

Comparison of Thermal and Infrared Spectroscopic Analyses in the Formation of Polyurethane, Unsaturated Polyester, and Their Blends

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Synopsis

Differential scanning calorimetry (DSC) and infrared spectroscopy (IR) are two widely used techniques for the measurement of polymerization kinetics. Reactions of several thermoset polymers: a polyurethane, two unsaturated polyester resins, and polyurethane-polyester blends, were measured by these two methods. Results indicate that the thermal method is easy to use, and can generate both kinetic and thermal information. It is, however, less accurate and cannot detect detailed reaction mechanisms because the measurement relies upon the overall heat generation during reaction. Fourier transform infrared (FTIR) spectroscopy, on the other hand, can provide detailed kinetic information for multicomponent reactions such as styrene-unsaturated polyester and polyurethane-polyester blends. Data analysis, however, is more tedious and requires reliable calibration. For an accurate kinetic measurement, both methods should be used because the results from both experiments can calibrate each other.

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 (SEC). Differential scanning calorimetry (DSC) is by far the most widely used experimental technique for measuring the reaction kinetics of thermoset polymers.¹⁻⁵ 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 reaction and cannot differentiate between chemical reactions and physical changes such as crystallization, phase formation, etc. It is also less sensitive at high conversions since measurement relies on the heat of generation of the reaction.

Spectroscopic methods like infrared (IR), ultraviolet (UV), or nuclear magnetic resonance (NMR) can be much more specific to particular bond formation. The recent development of computer-assisted Fourier transform infrared (FTIR) spectroscopy has enabled accurate monitoring of fast and complex polymerizations.⁶⁻¹⁰ 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

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both thermal and spectroscopic methods have been used in the analysis of polymerizations, the results from both methods are seldom compared in the quantitative manner.

In this work, the polymerizations of two widely used thermoset polymers, a polyurethane and unsaturated polyester resins, and their blends are studied using differential scanning calorimetry and infrared spectroscopy. The objective is to compare quantitatively the applicability of these two methods in the measurement of polymerization kinetics.

EXPERIMENTAL

Materials

The polyurethane chosen for this study consists of a poly(ϵ -caprolactone triol) (TONE310, Union Carbide) with a number-average molecular weight of 900 and 99% primary hydroxyl groups, and a liquid form of 4,4'-diphenylmethane diisocyanate (143L, Dow). They were used as received at equal stoichiometry. Dibutyltin dilaurate (DBTDL, T-12, M & T Chemicals) was used as a catalyst with a concentration of 7.6 ppm of triol. Table I lists the materials and compositions used in the polyurethane reaction. Isothermal polymerizations were carried out at 60°C.

Two unsaturated polyester resins were used in this study. They consist of maleic anhydride, isophthalic acid, and propylene glycol with differing molar ratios. The average number of C=C bonds per molecule ranges from 6.56 for sample S-6 to 10.13 for sample S-10. The number average molecular weights of these two resins are 1700 g/mol for S-6 and 1580 g/mol for S-10. Styrene was added to adjust the molar ratio of styrene to the unsaturation on polyester molecules to 2:1. Methyl ethyl ketone peroxide (MEKP, Lucidol) with 33% cobalt naphthanate promoter was used as an initiator. The concentration of the initiator and promoter was 1% by weight of total resin for both samples. Table II lists the materials and compositions used in the styrene-polyester reaction. Isothermal polymerizations were carried out at 30°C.

The blends of polyurethane and polyester consist of the same polyurethane mentioned before. The unsaturated polyester resin used is a 1:1 propylene-maleate polyester combined with 35 wt% of styrene (P325, OCF). Extra styrene was added to adjust the molar ratio of styrene to the unsaturation of polyester molecules to 2:1. MEKP with 33% cobalt naphthanate was used as a low-temperature initiator, while *t*-butyl peroxy-2-ethyl hexanoate (PDO, Lucidol) was used as a high-temperature initiator. Compositions of the blends are given in Table III. Isothermal polymerizations were carried out at 60°C.

TABLE I
Materials Used for Polyurethane Reaction

Ingredients	Parts by weight
Resins: Triol (TONE310, $f = 3.0$)	67.2
MDI (143L, $f = 2.3$)	32.8
Catalyst: T-12	5.1×10^{-4}

TABLE II
Materials Used for Styrene-Polyester Reaction

Unsaturated polyester resins	S-6	S-10
Composition (molar ratio)		
Maleic anhydride	2	1
Isophthalic acid	1	0
Propylene glycol	3	1
No. avg. mol. wt. (\bar{M}_n)	1700	1580
Avg. no. of C=C/polyester molecule	6.56	10.13

Ingredients	Parts by weight	
Resins: unsaturated polyester: S-10	42.9	—
S-6	—	57.1
Styrene	57.1	42.9
Initiator: methyl ethyl ketone peroxide	0.67	0.67
Promotor: cobalt naphthanate	0.33	0.33

TABLE III
Compositions of Polyurethane-Polyester Blends

Ingredients	Parts by weight	
	PU/PES 50/50	PU/PES 30/70
Polyurethane phase		
Resins: Triol (TONE310)	33.6	20.16
MDI (143L)	16.4	9.84
Catalyst: T-12	2.55×10^{-4}	1.53×10^{-4}
Polyester phase		
Resins: 65% Unsaturated		
Polyester in styrene (P325)	33.5	46.9
Styrene	16.5	23.1
Initiator: MEKP/cobalt naphthanate or PDO	0.335/0.165 0.5	0.469/0.231 0.7

Instrumentation and Experimental Procedure

A differential scanning calorimeter (Perkin-Elmer DSC-2C) was used to measure the exotherm rate during polymerization. Stainless steel sample pans were used, which have an internal O-ring seal to prevent the styrene monomer from volatilization during experiment. Sample weight was 15 to 40 mg with an empty pan as reference. Isothermal reactions were ended when there was no further exotherm. Samples were then reheated from room temperature to 250°C in the scanning mode with a heating rate of 5°C/min to detect the residual reactivity left in the isothermally reacted samples. The total heat of reaction during curing was calculated from the areas under both isothermal and residual scanning DSC curves. DSC cure was also carried out in the scanning mode from room temperature to 250°C at a heating rate of 10°C/min. The total heat of reaction was calculated from the area under the scanning curve, which is compared with that calculated from the isothermal experiments.

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

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

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

where $d\alpha/dt$ and α are the reaction rate and conversion at a given time; ΔH_t is the accumulated exotherm from $t = 0$ to the given time; ΔH_T is the total reaction exotherm; Δa_t is the accumulated area under the isothermal DSC curve from $t = 0$ to the given time; and Δa_T is the total area under both isothermal and residual scanning DSC curves for the isothermal cure, or the total area under the scanning DSC curve for the scanning cure.

Several assumptions are made for the above calculation. First, thermophysical properties such as heat capacity, density, and heat of reaction are assumed unchanged during reaction. This has been found acceptable for thermosetting and amorphous polymers.¹¹⁻¹³ Second, there is only one reaction taking place at the time and the reaction may reach completion in the scanning run. This may be inappropriate for multicomponent reactions such as polyurethane-polyester blends.

An FTIR spectrometer (Nicolet 20DX) with a resolution of 4 cm^{-1} in the transmission mode was also used for kinetic measurements. After the reactants were mixed, 1 drop of mixture was pasted between two sodium chloride plates which were then mounted on a sample holder located in the FTIR instrument. No spacer was used between the two NaCl plates. A temperature chamber (heating rate: $10^\circ\text{C}/\text{min}$, temperature stability: $\pm 1^\circ\text{C}$) was designed to maintain the reaction temperature isothermally. Three consecutive 1-s scans were taken at each sampling time, and their average was stored in a floppy disk for later data analysis. The sampling interval was 1 min during most of the reaction but was larger at higher conversions, since the reaction was slow in those regions. Measurement was ended at a preset time. All IR spectra in this study were expressed in absorbance.

Infrared absorption is based on the fact that each chemical group in a sample absorbs infrared radiation of some characteristic frequencies. The amount of light intensity of transmission relative to the amount of light intensity incident on the sample can be related directly to the concentration of the absorbing species by Beer's law¹⁴

$$A_i = \beta_i l C_i \quad (3)$$

where A_i is the absorbance of species which can be determined from the peak height or peak area, β is the absorptivity which is characteristic of the absorbing species, l is the sample length, and C_i is the concentration of the absorbing species i . To compensate for thickness changes in the sample during polymerization, a ratio is taken between the absorbance of the group of

interest and that of an internal standard, specifically, a group whose concentration does not change during reaction. In this study, the C—H peak at 2942 cm^{-1} is chosen as the internal standard and either the peak area or the peak height is used to calculate the absorbance. Reaction conversion can then be determined from the change of the normalized absorbance

$$\alpha = 1 - \frac{\bar{A}_t}{\bar{A}_o} \quad (4)$$

where \bar{A}_o and \bar{A}_t are normalized absorbances of the monomer functional group before the reaction and after a reaction time, t .

RESULTS AND DISCUSSION

Polyurethane Reaction

Figure 1 shows both isothermal and scanning reaction rate profiles for the polyurethane reaction measured by DSC. For a catalyzed step-growth polymerization such as polyurethane, the reaction started immediately after mixing. In the isothermal mode, the maximum reaction rate occurred at the beginning of the reaction and decayed when the functional groups were consumed. In the scanning mode, the location of the maximum reaction rate depended on the catalyst concentration and the scanning rate. The initial part of reaction could not be measured by DSC because sample preparation and

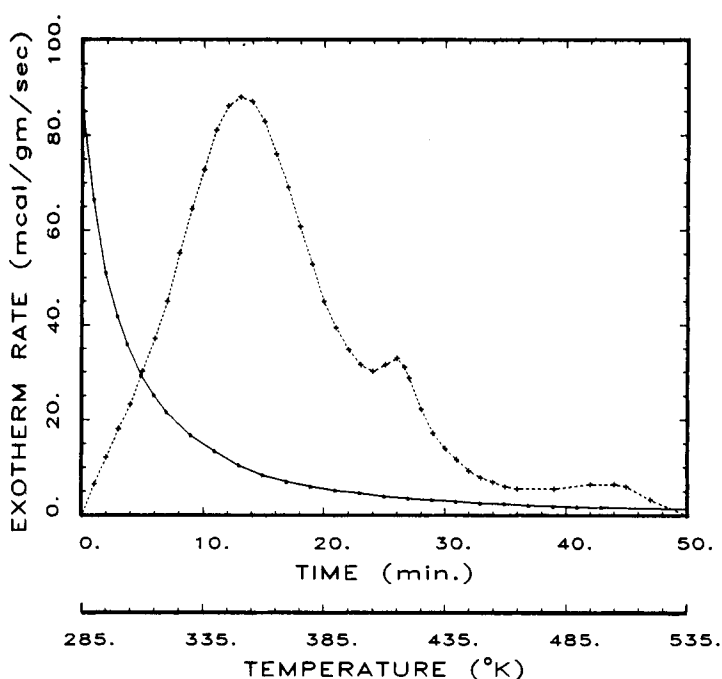


Fig. 1. Polyurethane reaction rate profiles measured by DSC. Solid line: rate vs. time, isothermal run at 60°C . Dashed line: rate vs. temperature, scanning run.

TABLE IV
Reaction Exotherm of Polyurethane Reaction

Total heat of reaction	cal/g
ΔH_I^a	43.94
ΔH_S^b	44.63

^a Isothermal DSC measurement followed by scanning measurement.

^b Scanning DSC measurement.

sample loading took certain amounts of time. The second and third peaks in the scanning measurement are probably due to the side reactions of isocyanate in the urethane polymerization. Between the two modes, the isothermal result was always less accurate than the scanning result since the sample needed to be heated quickly to the test temperature, which took about one minute. Table IV shows that the total heat of reaction resulting from scanning DSC measurement is slightly higher than that from isothermal DSC measurement at 60°C.

Figure 2 shows FTIR spectra for the polyurethane reaction at 60°C. The FTIR analysis is based on the peak change of functional groups or characteristic linkages during the reaction period. Therefore, there is more than one peak which may change when the reaction takes place. For polyurethane reaction, intensities of the isocyanate peak (2278 cm⁻¹), hydroxyl peak (3588 cm⁻¹), secondary amine peak (3349 cm⁻¹), and urethane peaks (*trans* at 1528 cm⁻¹, *cis* at 1414 cm⁻¹), can all be followed during polymerization. However, the

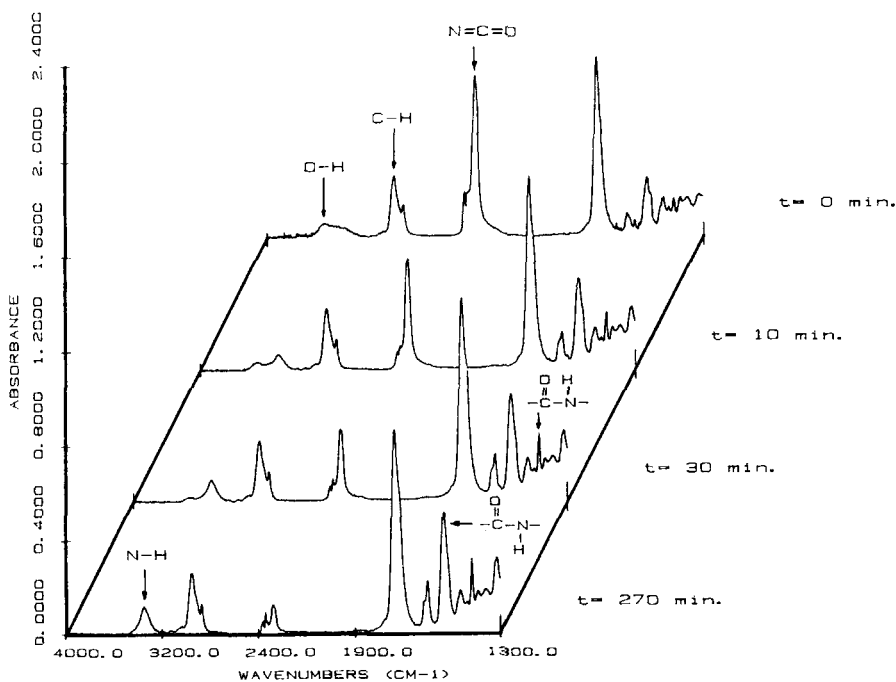


Fig. 2. FTIR spectra of polyurethane reaction at 60°C.

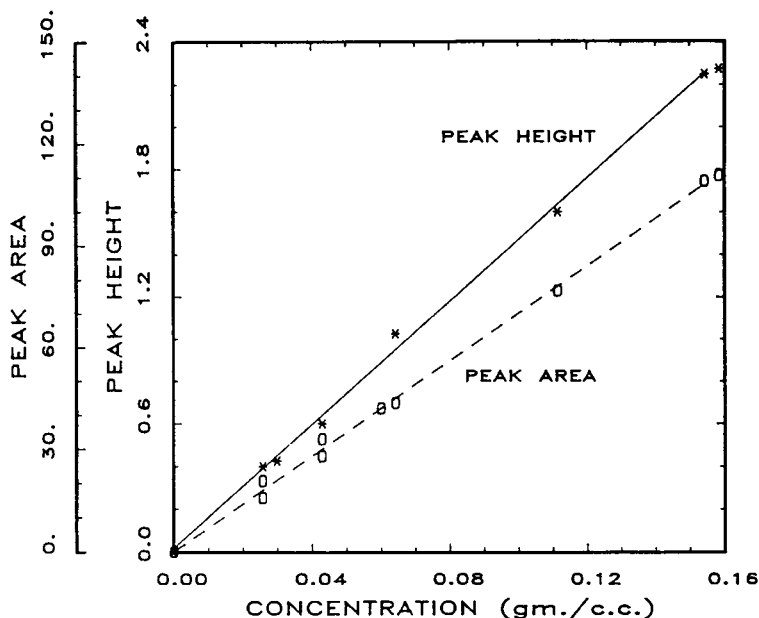


Fig. 3. Calibration curves of isocyanate peak at 2278 cm^{-1} .

urethane peaks are located in a multiplex region where most peaks overlap with one another. Also, the hydroxyl and secondary amine peaks overlap each other and are strongly influenced by hydrogen bonding. Therefore, only the isocyanate peaks can be followed easily during the polyurethane reaction, which are shown in Figure 2. The spectra are normalized based on the C-H peak.

Before applying Beer's law for any quantitative measurement, the absorptivities of reacting species need to be determined. Figure 3 shows the calibration curves of isocyanate peak based on the changes of both the peak height and the peak area. The calibration curves were established by preparing monomer-dichloromethane solutions of known concentrations. FTIR spectra of calibration solutions were measured at the test temperature to avoid the effect of temperature difference on the molar extinction coefficient.⁹ For the isocyanate peak, the calibration curves form straight lines for both the peak height and the peak area. Therefore, the change of isocyanate peak is followed to determine the reaction kinetics of polyurethane.

Figure 4 compares the conversion of polyurethane reaction measured by both DSC and FTIR in the isothermal condition. In order to match the sample heat-up time in DSC and FTIR, the DSC sample was first heated from room temperature to reaction temperature in the scanning mode at a rate equivalent to that of FTIR temperature chamber before being switched to the isothermal mode. FTIR results based on the change of either peak height or peak area agree well with the DSC result. Here, the total heat of reaction used to determine the conversion in DSC experiment was calculated from the isothermal and residual scanning runs. Since the sample preparation time and the sample heat-up time were about the same for both DSC and FTIR measurements, the experimental error was probably the same in both

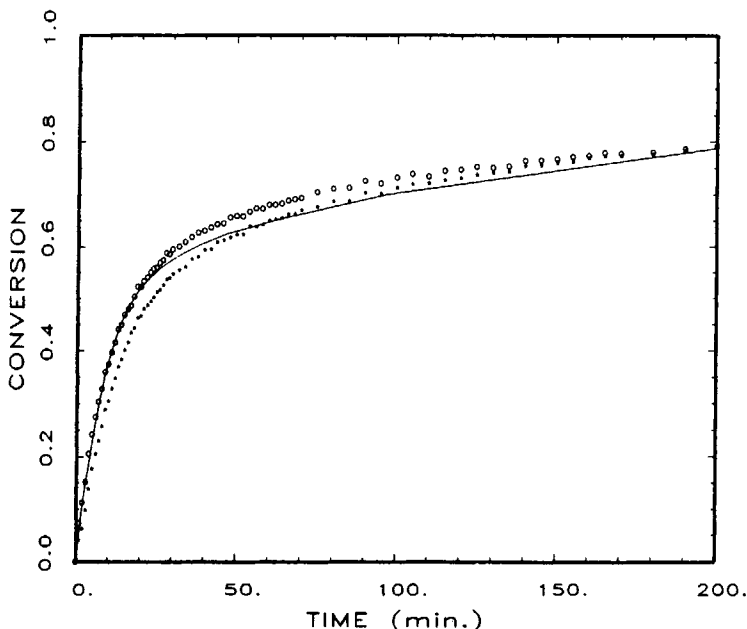


Fig. 4. Conversion vs. time of polyurethane reaction at 60°C. Solid line: DSC measurement; \circ : FTIR measurement, based on peak area changes; $*$: FTIR measurement, based on peak height changes.

measurements. Figure 4 demonstrates that both techniques are reliable for the kinetic measurement of polyurethane reaction.

Styrene-Polyester Reaction

Figure 5 shows the isothermal reaction rate profiles of the two polyester samples measured by DSC, while Table V summarizes the heat generated by the curing reaction, which includes the heat generated in isothermal cure (i.e., obtained by integrating the rate-time curve given in Fig. 5), the residual heat that was released when the sample was heated to 250°C upon completion of the isothermal cure, and the total heat of cure by adding the above mentioned two heats. It is interesting to note that the total heat of cure is much less for sample S-6 than that for sample S-10, even based on an equal molar C=C bonds. The conversion profiles of the two samples in Figure 5 were calculated based on ΔH_f shown in Table V. Figure 5 indicates that sample S-6 reacts much faster and reaches higher conversion than sample S-10 at 60°C. The second peak shown in the reaction rate curve of sample S-6 may be caused by the styrene homopolymerization.¹⁵

Figure 6 shows the scanning reaction rate and conversion profiles of the two polyester samples measured by DSC, while Table V lists the heat generated by the scanning reaction. Based on the equal molar C=C bonds, both samples resulted in almost the same heat of reaction, namely, 14.6 kcal/mol C=C bonds, which is higher than that obtained from isothermal DSC experiments. The scanning DSC results, again, show that sample S-6 reacts faster than sample S-10.

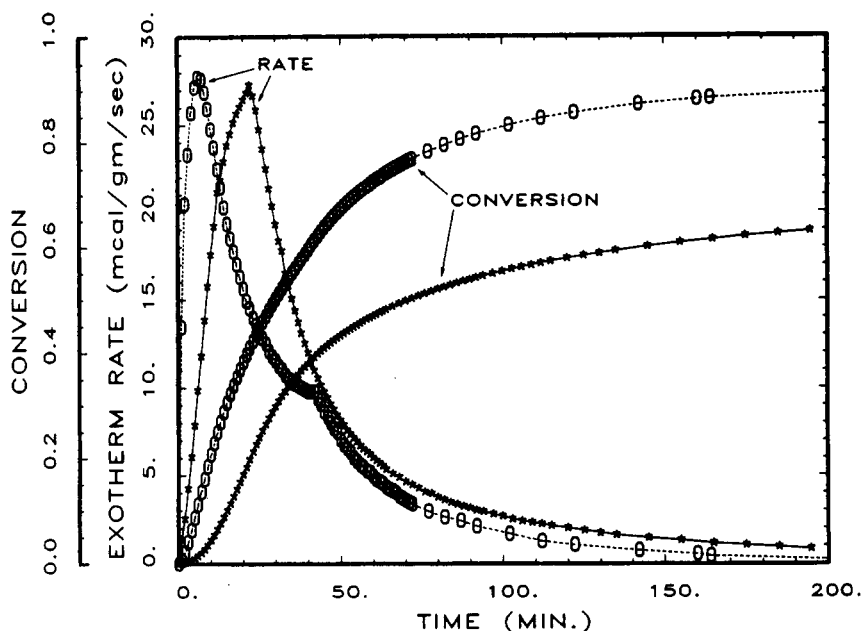


Fig. 5. Reaction rate and conversion profiles of styrene-polyester reactions at 30°C measured by DSC. •: styrene/S-10; ○: styrene/S-6. MEKP/cobalt naphthanate is the initiator.

The existence of two major exotherm peaks in Figure 6 suggests that two initiation reactions occur in the unsaturated polyester resins containing a peroxide as initiator and cobalt naphthanate as promoter. Lem and Han⁵ have demonstrated that the first peak arises from the redox-type initiation between the peroxide and the promoter, while the second peak is caused by the reaction initiated by thermal decomposition of peroxide.

Figure 7 shows FTIR spectra from wave number 850 to 1055 cm^{-1} for the reaction of sample S-10 at 30°C. Reaction conversion can be determined from the consumption of styrene C=C bonds at peaks 912 cm^{-1} and 992 cm^{-1} ($\text{CH}_2=\text{CHR}$ deformation), and the consumption of polyester C=C bonds at peak 982 cm^{-1} (*trans* CHR=CHR deformation). Polystyrene formation is indicated by a peak at 1598 cm^{-1} which is located in a multipeak region. The styrene consumption can be determined easily from the peak change at 912

TABLE V
Reaction Exotherm of Styrene-Polyester Copolymerization

Total reaction exotherm	Styrene/S-10		Styrene/S-6	
	cal/g	kcal/mol C=C	cal/g	kcal/mol C=C
Isotherm + scanning measurement				
ΔH_{iso}	70.70	8.58	60.29	9.39
$\Delta H_{\text{residual scan}}$	41.51	5.04	6.78	1.06
$\Delta H_{\text{I}} = \Delta H_{\text{iso}} + \Delta H_{\text{residual scan}}$	112.21	13.62	67.07	10.45
Scanning measurement				
ΔH_{S}	120.03	14.56	93.97	14.64

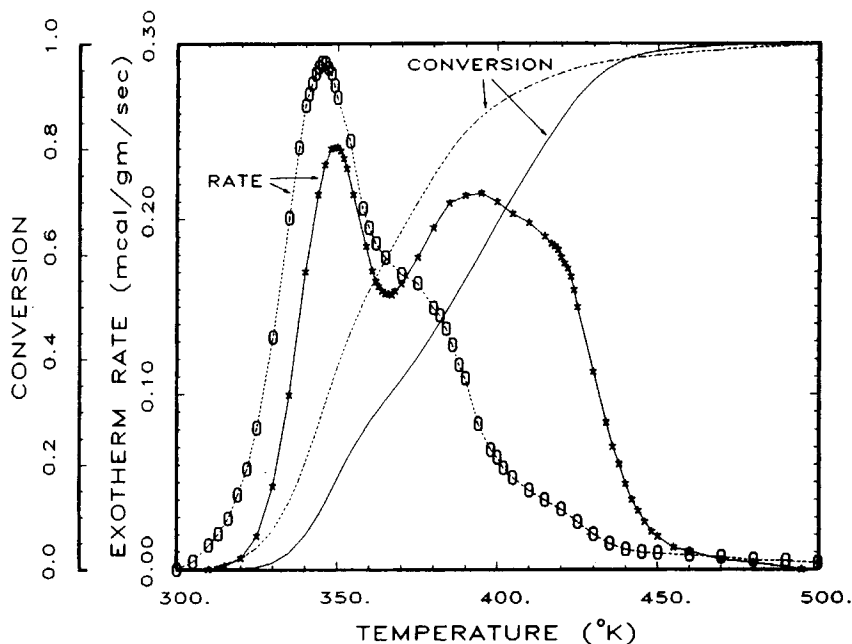


Fig. 6. Reaction rate and conversion profiles of styrene-polyester reactions measured by DSC in scanning mode. Solid lines: styrene/S-10; dashed lines: styrene/S-6. MEKP/cobalt naphthanate is the initiator.

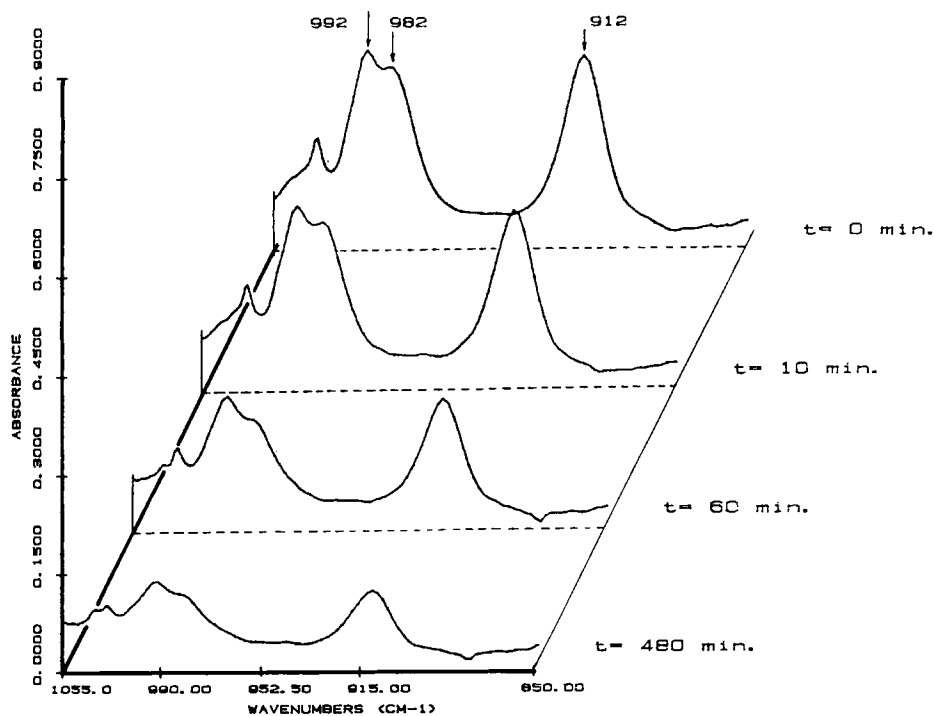


Fig. 7. FTIR spectra of styrene/S-10 reaction at 30°C with MEKP/cobalt naphthanate as initiator.

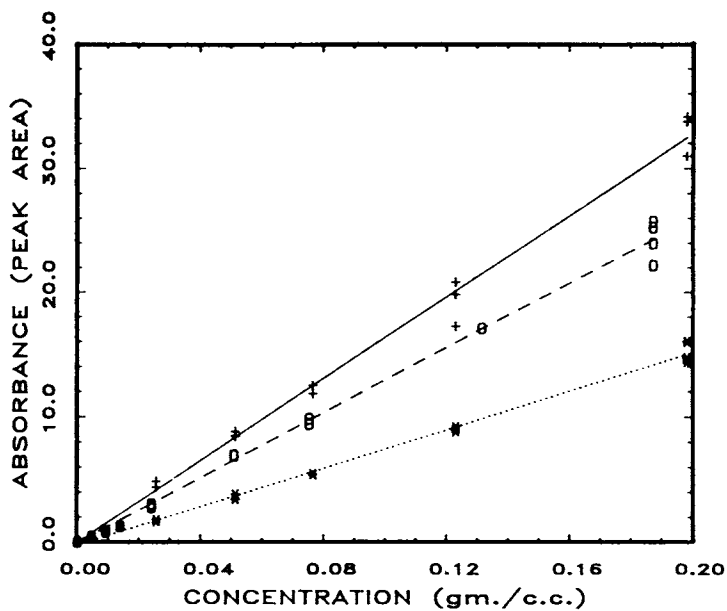


Fig. 8. Calibration curves of functional peaks of styrene and polyester. +: peak 912 cm^{-1} ; *: peak 992 cm^{-1} ; o: peak 982 cm^{-1} .

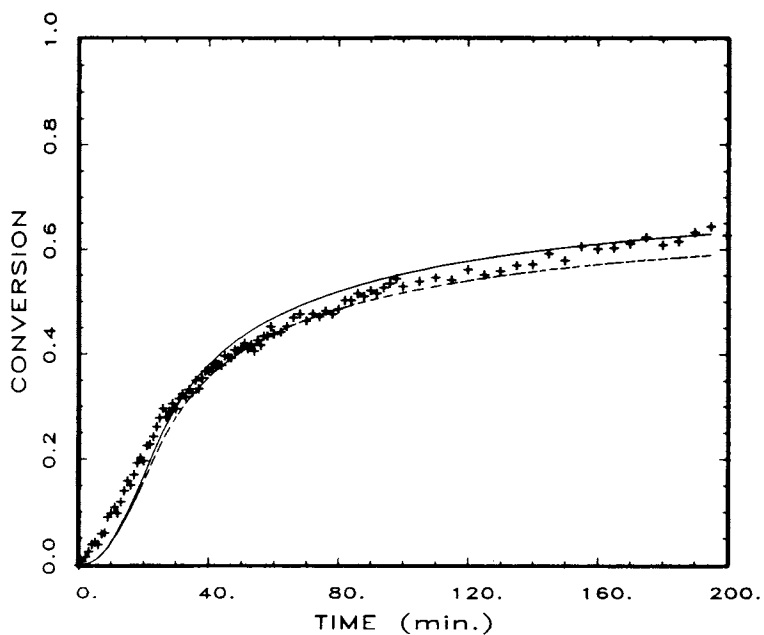


Fig. 9. Conversion vs. time of styrene/S-10 reaction at 30°C with MEKP/cobalt naphthanate as initiator. +: FTIR measurement; solid line: DSC measurement based on ΔH_7 ; dashed line: DSC measurement based on ΔH_5 .

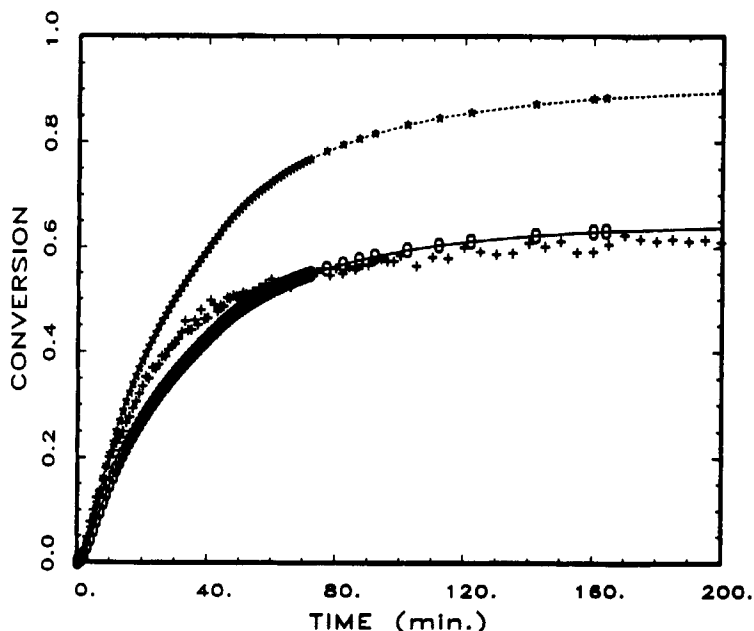


Fig. 10. Conversion vs. time of styrene/S-6 reaction at 30°C with MEKP/cobalt naphthanate as initiator. +: FTIR measurement; *: DSC measurement based on ΔH_f , °: DSC measurement based on ΔH_s .

cm^{-1} , but the consumption of polyester C=C bonds and the total consumption of C=C bonds cannot be followed directly from the peaks 982 cm^{-1} and 992 cm^{-1} because they overlap each other. A subtraction method was used to separate the overlapping peaks.¹⁰ Figure 8 shows the calibration curves of these three peaks based on the change of peak area. Again, the calibration curves are established by preparing monomer-dichloromethane solutions of known concentration. Linear relationship between absorbance and concentration is found for all three peaks.

Figures 9 and 10 compare the measured conversion of overall C=C bonds in the styrene-polyester reaction by both FTIR and DSC. Since the total heat of reaction measured by the isothermal DSC experiment, ΔH_f , is different from that measured by the scanning DSC experiment, ΔH_s , two DSC conversion curves are shown in Figures 9 and 10, where the lower curve is based on ΔH_s while the upper one is based on ΔH_f . For sample S-10, the difference between ΔI_s and ΔH_f is very small. Both DSC curves and the FTIR result are very close to each other as shown in Figure 9. Because of the experimental error, it is difficult to judge the accuracy of each measurement method. For sample S-6, the difference between ΔH_s and ΔH_f is quite significant. The comparison between DSC and FTIR results clearly demonstrates that the total heat of reaction for styrene-polyester resins should be determined by the DSC scanning method. The lower ΔH_f values shown in Table V indicate that permanent residual existed in isothermally cured unsaturated polyester resins. Reheating the isothermally cured samples to higher temperatures can increase the final conversion, but cannot promote the reaction to completion. The residual reactivity is apparently a function of the type of polyester resins.

Detailed discussion of reaction kinetics of unsaturated polyester resins can be found elsewhere.¹⁶

Reaction of Polyurethane-Polyester Blend

Figure 11 shows the isothermal reaction rate profiles of two polymer blends (30/70 and 50/50 PU/PES) measured by DSC at 60°C. PDO was the initiator used for the polyester reaction. The reaction curve can be divided into two parts, where the first peak is the polyurethane reaction while the second peak is the styrene-polyester reaction. Increasing the polyester content from 50% to 70% speeded up the polyester reaction greatly, but this reaction still occurred after the completion of urethane reaction. For such sequential reactions, DSC is capable of measuring the reaction rates of constituent components. When PDO was replaced by MEKP and cobalt naphthanate as the initiator for styrene-polyester reaction, the PES phase reaction took place almost at the same time as the polyurethane reaction except that the latter had a maximum reaction rate at the beginning of the reaction, while the former would not reach the peak rate until a certain reaction time was passed. The isothermal reaction rate profiles measured by DSC for the two polymer blends are shown in Figure 12. Again, increasing the polyester content speeded up the polyester reaction, but the heavy overlap of the two reaction peaks in the DSC curves makes it impossible to analyze the reaction kinetics of individual polymerization. Scanning of the isothermally cured samples indicated that the conversion was incomplete as shown in Figure 13, but DSC was not able to distinguish the residual exotherm of polyurethane reaction from that of polyester reaction.

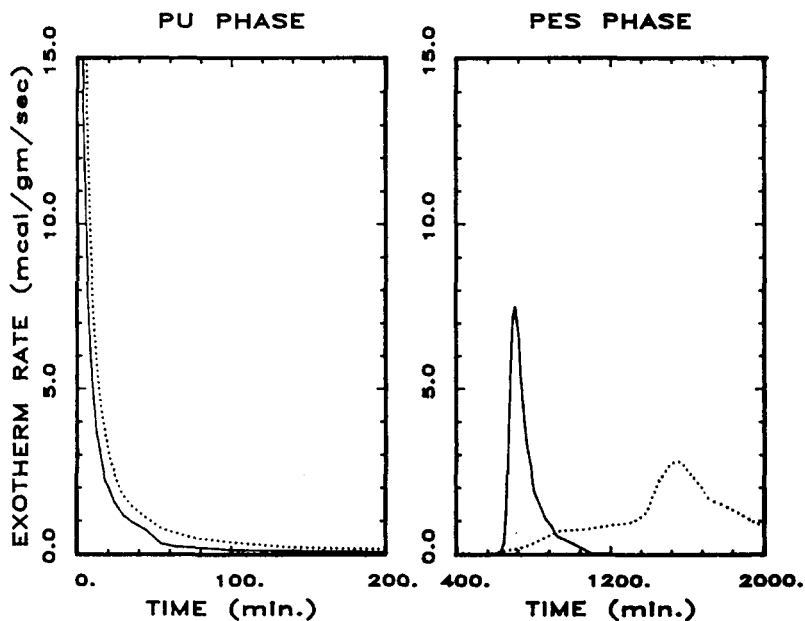


Fig. 11. Reaction rate profiles of polyurethane-polyester blends measured by DSC at 60°C with PDO as initiator. Solid line: 30/70 PU/PES; dot line: 50/50 PU/PES.

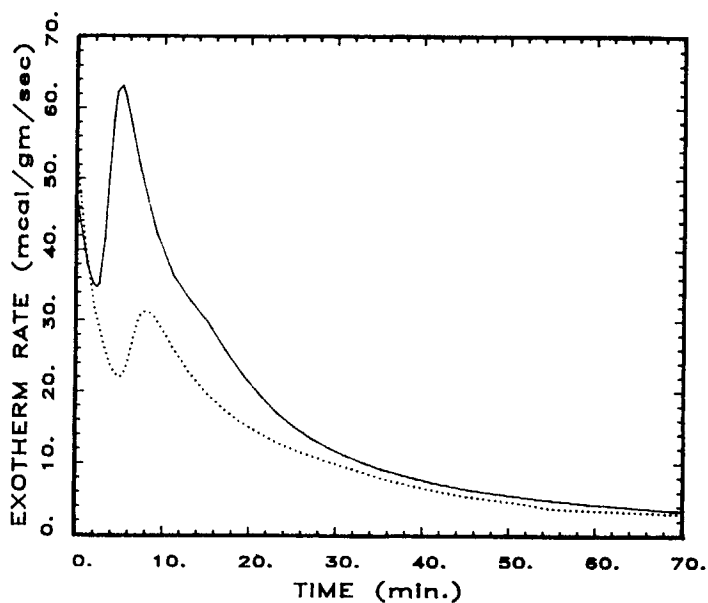


Fig. 12. Reaction rate profiles of polyurethane-polyester blends measured by DSC at 60°C with MEKP/cobalt naphthanate as initiator. Solid line: 30/70 PU/PES; dot line: 50/50 PU/PES.

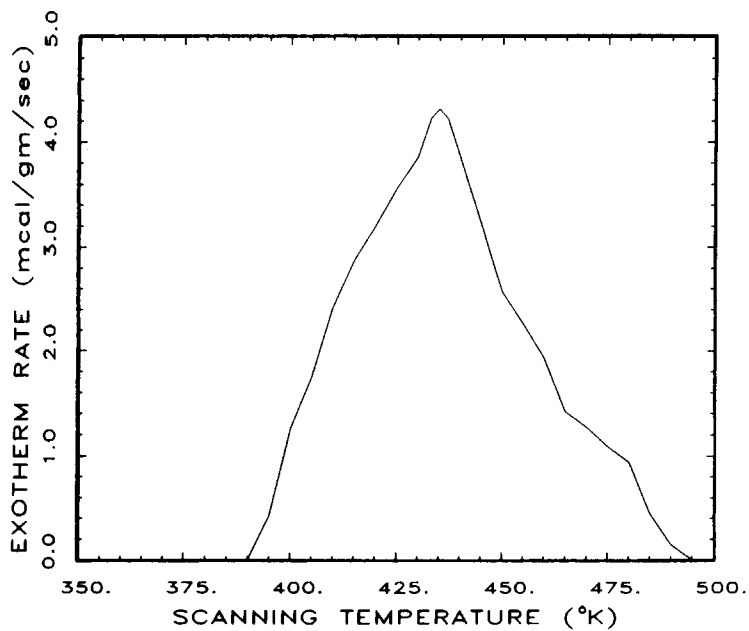


Fig. 13. Residual exotherm of 60°C cured 50/50 PU/PES blend, with MEKP/cobalt naphthanate as initiator.

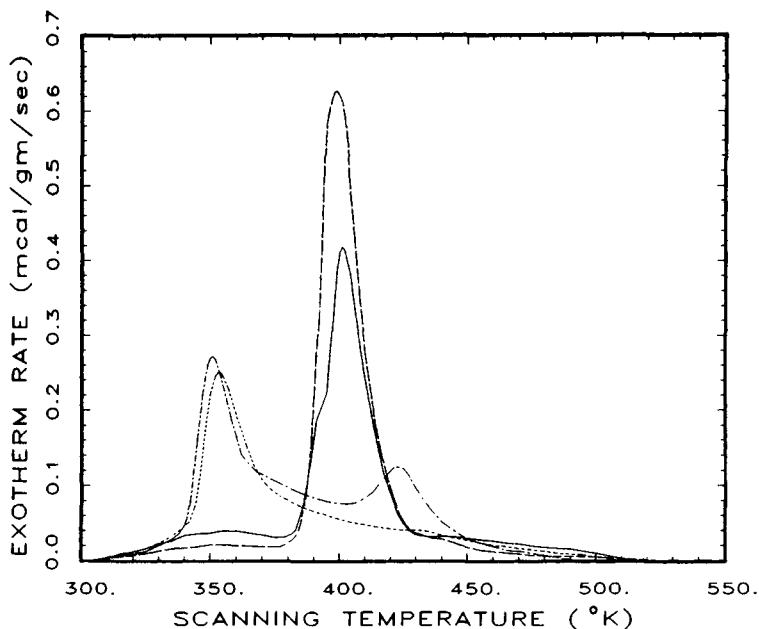


Fig. 14. Reaction rate profiles of polyurethane-polyester blends measured by DSC in scanning mode. (---) 30/70 PU/PES with MEKP/cobalt naphthanate; (....) 50/50 PU/PES with MEKP/cobalt naphthanate; (—) 30/70 PU/PES with PDO; (——) 50/50 PU/PES with PDO.

Figure 14 shows the scanning reaction rate profiles for all polyurethane-polyester blends. There are two major peaks in each reaction. For PDO-initiated reactions, the peak around 350K was due to urethane polymerization (see Fig. 1), while the peak around 400K was a result of styrene-polyester reaction. Increasing the polyester content from 50% to 70% increased the polyester reaction rate and decreased the polyurethane reaction rate. For MEKP-cobalt naphthanate-initiated reactions, the peak around 350K is quite large, which indicates that the two polymerizations occurred simultaneously. The second peak is believed to be caused by the reaction initiated by thermal decomposition of MEKP as discussed before. It is interesting to note that this peak is located at a higher temperature and is much more suppressed for the 50/50 PU/PES blend than for the 30/70 PU/PES blend.

Table VI lists reaction exotherms of all the blends measured by DSC in the scanning mode. For comparison, the total heat of reaction calculated by the additivity rule of constituent ingredients is also given in the table. The results show that all blends have reaction exotherms lower than the calculated values, and the blends with a sequential reaction order can generate more heat than those with simultaneous reactions. This fact reveals that it is more difficult to reach a higher conversion in a dual-reaction system than in a single reaction system. Physical interactions between the two reacting phases may have caused the difference.¹⁷ DSC is able to measure the overall reaction rate. It cannot, however, totally differentiate one reaction from the other.

FTIR spectroscopic analysis does not have such limitations as thermal analysis. Figure 15 shows the FTIR spectra of the isothermal reaction of the

TABLE VI
Reaction Exotherm of Polyurethane-Polyester Blends

Total heat of reaction (cal/g) ^a	PU/PES 50/50	PU/PES 30/70
Simultaneous PU-PES reaction ^b	63.00	78.37
Sequential PU-PES reaction ^c	75.77	89.01
Calculated ΔH	82.33	97.41

^a Measured by scanning DSC experiments.

^b MEKP/cobalt naphthanate is the initiator for polyester reaction.

^c PDO is the initiator for polyester reaction.

30/70 PU/PES blend initiated by MEKP and cobalt naphthanate. The change of functional peaks of polyurethane reaction (i.e., wave number 2278 cm^{-1}) and styrene-polyester reaction (i.e., wave numbers 912, 982, and 992 cm^{-1}) can be followed independently. Through appropriate calibration and calculation, one can establish the conversion profiles for both reactions as shown in Figure 16. Furthermore, the consumption rates of styrene monomer and polyester C=C bonds during reaction can also be calculated.¹⁰ Compared with Figure 4, Figure 16 indicates that, at a given temperature, adding polyester resin to the polyurethane reaction may increase the final conversion of polyurethane. This phenomenon has been explained as the "solvent effect" of polyester phase on the polyurethane reaction.^{10,18} On the other hand, the polyester conversion (the overall C=C bonds, styrene monomer and polyester

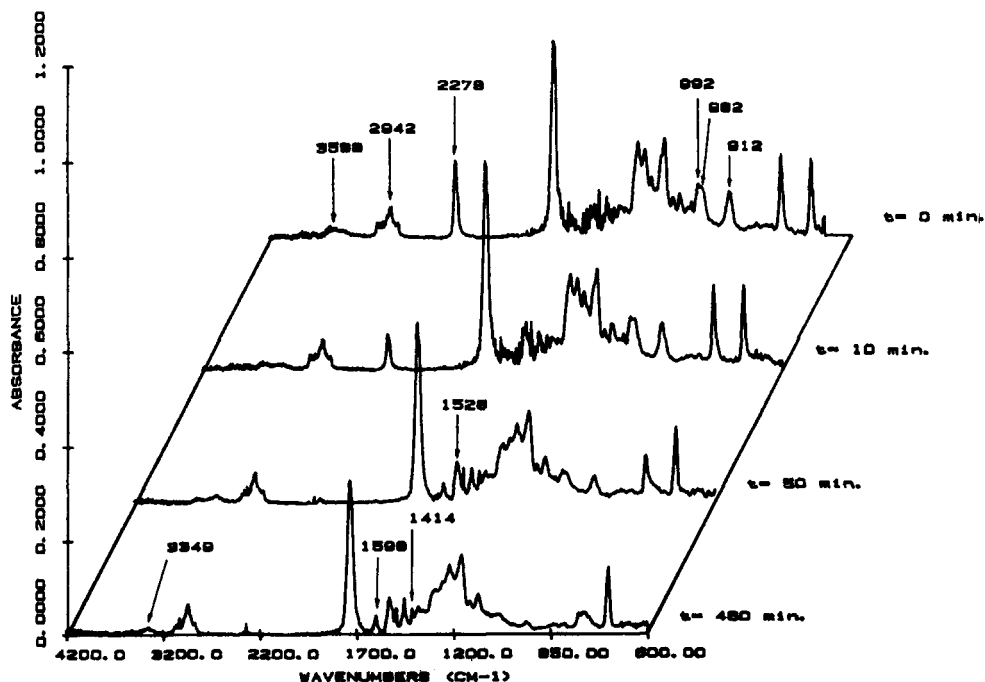


Fig. 15. FTIR spectra of a reaction of 30/70 PU/PES blend at 60°C with MEKP/cobalt naphthanate as initiator.

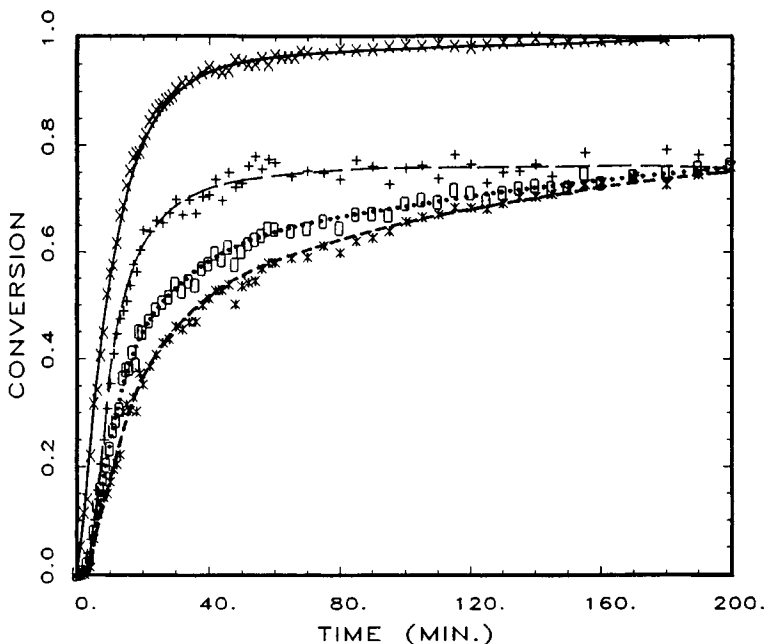


Fig. 16. Conversion vs. time measured by FTIR at 60°C for a reaction of 30/70 PU/PES blend with MEKP/cobalt naphthanate as initiator. X: PU; *: styrene monomer; +: polyester C=C bonds; o: overall C=C bonds.

C=C bonds) is much lower at given conditions. Since residual styrene monomer and polyester C=C bonds may affect the physical properties of reacted products in different ways, it is important to measure them independently. For example, residual styrene monomers may cause blisters and voids on the surface of molded products at elevated temperatures because of their volatile nature, while residual polyester C=C bonds are an indication of lower crosslinking density of reacted polyester resins.

CONCLUSIONS

Both DSC and FTIR are useful for the kinetic measurement of various polymerizations. The thermal method is easy to perform but only suitable for a single-reaction system. The spectroscopic method can detect the detailed reaction mechanism of complex polymerization. It, however, needs to be carefully calibrated when used in the quantitative analysis. The calculation is also much more time consuming compared with thermal analysis. For engineering applications, DSC is a better tool because it can generate kinetic as well as thermal information for the reaction system. For an accurate kinetic measurement, it is recommended that both DSC and FTIR experiments be carried out, since DSC provides reaction rate profiles while FTIR provides detailed reaction conversions. Furthermore, results from both experiments can be used to calibrate with each other.

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