 30 and 60°C were obtained by FTIR measurements in the transmission mode,<sup>16</sup> while the 120°C curing results were obtained by FTIR-PLC measurements. Curing temperature can change the relative reaction rates because each reaction has its own activation energy. Figure 19 shows the effect of cure temperature on the styrene conversion vs. polyester C=C bond conversion for sample S-10. Increasing the cure temperature tends to shift the curve toward the azeotropic reaction line. The sample S-6 also shows the similar trend.<sup>17</sup> The results shown in Figure 19 indicate that increasing the cure temperature favors the styrene reaction. In other words, the styrene reaction is enhanced more than the polyester C=C bond reaction by increasing the cure temperature. This implies that the activation energy of styrene reaction is lower than that of polyester C=C bond reaction.



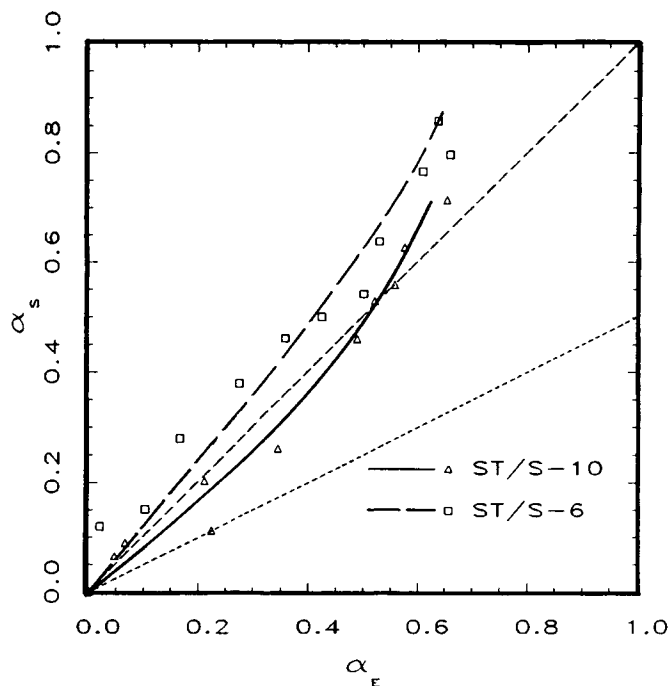


Fig. 18. Relative conversion of styrene ( $\alpha_S$ ) vs. polyester C=C bonds ( $\alpha_E$ ) for samples S-10 ( $\triangle$ ) and S-6 ( $\square$ ) at 120°C and 300 psig (2.07 MPa).

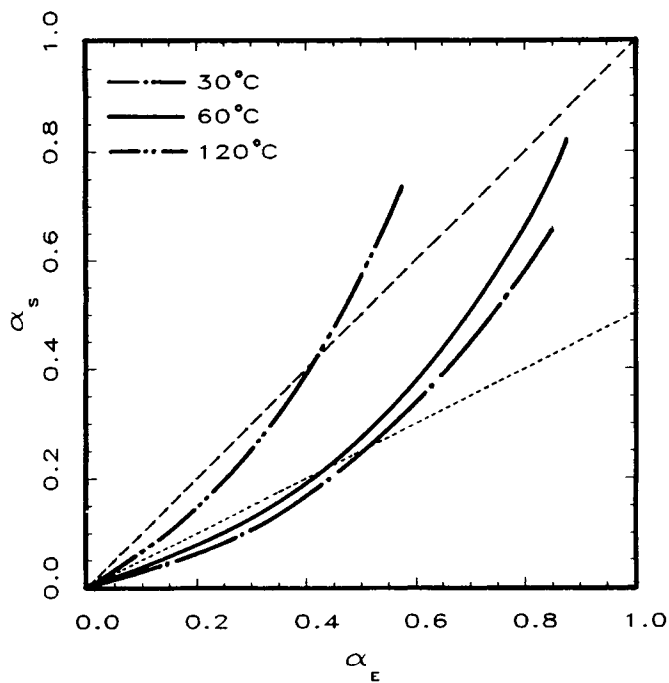


Fig. 19. Relative conversion of styrene ( $\alpha_S$ ) vs. polyester C=C bonds ( $\alpha_E$ ) for sample S-10 at 0 psig and three temperatures (°C): (---) 30; (—) 60; (····) 120.

## CONCLUSIONS

Both pressure DSC and FTIR-PLC are useful for the kinetic measurement of unsaturated polyester resins at high temperatures and pressures. Within the experimental error, the results from both methods agree with each other fairly well. The thermal method is easy to perform but only provides an overall reaction exotherm. The spectroscopic method can detect the detailed reaction mechanism of copolymerizations. It is, however, less quantitative, and the calculation is much more time-consuming. FTIR-PLC in the internal reflection mode provides a good means to measure fast reactions at high pressures. It can also be used for samples with strong IR light scattering (e.g., samples with fillers).

There are, however, several limitations associated with IR measurement in the reflection mode. First, the throughput of IR light intensity in the internal reflection mode is much lower than that in the transmission mode even with a beam condenser. To obtain spectra with a high signal-to-noise ratio, more scans need to be taken at each sampling time. For the materials studied, three consecutive scans at each sampling time could provide spectra with a low noise level in our FTIR if it was in the transmission mode.<sup>10,11</sup> In the internal reflection mode, even we increased the number of scans to seven and used a nine-point smoothing method to reduce noise, the spectra obtained still had a low signal-to-noise ratio as shown in Figure 11. Because of high reaction rates, not very many scans could be taken at each sampling time. Better results can be obtained by using a FTIR with higher scanning rate, higher resolution, and a more sensitive detector.

The second limitation of PLC in the internal reflection mode is that the optical contact between the sample and the prism surface tends to change during the polymerization, primarily resulting from the polymerization shrinkage. This further reduces the intensity of IR beam and makes the calculation more difficult, especially at high conversions.

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