A Study of Reaction Kinetics by Near-Infrared Spectroscopy. 1. Comprehensive Analysis of a Model Epoxy/Amine System

Jovan Mijović* and Saša Andjelić

Chemical Engineering Department, Polytechnic University, Six Metrotech Center, Brooklyn, New York 11201

Received September 28, 1994; Revised Manuscript Received December 15, 1994®

ABSTRACT: An investigation of model epoxy/amine reactions was carried out by near-infrared (IR) spectroscopy. A comprehensive account of the origin, location, and shifts during reaction of all major absorption peaks in the spectral range between 4000 and 7100 cm^{-1} is provided. Reaction kinetics derived from the near-IR data were in excellent agreement with the results obtained by high-performance liquid chromatography (HPLC). A most interesting and equally unexpected finding was the observed discrepancy between the kinetic predictions of near-IR and mid-IR analyses. It was established that the kinetics of epoxy/amine reactions can be accurately deduced from the near-IR data, while the "standard" mid-IR epoxy absorption band at 915 cm^{-1} was not a unique measure of the epoxy concentration, and hence its utilization in kinetic calculations is questionable unless appropriate corrections are made. Evidence was presented for the formation of hydrogen bonding that is directly related to a critical viscosity of the reactive mixture.

I. Introduction

This paper, which is the first of two parts, focuses on the application of FTIR spectroscopy to studies of reactive organic systems in the near-infrared frequency range, hereafter referred to as near-IR. The near-IR region, which covers the interval between approximately 14 000 and 4000 cm^{-1} (0.7–2.5 μm), encompasses bands that result from the harmonic overtones of fundamental and combination bands associated with hydrogen atoms, which is why compounds containing O–H, N–H, and/or C–H bonds lend themselves favorably to analysis by near-IR spectroscopy. The vast majority of the reported FTIR studies of reactive systems, however, have been carried out in the mid-IR range, which extends between about 4000 and 400 cm^{-1} (2.5–25 μm) and is replete with fundamental absorption bands. Only a handful of mostly qualitative investigations of reactive or interactive systems have been conducted in the near-IR range.[1–11]

In recent years, there has been a notable increase in research activity in the near-IR range, particularly in conjunction with the application of in-situ real time remote spectroscopy to "smart" processing. One major advantage of the near-IR frequency range is that it can be transmitted through silica type optical fibers, which are relatively inexpensive and readily available in a variety of types and forms. In the mid-IR range, on the other hand, only exotic state-of-the-art chalcogenide and metal halide fibers have the required transmission capabilities, and even then usually over a limited frequency interval.[12]

The principal objective of this paper is to provide a hitherto unavailable comprehensive quantitative characterization of near-IR spectra during reactions in a model epoxy/amine system. Our goal is to identify the characteristic near-IR band assignments, monitor their change during reaction, use them to evaluate the reaction rate, and contrast the kinetic results obtained by near-IR and mid-IR analyses. This study is a part of an ongoing program at Polytechnic on in-situ real time characterization of reactive organic systems of both polymer-forming and non-polymer-forming type.

II. Experimental Section

Materials. The epoxy/amine model system used in this study consisted of 1,2-epoxy-3-phenoxypropane, also known as phenyl glycidyl ether, or PGE, and aniline. Both compounds were supplied by Aldrich. Additional compounds were used to help identify and assign different absorption peaks observed in the course of our investigation. Those include *N*-methylaniline, 4,4′-methylenedianiline, diaminodiphenyl sulfone, 2,3-epoxypropylbenzene, and two multifunctional epoxy resins: diglycidyl ether of Bisphenol A (DGEBA) and tetraglycidyl diaminodiphenyl methane (TGDDM).

Sample Preparation. A stoichiometric amount of epoxy group (PGE) and amine hydrogens (aniline) was used. The reactants were mixed at room temperature and immediately tested under isothermal conditions at a series of selected temperatures in the range between 90 and 130 °C.

Technique. Fourier transform infrared spectroscopy was performed using a Nicolet Magna-IR system 750 spectrometer with spectral range coverage from 15 800 to 50 cm^{-1} and a Vectra scanning interferometer with a better than 0.1 cm^{-1} resolution. Mid-IR data were collected using a KBr beamsplitter, an IR source, and a DTGS KBr detector. Near-IR data were obtained using a calcium fluoride beamsplitter, a white light source, and a PbSe and/or MCT detector. All spectra were measured at 4 cm^{-1} resolution using 35 scans.

Highly accurate measurement of the sample temperature is essential in kinetic studies, and that places a premium on the experimental precision. The heated cell (Spectra Tech. Inc.) supplied with the Magna spectrometer was insufficiently accurate in monitoring the actual sample temperature and had to be modified. Calibration runs were performed using Luxtron's Model 750 multichannel fluoroptic thermometer. The optical fiber probe was immersed directly in the sample which was located inside a Teflon-insulated cell. In subsequent runs, a fine-gauge Omega thermocouple was placed inside the sample to record temperature during reaction.

High-performance liquid chromatography (HPLC) analysis was utilized to generate complementary information. The analysis was performed on a Perkin-Elmer LCI laboratory computing integrator equipped with a reverse-phase C18 column. Gradient elution of the acetonitrile–water mixture was utilized at a constant flow rate of 2 mL/min for about 20 min. Further details of the experimental procedure are given elsewhere.[13]

* To whom correspondence should be addressed.
® Abstract published in *Advance ACS Abstracts,* March 1, 1995.

0024-9297/95/2228-2787$09.00/0

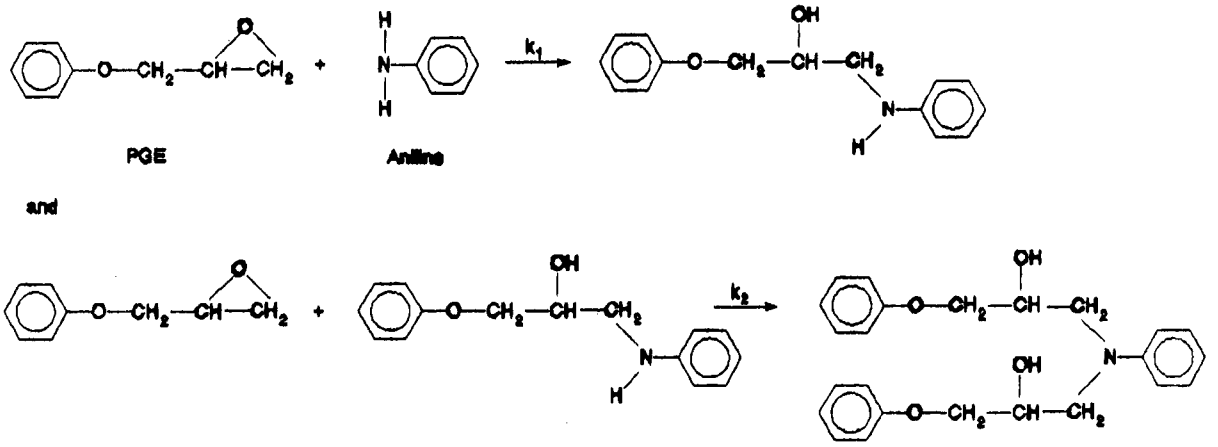

Figure 1. Chemical reactions in the PGE/aniline system.

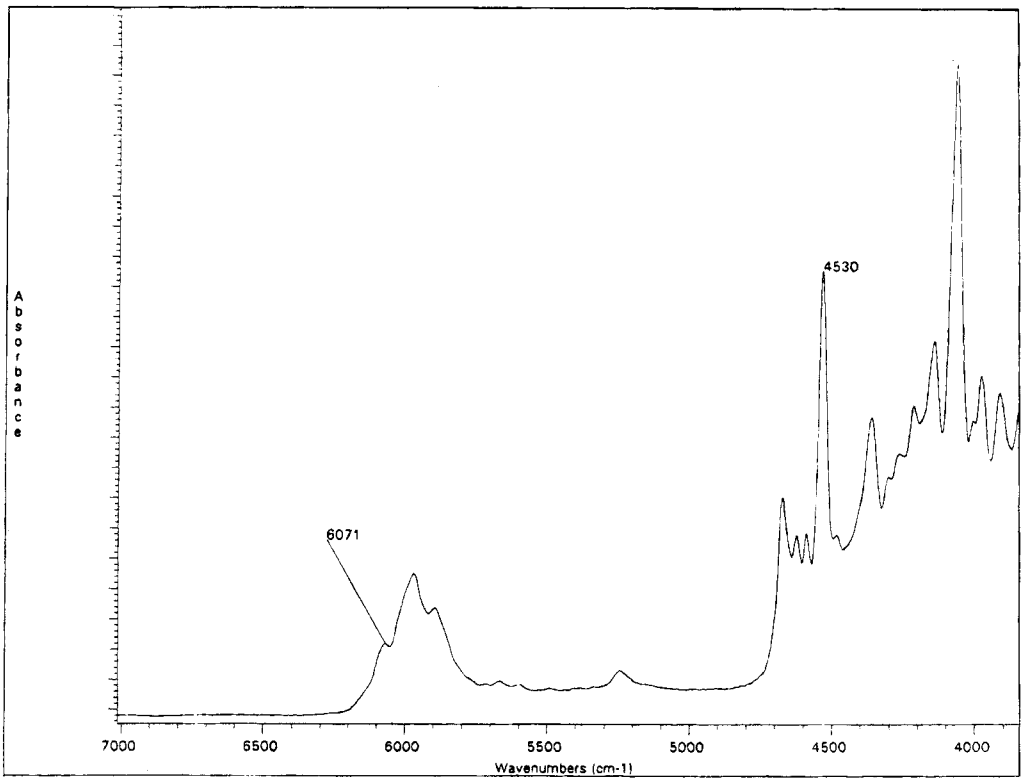

Figure 2. Near-IR spectrum of PGE.

III. Results and Discussion

The presentation of our results is divided into five sections. An introductory paragraph contains brief comments regarding the model system. A comprehensive account of the location and origin of observed near-IR absorption peaks is given in section 2. Changes in the absorption characteristics of various peaks during reaction are described qualitatively in section 3 and quantitatively in section 4. Finally, an interesting revelation regarding the observed difference in near-IR versus mid-IR kinetics is presented and discussed in section 5.

1. Model System. The PGE/aniline reaction proceeds according to the sequence shown in Figure 1. This figure is intended only to illustrate the events on the molecular level; the exact mechanism and the chemorheological aspects of those reactions will not be discussed here, and the interested reader is referred to the pertinent literature.[13] The rationale in choosing the model system was based upon the lack of evolution of small molecules during reaction, its importance in modeling of cure of multifunctional epoxy systems, and our considerable experience with the chemorheological characteristics of this genetic group of materials.

2. Assignment of Near-IR Absorption Peaks in the Initial Components. We begin our discussion by presenting the near-IR spectra of PGE and aniline in Figures 2 and 3, respectively. The spectral region between approximately 4000 and 7100 cm^{-1} was investigated in this study. For convenience sake, we shall subdivide this region into three zones, termed A, B, and C, whose main features are described below.

Zone A, which extends from ca. 3600 to 4800 cm^{-1}, is the "fingerprint" section which contains specific information about the chemical structure of the material and hence is useful for identification purposes. This zone is of major importance in our study since it contains the combination band of epoxy stretching and bending vibration, at 4530 cm^{-1}, whose absorption intensity decreases systematically during reaction and can there-

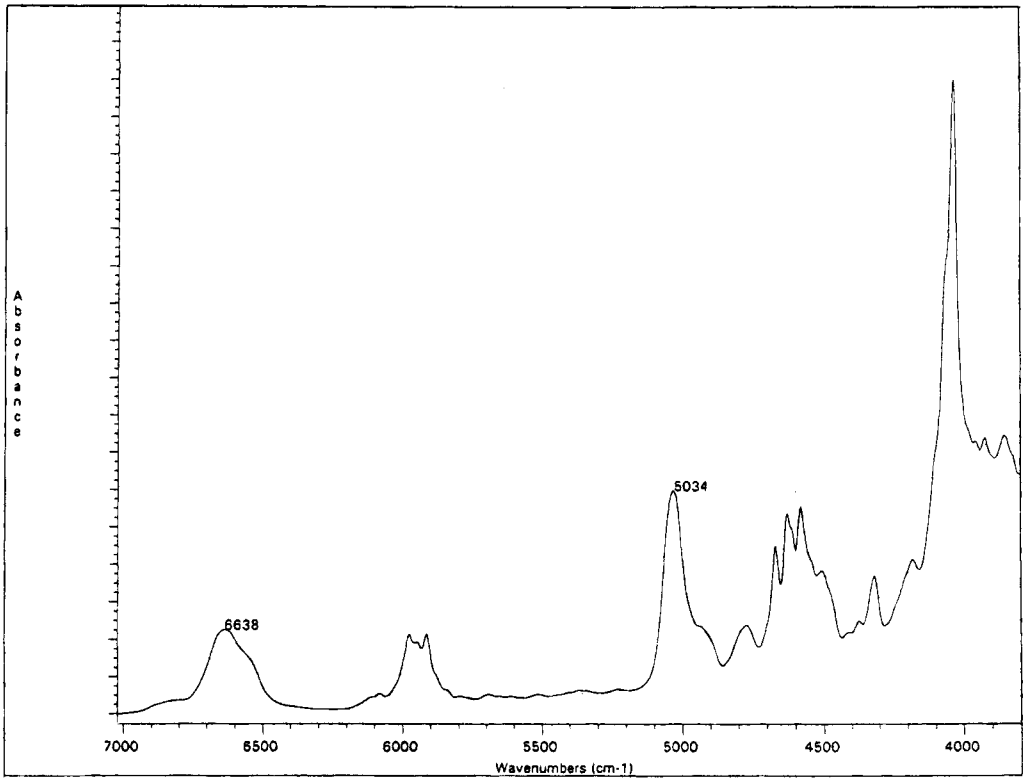

Figure 3. Near-IR spectrum of aniline.

fore be used in the kinetic studies. The presence of this peak has been first reported and analyzed in the late 1950s and early 1960s.[1,2]

A most interesting peak was noted at 4300 cm^{-1}. Its small initial absorption area remains unchanged until about 55% conversion, at which point it begins to increase and becomes pronounced at the end of reaction. This peak is probably related to the presence of −OH groups, or some form of their interactions in the mixture, and the onset of its increase at the critical concentration of −OH groups is intriguing.[13]

There are three important absorption bands in zone B, which covers the range between ca. 4800 and 6000 cm^{-1}. The primary amine combination (bending and stretching vibrations), located at 5056 cm^{-1}, yields a useful measure of the decrease in primary amine concentration during reaction. The first detailed near-IR analysis of aromatic primary amines was done by Whetsel et al.,[14] who reported peak positions and intensities for various aromatic amines and analyzed the effect of the benzene ring substituents. This peak was located at 5067 cm^{-1} by George et al.[7] and utilized in their study of the kinetics of a tetrafunctional epoxy/aromatic amine formulation by remote spectroscopy. The spectral cutoff of their fibers was 4700 cm^{-1}, and hence these authors did not monitor the major near-IR epoxy absorption at 4530 cm^{-1}. Another interesting peak is due to the hydroxyl combination band, which is found in the broad range between 4800 and 4900 cm^{-1}. The absorption at 5240 cm^{-1} is representative of hydroxyl−water interactions and can be used for the evaluation of moisture content.[15] The effect of moisture on this band was also experimentally confirmed in our laboratory.

Zone C extends from 6000 to ca. 7100 cm^{-1}. An important peak appears here at approximately 6670 cm^{-1}, as a result of the combined absorption of primary and secondary amine. This peak is particularly useful for the kinetic studies in the later stages of reaction, when primary amine groups are depleted and only secondary amine−epoxy reactions take place. The first overtone of the hydroxyl group stretching vibration, found at ca. 7000 cm^{-1}, is another important band. Although every reaction between an epoxy group and an amine hydrogen produces a hydroxyl group, the use of this band to monitor reaction kinetics in terms of the appearance of hydroxyl groups is complicated by the simultaneous occurrence of hydrogen bonding and a 30-fold decrease in the absorptivity ratio of free to bonded hydroxyl in near-IR versus mid-IR spectra.[16] It is well-known that the hydrogen-bonded hydroxyl group absorbs at longer wavelength than the free hydroxyl group. The question of the influence of hydrogen bonding on the intensity and shifts of the peak at 7000 cm^{-1} was first addressed by Dannenberg,[2] in his excellent early work on the development of a near-IR method for the determination of functional groups in epoxy resins. He found that the absorption intensity at 7000 cm^{-1} increased during cure of a bifunctional epoxy with ethylenediamine, but the peak maximum did not shift with frequency. He further noted the appearance of a shoulder at longer wavelength in the later stages of cure and ascribed it to the formation of another type of hydrogen bonding originating from the physical changes in the curing system. Similar results were obtained in our study of PGE/aniline reactions; we did not notice a change in either shape or wavelength-at-maximum for the 7000 cm^{-1} peak. The influence of hydrogen bonding was manifested by an upward shift in the baseline at the lower wavenumber tail of the peak. An important point, seldom explicitly invoked and often overlooked in the reported FTIR studies of epoxy/amine kinetics, is the effect of temperature on hydrogen bonding. Stronger absorption due to hydrogen bonding occurs at lower temperatures, and hence the results of an in-situ measurement at higher temperature (e.g., over 100 °C) cannot be directly compared to those generated "off-line" at, for instance, room temperature. Comparison and

Table 1. Major Near-IR Peaks in a PGE/Aniline System between 4000 and 7100 cm^{-1}

peak maximum (wavenumber, cm^{-1})	assignment	remarks
7000	−OH stretching vibrations (first overtone)	baseline shift at lower wavenumber peak tial due to hydrogen bonding
6878	$-NH_2$ asymmetric stretching vibrations	weak band
6670	$-NH_2$ combination of symmetric and asymmetric stretching vibrations	region of both primary and secondary amine absorptions
6570	$-NH_2$ symmetric stretching vibration	partial overlap with neighboring combination band
6080	strecthing vibrations (first overtones)	weak band
just below 6000	−CH and $-CH_2$ stretching vibrations (first overtones)	overlap with second overtone epoxy group absorptions
5240	−OH stretching vibration due to moisture	useful for evaluation of moisture content in materials
5056	$-NH_2$ combination band (stretching and bending vibrations)	represents the absorption of primary amine only
4900−4800	−OH combination band	abrupt shift in baseline due to hydrogen bonding
4670 and 4623	−CH stretching vibration due to benzene ring	can be used as reference-standard peak
4586	nonassigned peak	related to epoxy group content
4530	combination band (strecthing and bending vibrations)	useful in kinetic studies; strong, well-separated peak
4300	−OH absorption interactions	remains constant until about 55% conversion and then increases
4210 and 4134	nonassigned peaks	decrease during reaction; same phenomenon observed in DGEBA−MDA system
4055	−CH stretching vibration due to benzene ring	possible existence of another peak in the same region

interpretation of such data require prudence. Scherzer[11] recently used near-IR spectroscopy to study a bifunctional epoxy resin modified with aliphatic diols. He reported hydroxyl group absorption at 6983 cm^{-1} and tentatively assigned it to a "combined effect of dimeric intermolecular and intramolecular interactions" but offered no evidence to support his hypothesis. Ghebremeskel et al.[10] studied specific interactions in the blends of poly(caprolactone) (PCL) and phenoxy[poly-(hydroxypropylether of Bisphenol A)] and found that the maximum of the OH stretch peak shifts to a higher wavenumber (from 6988 to 7015 cm^{-1}) when the concentration of PCL in the blend was increased but offered no explanation for it. The first overtone of epoxy vibrations also occurs in zone C, at ca. 6080 cm^{-1}, but it cannot be readily used for quantitative kinetic studies due to a significant overlap with absorptions due to C−H and $C-H_2$ stretching vibrations centered around 6000 cm^{-1}.

Table 1 contains a list of major absorption peaks observed in this study, their molecular origin, and some relevant comments regarding their utility. We have omitted several peaks found in zone A whose absorption intensities do not vary during the reaction.

3. Changes in Near-IR Spectra during Reaction. Once the initial components were characterized, we proceeded to monitor the changes in the near-IR spectra during PGE/aniline reactions at a series of temperatures between 90 and 130 °C. An example of our results is given in Figure 4, which contains a series of spectra taken at various times during PGE/aniline reaction at 110 °C. Analogous results were obtained at other temperatures. The trends displayed by major peaks of relevance in the epoxy/amine kinetic studies are evident: a decrease in epoxy absorption (4530 and 6080 cm^{-1}); a decrease in amine absorption (5056 and 6670 cm^{-1}); an increase in hydroxyl absorption (7000 and 4800−4900 cm^{-1}). An enlarged view of a portion of zone A is shown in Figure 5. In addition to the major epoxy peak at 4530 cm^{-1}, which decreases systematically and in a highly reproducible manner during reaction, three new absorption peaks were observed at 4586, 4210, and 4134 cm^{-1}, all of which also decrease during reaction. Interestingly, the last two peaks were also observed in a diglycidyl ether of Bisphenol A (DGEBA) type epoxy, while the peak at 4586 cm^{-1} appeared in PGE only. We are not quite sure, at present, what the molecular origin of those peaks is.

4. Evaluation of PGE/Aniline Reaction Kinetics from Near-IR Spectra. The use of FTIR spectroscopy to study reaction kinetics has been documented in the literature (e.g., refs 17 and 18), and only the salient points of our analysis will be recapped here. The extent of reaction (α) at any time t is calculated from the initial areas of epoxy and reference peaks, $A_{e,0}$ and $A_{r,0}$, respectively, and their corresponding values at time t, $A_{e,t}$ and $A_{r,t}$, according to the following equation:

$$\alpha = 1 - [(A_{e,t})(A_{r,0})]/[(A_{e,0})(A_{r,t})] \quad (1)$$

The peak at 4530 cm^{-1} was used to monitor the disappearance of the epoxy group. Various reference peaks were utilized and the most reproducible results were obtained using the peak due to the C−H stretching vibration of the benzene ring at 4673 cm^{-1}. The extent of reaction at 110 and 120 °C, calculated from eq 1, is plotted as a function of reaction time in Figure 6. A direct comparison with the extent of reaction for the same system measured by high-performance liquid chromatography (HPLC), which was reported in an earlier paper from our laboratory,[13] revealed excellent agreement between these two methods. We emphasize that the HPLC results were in excellent agreement with the predictions of our mechanistic kinetic model of epoxy/amine reactions described in the same paper.[13]

5. Direct Comparison of PGE/Aniline Kinetics Obtained by Near-IR and Mid-IR Analyses. Epoxy absorption in the mid-IR range at approximately 915 cm^{-1} has been used over the years by numerous authors in their investigations of the reaction kinetics of an array of epoxy formulations. We decided to analyze the kinetics of PGE/aniline reactions in the mid-IR range as a further test of the accuracy of our near-IR results. Several reference peaks were tried and found not to affect the kinetics; for instance, identical results were obtained using either the ether stretching vibration band at 1040 cm^{-1} or the benzene ring peak at 693 cm^{-1}.

When the kinetic results of our mid-IR and near-IR analyses were compared, a most interesting and equally surprising finding was obtained: the kinetics of reaction

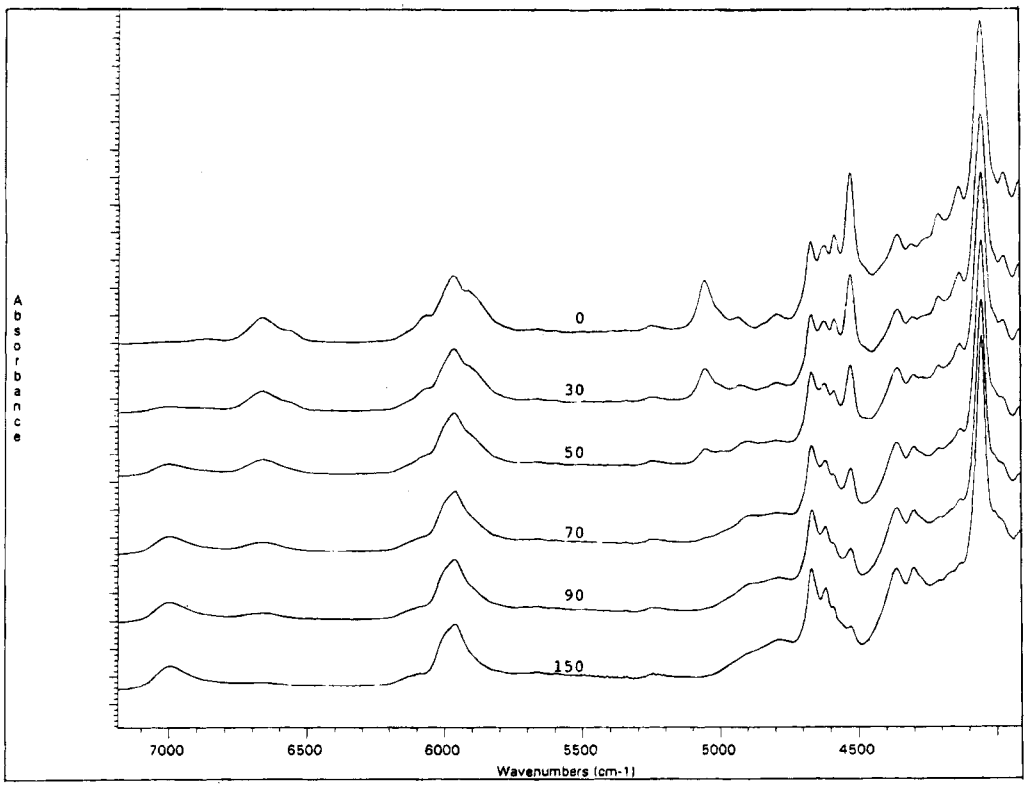

Figure 4. Near-IR spectra of a PGE/aniline system during reaction at 110 °C, with reaction time in minutes as a parameter.

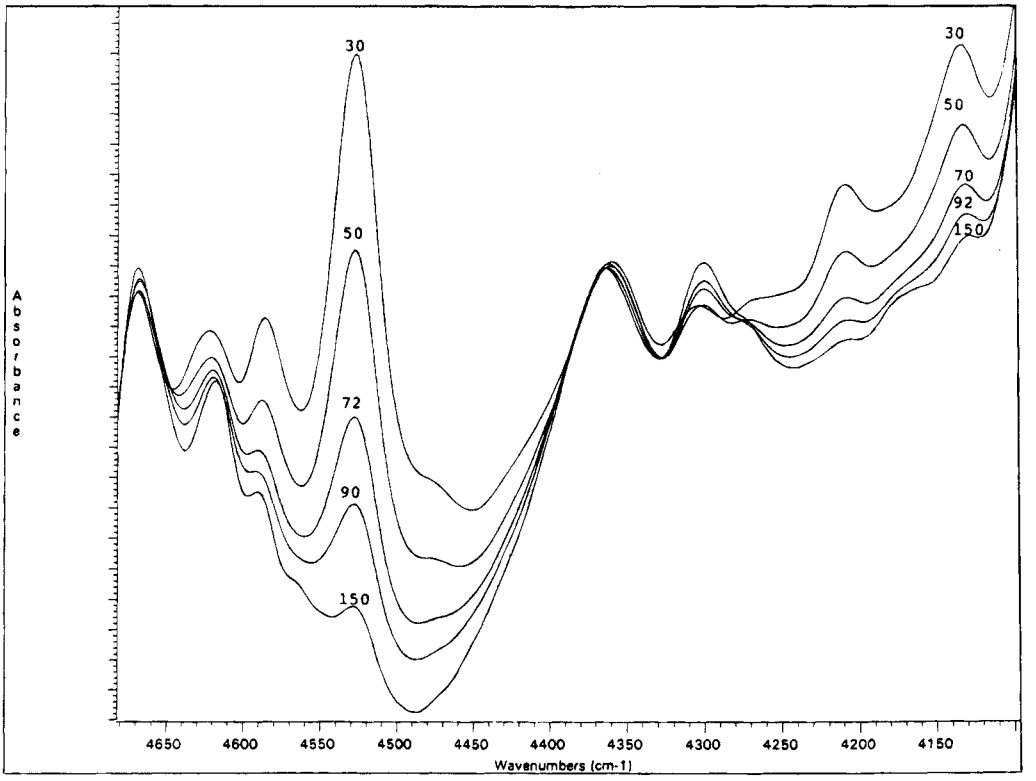

Figure 5. Enlarged view of zone A in near-IR spectra of a PGE/aniline system during reaction at 110 °C, with reaction time in minutes as a parameter.

measured by the disappearance of the epoxy group in near-IR and mid-IR spectra were found to differ consistently and in a reproducible manner.

A direct comparison of the extent of reaction at 110 and 120 °C calculated from near-IR and mid-IR data is shown in Figure 7. The two curves of extent of reaction for a given temperature appear horizontally shifted with respect to one another but retain similar slopes (hence rates) between approximately 10 and 60% conversion. The observed difference in initial rates and the corresponding horizontal shift are caused, at least partly, by the difference in sample size and configuration and the associated unavoidable discrepancy between thermal histories in the preisothermal stage. A thermal lag of a few degrees in the heating stage can have a noticeable effect on kinetics. Most importantly, however, the

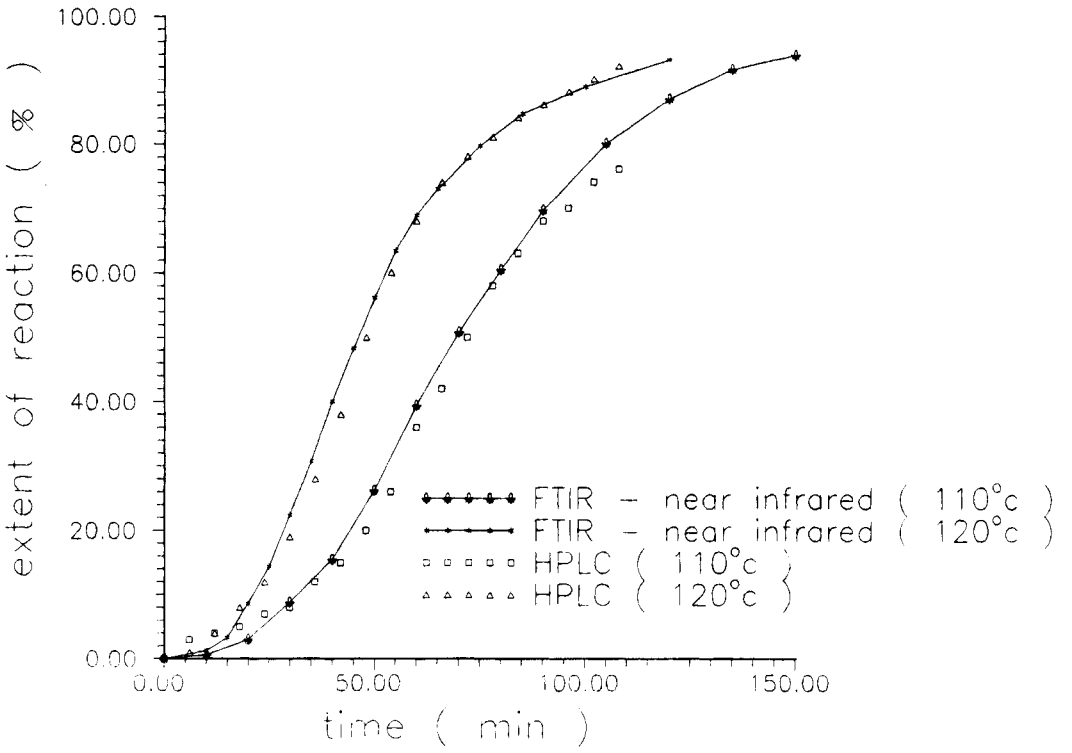

Figure 6. Extent of reaction of a PGE/aniline system at 110 and 120 °C as a function of time, calculated from near-IR and HPLC measurements.

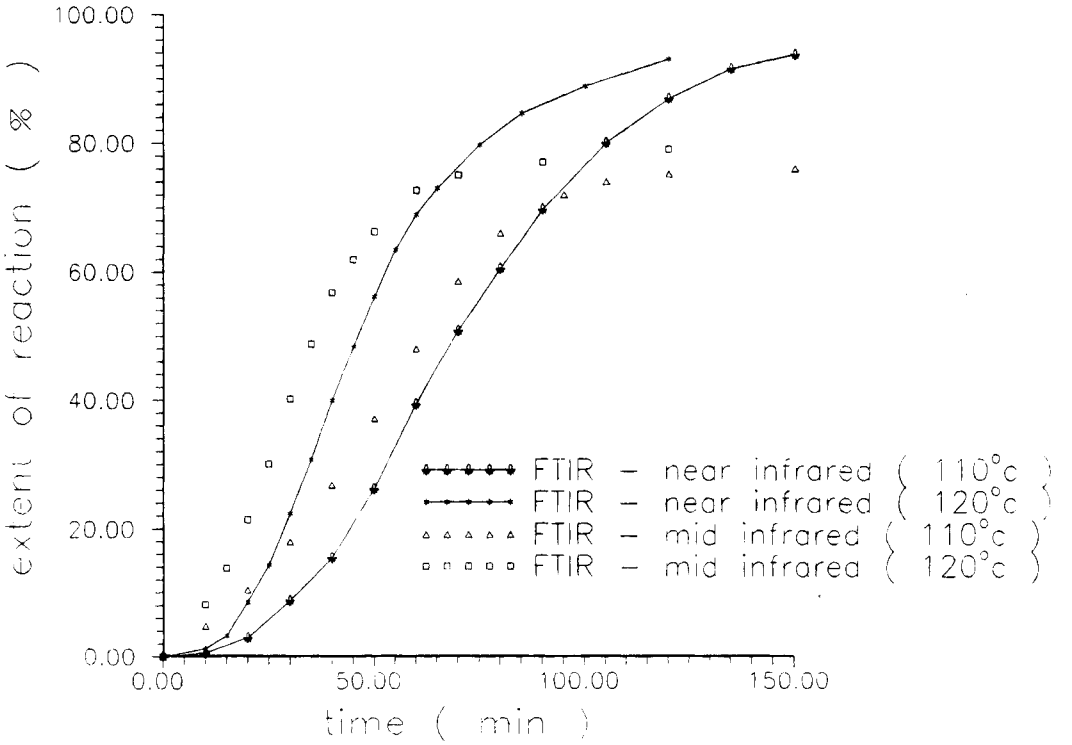

Figure 7. Extent of reaction of a PGE/aniline system at 110 and 120 °C as a function of time, calculated from near-IR and mid-IR measurements.

difference between the final portions of the two curves is evident, reproducible, and not in question. The mid-IR analysis predicts leveling off at about 78% conversion, while according to the near-IR results, the reaction eventually reaches conversion levels which, at the conditions of this study, exceed 93%.

Since the kinetics of a reactive system are its inherent characteristic and cannot be a function of the measuring method, and in the view of many published reports of epoxy kinetics based on the mid-IR data, we were intrigued by our findings and have set out to establish which of these two methods of analysis was correct. The accuracy of temperature control, the constancy of mixture composition, and the reproducibility and reliability of data have all been firmly established and are not in question. To verify if our findings were specific to aniline, we first ran a series of tests using *N*-methylaniline in lieu of aniline and obtained analogous results. We then addressed the key unresolved question of the significantly different final conversion calculated from

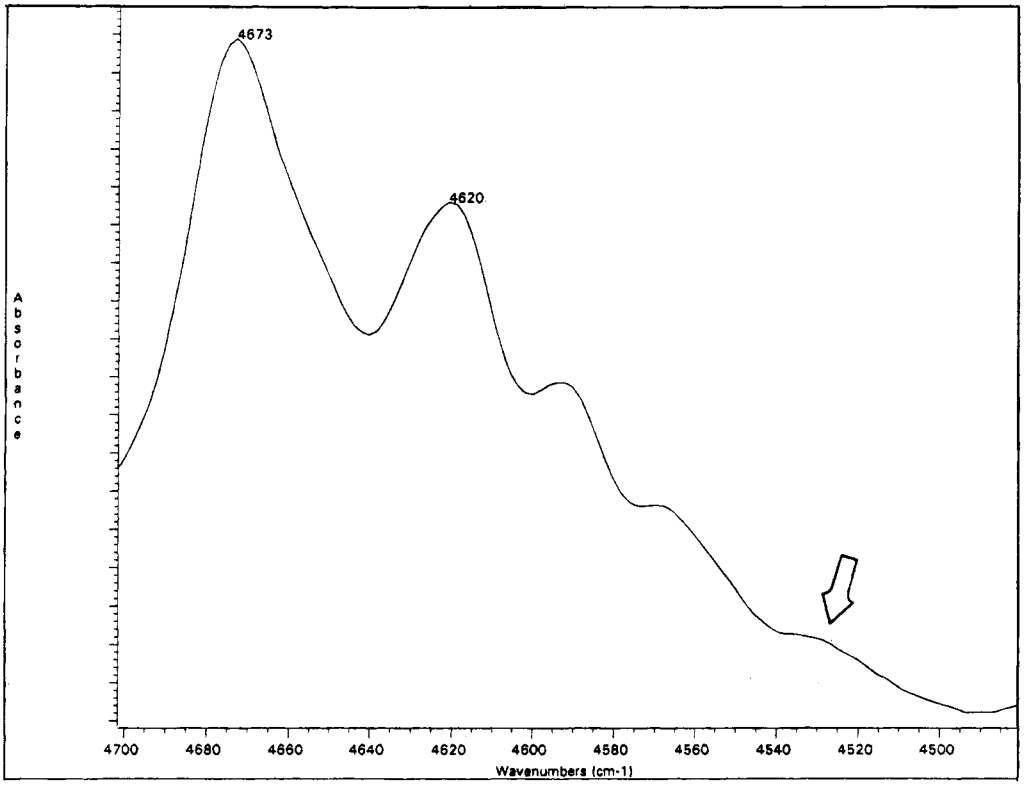

Figure 8. Epoxy absorption (4530 cm^{-1}) zone of the near-IR spectrum of a PGE/aniline system reacted at 105 °C/5 h + 160 °C/5 h.

near-IR and mid-IR analyses. For that purpose, a PGE/aniline reaction mixture was placed in a 25-mL vial and heated in an oven for 5 h at 105 °C, followed by an additional 5 h at 160 °C, at which point the reaction was assumed to be completed. A small amount of the product was dissolved in carbon tetrachloride, coated on a KBr window, and heated to remove the residual solvent. The sample was then tested in both near-IR and mid-IR, and the obtained results were identical to those shown in Figure 7; the initially observed difference in the spectra persisted. The near-IR spectrum of enlarged zone A, shown in Figure 8, revealed a 99% epoxy conversion (see arrow), while in the mid-IR spectrum of Figure 9, that number was considerably different and did not surpass 80%! The same results were obtained using a sample with excess aniline. Next, an HPLC analysis was performed on the individual components (PGE and aniline) and the final product of the above-described oven-heating sequence. A lone peak was observed in the chromatogram of the final product, and no trace of other compounds was detected. At this point, with overwhelming supporting evidence in hand, we felt confident that the near-IR and not the mid-IR results represented the actual kinetics of epoxy reactions. We believe that the 915 cm^{-1} mid-IR peak, unlike the 4530 cm^{-1} near-IR peak, is not a unique measure of the concentration of free epoxy groups, and hence its direct use for the quantitative analysis of epoxy/amine kinetics is questionable unless appropriate corrections are made. We have identified two additional mechanisms that affect absorption in the vicinity of 915 cm^{-1} and could be invoked to explain the observed anomaly in the mid-IR results. These two mechanisms are not mutually exclusive and are described below.

The first mechanism is deduced from the mid-IR spectra of epoxy absorption peaks at 915 and 840 cm^{-1}, whose gradual change during cure is displayed in Figure 10. As the reactions progress, the intensities of both peaks decrease and the 840 cm^{-1} peak also becomes skewed. An inspection of the spectra in Figure 10 clearly shows that after 120 min the 840 cm^{-1} peak diminishes in intensity and shifts to a lower wavenumber. But the 915 cm^{-1} peak remains strong even after 120 min of reaction, apparently suggesting a continuing presence of free, unreacted epoxy groups in the mixture which, we believe, is not the case. A more likely explanation is that there is an overlapping nonreactive peak in the 915 cm^{-1} region, whose residual absorption at the end of the reaction is mistakenly interpreted as being due to the remaining epoxy and which accounts for the observed difference between the near-IR and mid-IR kinetics. The most probable candidate is the C−O−C group, whose stretching absorptions in phenetoles[19] are found at 1240, 1040, and 920 cm^{-1}. The first two peaks are evident in our spectra. The 920 cm^{-1} peak overlaps with the 915 cm^{-1} epoxy peak and hence is not easily distinguishable, though its presence must be appropriately accounted for in a kinetic analysis.

To describe the second mechanism that possibly contributes to our (unexpected) findings, we shall first invoke the salient features of the epoxy/amine reaction mechanism. We reported earlier that the reaction rate order for the formation of tertiary amine in epoxy/amine systems changes at a critical concentration of hydroxyl groups.[13] For a PGE/aniline system, this critical concentration was observed at approximately 55% conversion and was independent of temperature. Above the critical value, we suggested the rising importance of hydroxyl groups in the formation of new hydrogen-bonded complexes during reaction necessitated that an additional reaction path be included in the mechanistic kinetic model. Interestingly, that scheme parallels the herein observed shift of the epoxy peak at 965 cm^{-1}, shown in Figure 11, which initially decreases during

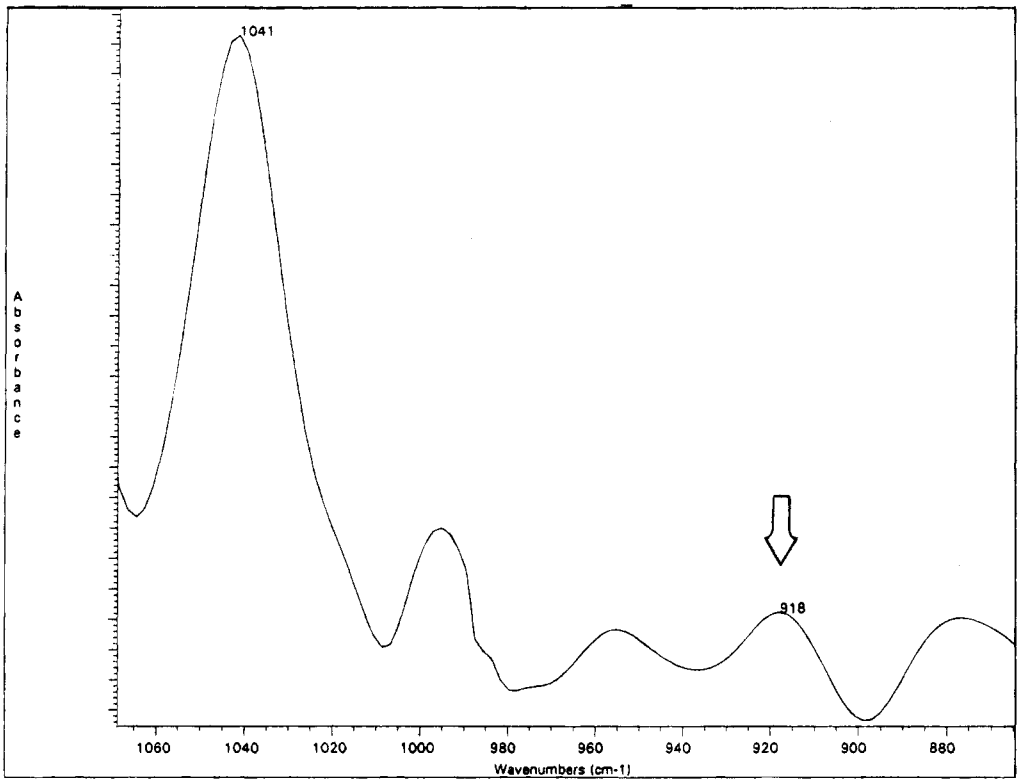

Figure 9. Epoxy absorption (915 cm^{-1}) zone of the mid-IR spectrum of a PGE/aniline system reacted at 105 °C/5 h + 160 °C/5 h.

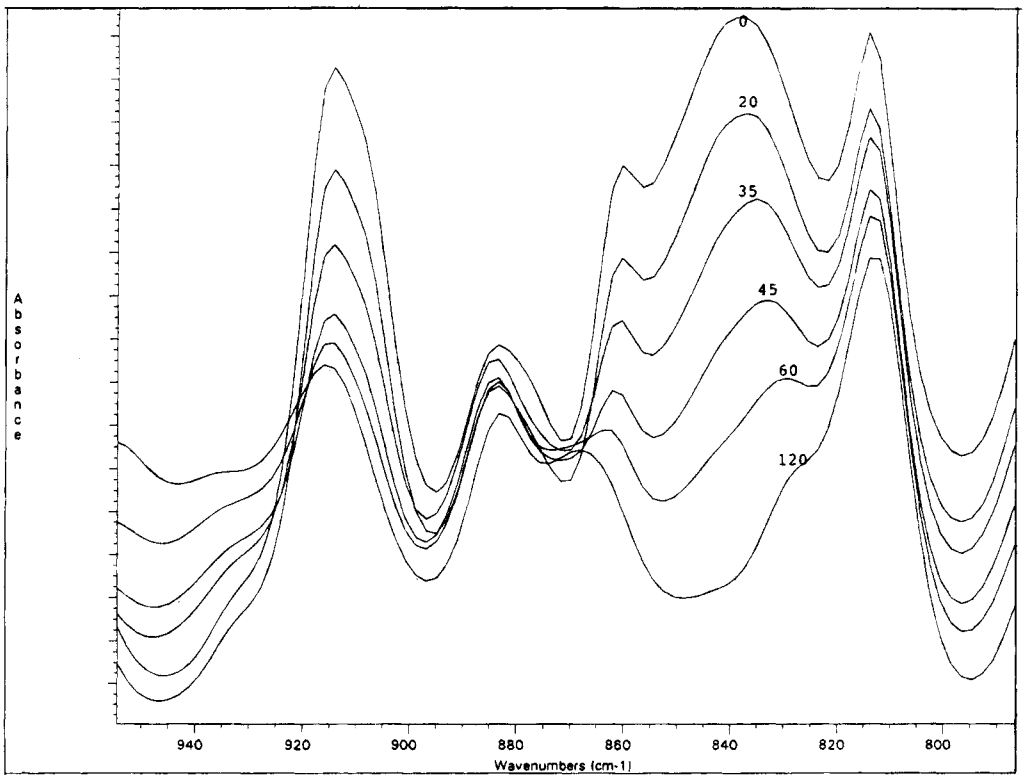

Figure 10. Epoxy absorption peaks at 915 and 840 cm^{-1} during reaction of a PGE/aniline system at 120 °C, with reaction time in minutes as a parameter.

reaction and then suddenly begins to shift to longer wavelengths at about 58% conversion independent of the reaction temperature. This conversion is very close to the gel point in tetrafunctional epoxy/amine formulations, and it also coincides with an increase in viscosity in the non-polymer-forming PGE/aniline system. It is suggested that a new form of hydrogen bonding appears, related to the increase in viscosity of the reactive mixture. We are currently looking into a possible quantitative correlation between these two events.

To elucidate further the influence of hydrogen bonding on epoxy absorption peaks at 915 and 965 cm^{-1}, an additional experiment was designed and performed. The spectral changes during that experimental sequence are described in Figure 12a–c. The PGE/aniline reaction was first run in a heated cell at 125 °C, and the peaks

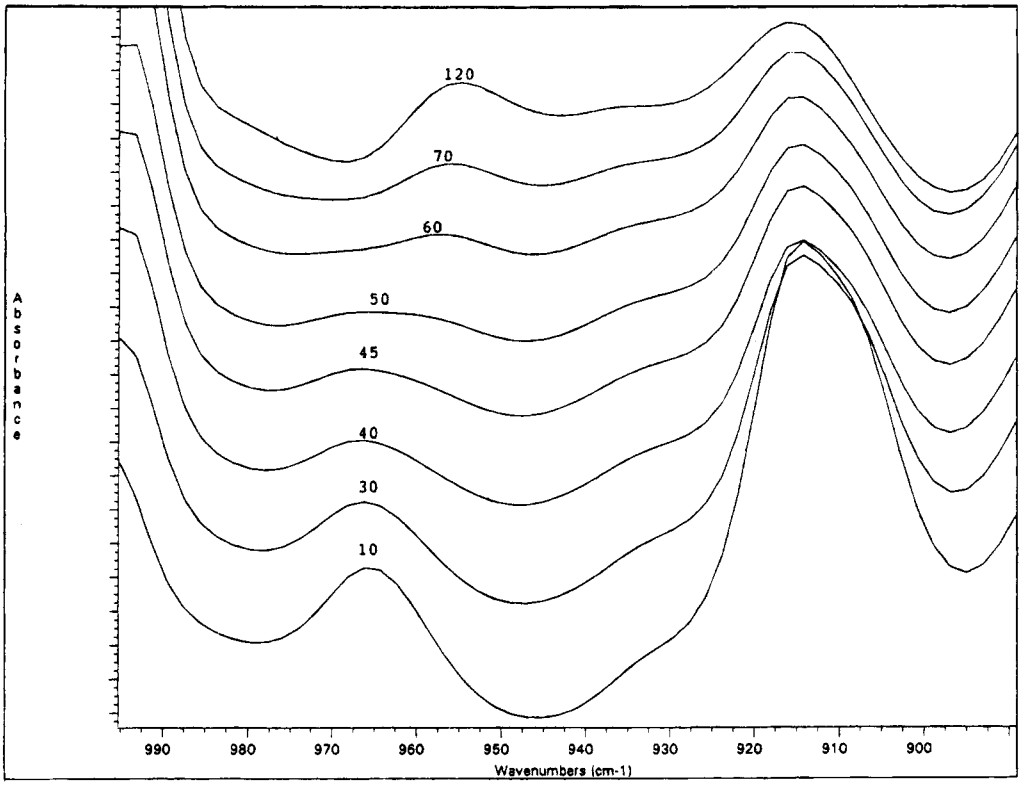

Figure 11. Epoxy absorption peaks at 965 and 915 cm^{-1} during reaction of a PGE/aniline system at 120 °C, with reaction time in minutes as a parameter.

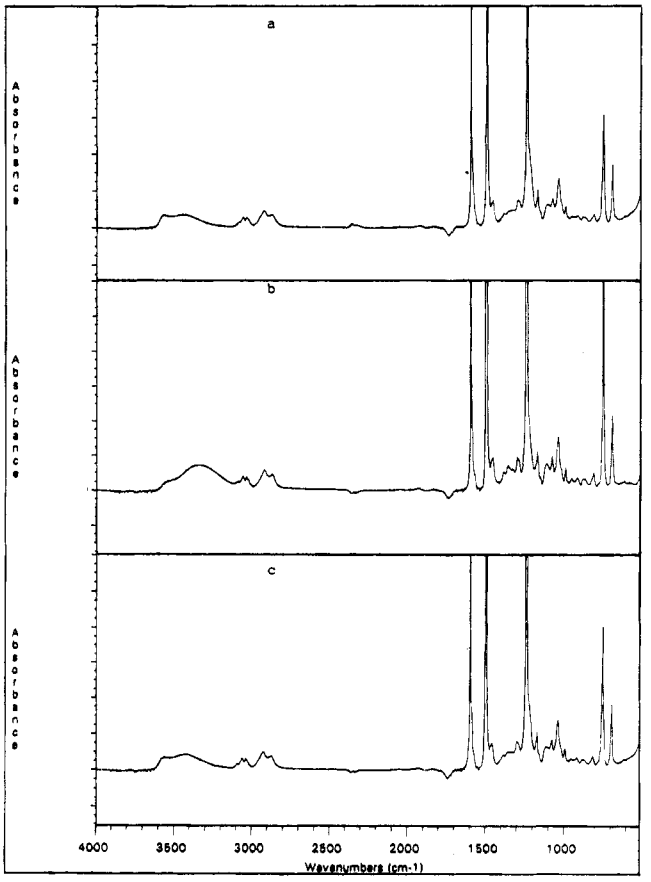

Figure 12. Mid-IR spectrum of PGE/aniline: (a) at 125 °C after reaction at that temperature for 340 min; (b) at room temperature upon cooling; (c) at 125 °C after reheating.

at 915 and 965 cm^{-1} were monitored up to the point where no further change in the former was observed (Figure 12a). Upon increasing the temperature to 133 °C, both peaks started to decrease slowly and then leveled off. The sample was then cooled to room temperature and scanned. A most interesting result was obtained; there was a strong increase in hydroxyl absorption, at ca. 3300 cm^{-1}, and in both epoxy peaks, at 915 and 965 cm^{-1} (Figure 12b). The peaks at 915 and 965 cm^{-1} increased by about 15% and 40%, respectively! This measured increase was precisely determined by normalizing the peak areas with respect to the benzene ring absorption at 693 cm^{-1} and was very reproducible. The observed phenomenon was thermally reversible, however, and the initial absorbance levels were attained upon reheating (Figure 12c). If the 915 cm^{-1} peak were used to evaluate the extent of reaction before and after cooling, the observed 15% decrease in its intensity upon cooling would translate into a simultaneous decrease in the extent of reaction from 82.5 to 70.5%, which is clearly impossible on physical grounds. This observation strongly supports our tenet that the absorption band at 915 cm^{-1} is also influenced by hydrogen bonding and hence is not a measure of the concentration of free epoxy groups **only**, raising doubts regarding its use for the quantitative kinetic analysis of reactive epoxy systems.

IV. Conclusions

We have carried out an investigation of model epoxy/amine reactions by near-infrared spectroscopy. Characteristic near-IR band assignments were identified and used in evaluation of reaction kinetics. An excellent agreement was observed between the kinetics deduced from the near-IR results and those obtained from high-performance liquid chromatography. A direct comparison of near-IR and mid-IR spectra led to the conclusion that the standard mid-IR epoxy absorption at 915 cm^{-1} is not an exclusive measure of free epoxy groups and is affected by other absorption mechanisms, including hydrogen bonding and an overlapping group absorption.

Appropriate corrections should be made in kinetic analyses of mid-IR results based on that peak. Near-IR spectroscopy, on the other hand, was shown to be an attractive method for qualitative and quantitative evaluation of the progress of reaction. Due to its compatibility with silica type optical fibers, this technique is particularly promising for in-situ real time remote sensing of reactive systems.

Acknowledgment. Funding by the Air Force Office of Scientific Research (AFOSR) under Grant No. F49620-93-1-0603 for the purchase of FTIR equipment is gratefully acknowledged.

References and Notes

(1) Goddu, R. F.; Delker, D. A. *Anal. Chem.* **1958**, *30*, 2013.
(2) Dannenberg, H. *SPE Trans.* **1963**, *3*, 78.
(3) Lee, H.; Neville, K. *Handbook of Epoxy Resins*; McGraw-Hill: New York, 1967.
(4) Osborne, B. G.; Fearn, T. *Near Infrared Spectroscopy in Food Analysis*; Wiley: New York, 1986.
(5) Archibald, D.; Miller, C. E.; Lin, L. T.; Honigs, D. E. *Appl. Spectrosc.* **1988**, *42*, 1549.
(6) Paputa Peck, M. C.; Carter, R. O., III; Qaderi, S. B. A. *J. Appl. Polym. Sci.* **1987**, *33*, 77.
(7) George, G. A.; Cole-Clark, P.; St. John, N.; Friend, G. *J. Appl. Polym. Sci.* **1991**, *42*, 643.
(8) St. John, N.; George, G. A. *Polymer* **1992**, *33* (13), 2679.
(9) Fu, J. H.; Schlup, J. R. *J. Appl. Polym. Sci.* **1993**, *49*, 219.
(10) Ghebremeskel, Y.; Fields, J.; Garton, A. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 383.
(11) Scherzer, T. *J. Appl. Polym. Sci.* **1991**, *51*, 491.
(12) Mijovic, J.; Kenny, J. M.; Nicolais, L.; Pejanovic, S. *SAMPE J.* **1992**, *28* (5), 39.
(13) Mijovic, J.; Fishbain, A.; Wijaya, J. *Macromolecules* **1992**, *25*, 978.
(14) Whetsel, K. B.; Robertson, W. E.; Krell, M. W. *Anal. Chem.* **1958**, *30* (10), 1594.
(15) Ciurezak, E. W. *CHEMTECH* **1992**, June, p 374.
(16) England-Kretzer, L.; Fritzsche, M.; Luck, W. A. P. *J. Mol. Struct.* **1988**, *175*, 277.
(17) Morgan, R. J. *Adv. Polym. Sci.* **1985**, *72*, 1.
(18) Mertzel, E.; Koenig, J. L. *Adv. Polym. Sci.* **1985**, *75*, 73.
(19) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1964.

MA946025Y