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Chemical Composition Monitoring Using An In-Situ Infrared Probe

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This paper describes a new approach to process analysis utilizing an infrared probe which can be immersed within a volume of liquid chemical. Based on the internal reflectance principle, the immersion probe can be coupled to a process FTIR spectrometer to provide essentially real-time analysis of either batch or continuous reactions. After describing the design of the probe, the paper presents the results of a series of laboratory scale experiments in which a small version of the immersion probe was used to monitor various polymerization reactions.

1. Introduction

Over the past several years, infrared spectroscopy has emerged from the laboratory to become a powerful "new" tool for on-line chemical process monitoring. Several developments have come together to make this important advance possible. These include high performance FTIR spectrometers exhibiting the stability and ruggedness demanded by the manufacturing environment, software capable of converting the wealth of spectral information available into readouts of the desired process variable, and highly reliable sampling equipment to couple the IR instrumentation to the process line.

As of this writing, over one hundred dedicated process FTIR systems have been placed in operation with applications ranging from process gas analysis to monitoring the composition of hot polymer melts. These spectrometers operate in either the near-IR or mid-IR regions of the spectrum. In the near-IR, FTIR technology provides the high stability needed to separate the contributions from chemical species with broadly overlapping absorption bands. When used in mid-IR, FTIR provides an additional important benefit - the ability to directly monitor the sharp spectral bands which characterize functional groups. Since it is the functional groups that control chemical reactivity, mid-infrared FTIR can be said to provide a "window" into the chemical process.

Most of the present on-line FTIR systems are being used to monitor continuous processes. In these, systems, a portion of the process stream flows through a sampling device employing either the transmission or the attenuated total reflectance (ATR) principle.

The present paper reports on a new sampling capability which has made it possible to extend the power of process FTIR to batch processes while, at the same time, promising to provide enhanced performance for many continuous processes (1). This capability involves the use of a family of infrared immersion probes which can be inserted into a batch process kettle or large diameter process line to provide true in-situ chemical analysis during the manufacturing process. This makes it possible, for example, to monitor the concentrations of individual constituents in a batch reaction so as to terminate the process when the optimum concentrations have been reached.

The new "Deep Immersion Probes" have been developed within the past two and one-half years. Within ten months of the first commercial application of the principle on a laboratory scale, the immersion probes had made the transition to full scale on-line application. This rapid conversion was made possible by the generally high level FTIR technology available and by the skills of key scientists within the process industry. The use of the infrared immersion technique is already starting to have significant impact on quality, efficiency, and yields in a variety of chemical processes.

2. Deep Immersion Probe Design

The optical design of the immersion probes is illustrated in

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Figure 1. As this figure suggests, the design is conceptually quite simple, involving the use of the hollow metallic light guides to transmit IR radiation to and from an ATR element at the lower end of the probe. This apparent simplicity prompts the obvious question as to why this technology wasn't available sooner. The answer is two-fold. First, the potential utility of an in-situ IR probe for process use wasn't recognized until FTIR hardware had reached the level of performance required for process application. Second, the development of the probe did require technical advances - the design of sufficiently rugged and compact sensing head optics and an efficient means of coupling the IR radiation between the spectrometer and the probe.

The use of metallic light guides for this application may at first seem obvious. However, this approach had been generally rejected in the past due to the inherent divergence of incoherent IR radiation coupled with the fact that the reflectance of most materials is poor for angles far from normal incidence. The present system overcomes these obstacles by using radiation which is very nearly collimated and a light guide coating which exhibits especially high reflectance at angles very close to grazing.

An alternative approach to transmitting the radiation to and from the probe might be the use of infrared fiber optics[2]. However, this approach has two fundamental problems. First, suitable mid-IR fibers have yet to be developed. Second, the relatively low energy of thermal radiation sources in the mid-IR necessitates the use of optical systems with high geometric thoughput. In the case of fiber optics, this would require either the use of individual fibers with diameters of the order of a millimeter or equally large fiber bundles with a very high collection efficiency.

The operation of the probe sensing head is based on the attenuated total reflectance (ATR) method[3] In this method, the IR radiation is transmitted through an optical element having a high index of refraction in such a way that it alternatively reflects from opposite sides of the element at an incidence angle of approximately 45°. Due to the high refractive index, the radiation is totally reflected at this angle when the element is surrounded by air. However, when the element is immersed in an absorbing medium, a portion of the radiation is absorbed at each reflection, making it possible to obtain an absorption spectrum of the surrounding medium. Since the effective penetration depth on each reflection is rather small, this technique is especially useful for the very strong absorption bands encountered in the mid-IR.

The design of the sensing head had been discussed in detail previously[1][4]. Thus I will only outline it briefly here. The heart of the probe is a cylindrical rod of an infrared transmitting material with a relatively high index of refraction. The
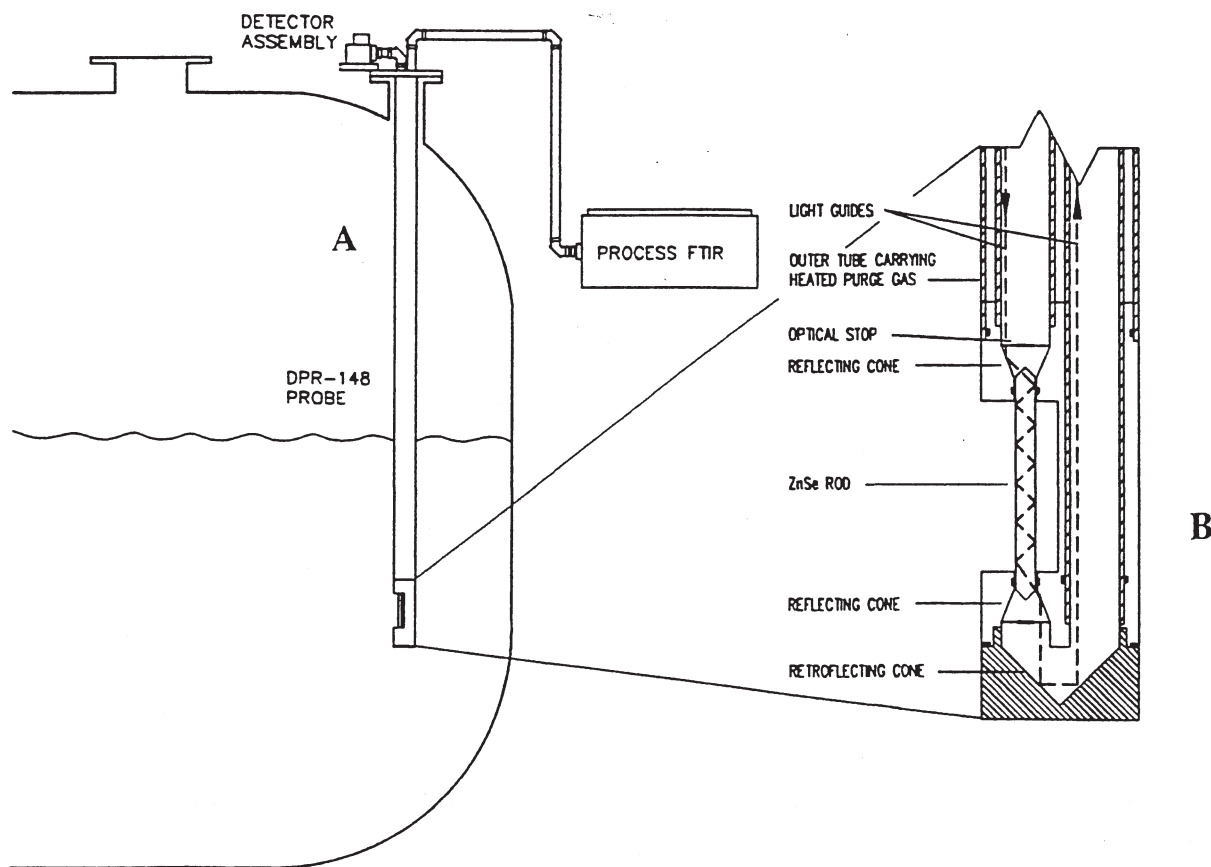

Figure 1 A - Process scale deep immersion probe mounted in a batch reaction vessel
        B - Probe Sensing head construction

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ends of the rod are in the form of 90° cones. As illustrated in Figure 1, the collimated radiation traveling down through one of the internal light guides first strikes a reflecting cone the sides of which are at an angle of 22.5° to the light guide axis. The reflected radiation then enters the rod approximately normal to the conical end surface, after which it travels through the rod at an angle of 45° to its axis, alternately being reflected from one side and then the other. After leaving the lower end of the rod, the radiation is recollimated by reflection from a second 22.5° cone. Optical stops at each end eliminate radiation which would otherwise travel through the rod without striking the reflecting cones. A large reflecting cone at the bottom of the probe redirects the radiation up through a second light guide.

The design outlined above was initially developed to meet the size constraints imposed by the ports available on typical reaction vessels. However, it also provides several additional benefits. For example, the optical characteristics are essentially machined into the structure. Since there are no adjustments, nothing can change. The result is a very high degree of performance stability and repeatability, even from probe to probe. In addition, the design concentrates the radiation at the optimum angle of incidence. The result is enhanced sensitivity compared to other ATR devices and a very high degree of absorbance linearity. Along with these benefits, goes the ruggedness which results both from the lack of adjustable parts and the solid stainless steel construction.

2. Scaling Considerations

An important consideration in designing any process monitoring system is the need to employ the system on a small scale to model the process and then to scale it up for full scale on-line operation - with minimal change in performance. In our program, this need was met by developing a series of probes having essentially identical spectroscopic characteristics but designed to mate to reaction vessels ranging in capacity from a few hundred milliliters to thousands of gallons.

To date, we have constructed probes with diameters of 0.98, 2, and 3.5 inches and lengths ranging from 9 inches to 8 feet. The diameters of the ATR elements corresponding to the three probe diameters are 0.125, 01.25, and 0.5 inches respectively. However, in each case the length to diameter ratio of the element was kept constant so as to provide approximately the same number of reflections at the interface between the ATR rod and the surrounding sample. For a given combination of ATR element material and sample species, the measured infrared band strength will depend on the angle of incidence of the radiation and the number of reflections. Thus, all of our probes produce essentially the same measurements, independent of overall size.

The structural designs of all the probes are quite similar, the main difference being the method of attachment to the reaction vessel. In the case of the laboratory scale (0.98" diameter) probes, the interface is in the form of a sliding tapered joined to mate to a 29-42 joint on a typical glass reaction vessel. For
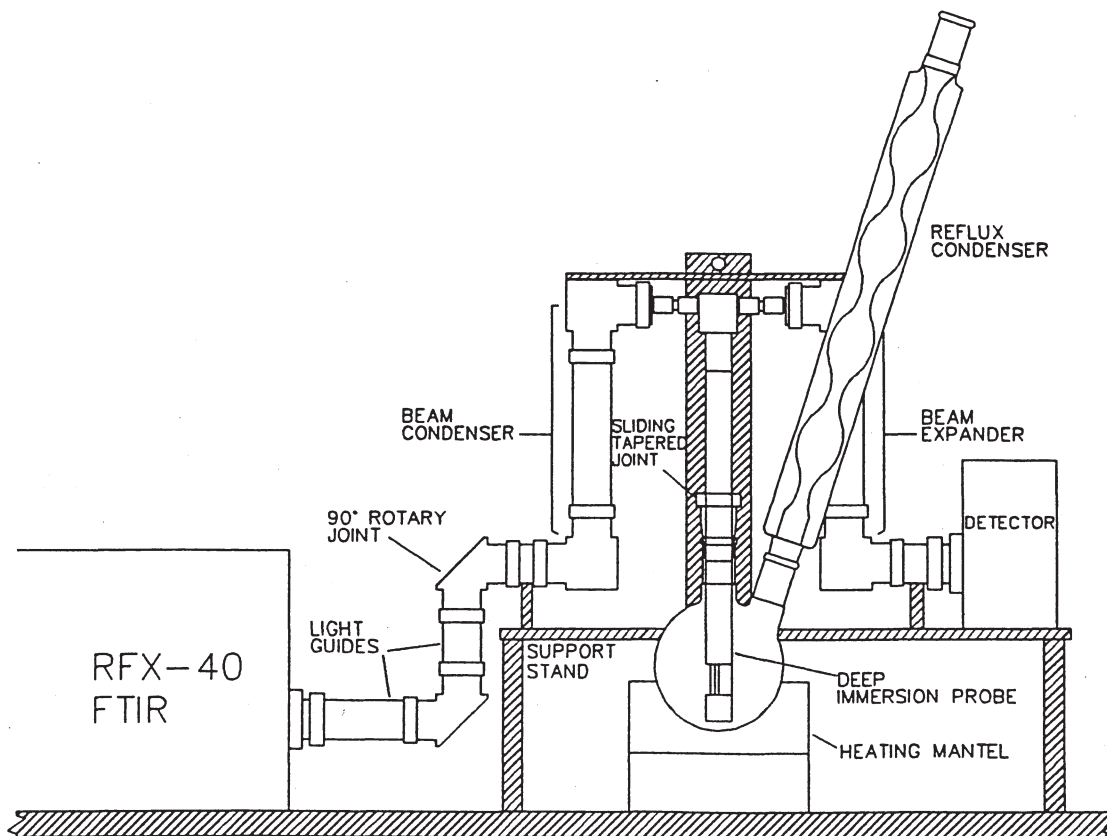

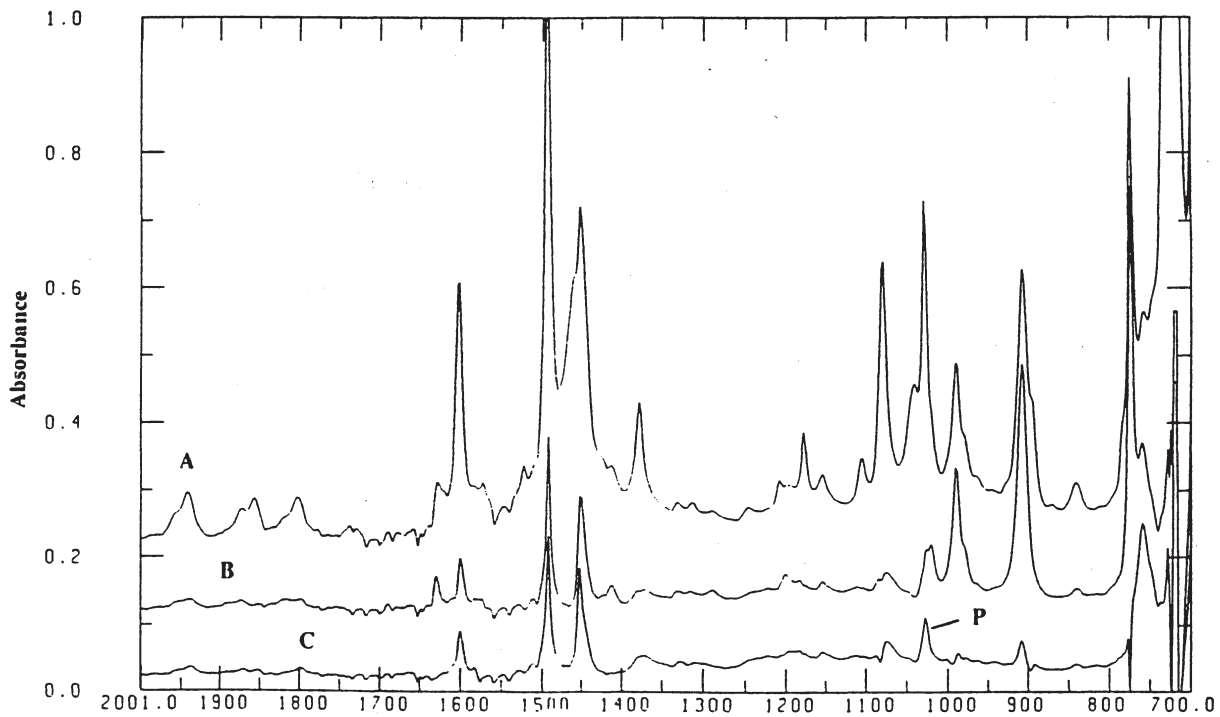Figure 2: Experimental arrangement using a laboratory scale Deep Immersion Probe.

Figure 3: A - Spectrum of a 20% solution of styrene monomer in toluene. "T" indicates the band used for toluene quantization.
B - Spectrum of toluene.
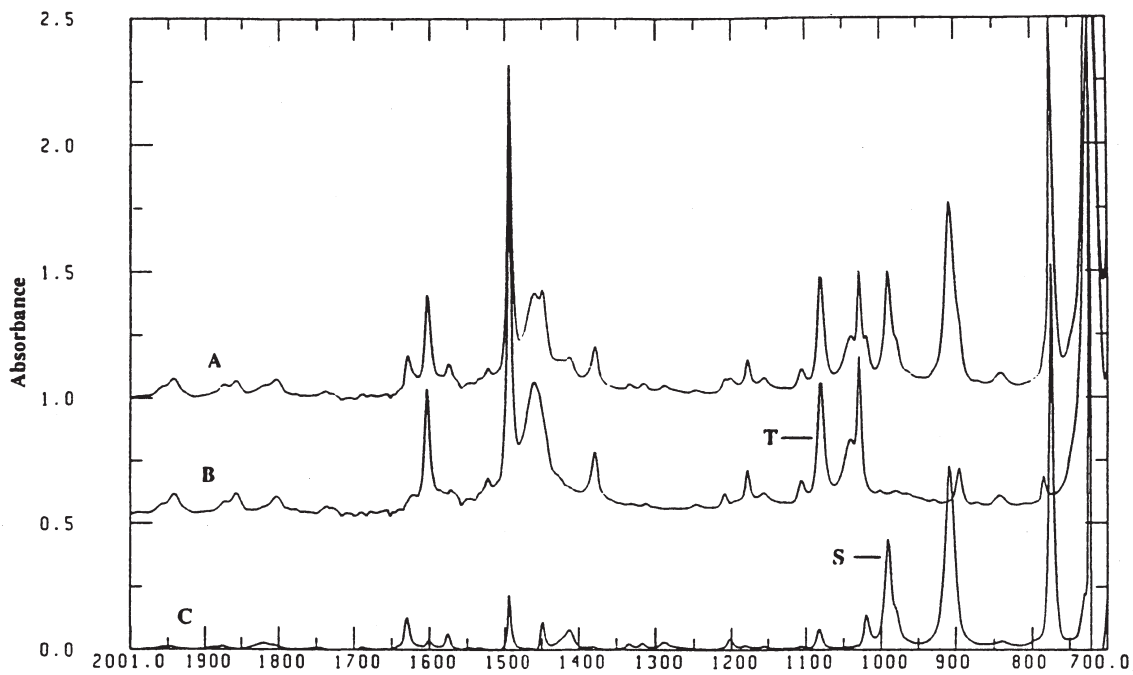C - Spectrum A minus spectrum B. This is the spectrum of styrene.

Figure 4: A - Acid catalyzed reaction mixture after 25 minutes.
B - Spectrum A less toluene.
C - Spectrum B less styrene (spectrum 3,C). This is a spectrum of polystyrene.

larger probes, we use standard industrial flanges, gusseted when necessary to withstand the torques encountered in the typical stirred process kettle.

3. Laboratory Scale Experimental Configuration

The experimental arrangement used for the measurements to be discussed below is shown in Figure 2. The collimated radiation obtained from the side port of an FTIR spectrometer (in this case, Laser Precision Analytical's Model RFX-40) is routed to be the experiment by a series of light guides and 90 degree rotary mirror assemblies. Any number of these can be used as long as the total length is less than roughly fifty feet. A 4x beam condenser is used to reduce the diameter of the collimated beam from 1.25" to 0.312" so as to match the small light guides used within the probe. After passing down through the probe, interacting with the liquid chemicals, and returning back to the top of the probe, the beam is expanded back to 1.25" in diameter so as to match the detector assembly optics. For our experiments, we used a wide-band HgCdTe detector operating at liquid nitrogen temperature.

The round bottom flask shown in Figure 2 was used for our heated free radical polymerization experiments discussed below. In this case, the probe was inserted through the central 29/42 ground glass joint of the flask. The probe is equipped with a sliding tapered joint which was lowered and clamped in place. A reflux condenser was mounted on a second ground glass joint, and a thermocouple temperature sensor (not shown) was inserted into the solution through the reflux condenser. Since the experiments were carried out primarily under reflux conditions, no mechanical stirring was used.

For the room temperature acid catalyzed experiments, the round bottom flask was replaced by an Erlenmeyer flask equipped with a magnetic stirring rod.

4. Process FTIR Software

A wealth of quantitative software is available for use in converting the large amounts of data obtained in FTIR spectroscopy into numeric readout of process variables[5]. All of these rely on the fact that, in most situations, infrared absorbance at a given spectral frequency will be linearly dependent on the concentrations of the various chemical species present in the solution. The work discussed below employed the "P-matrix" approach, in which the concentrations of the various species present are considered as functions of the absorbencies, ie: C = PA. Here, C represents the set of concentrations of the various species present, A is the set of IR absorbencies at selected frequencies, and P is the matrix of coefficients which relates concentration to absorbance.

In calibrating the system to monitor a given process, one normally prepares a set of samples containing measured quantities of each constituent of the process, with concentrations covering the full range of values to be encountered. The computer then performs a least squares fit to determine the set of matrix coefficients which best characterizes the calibration
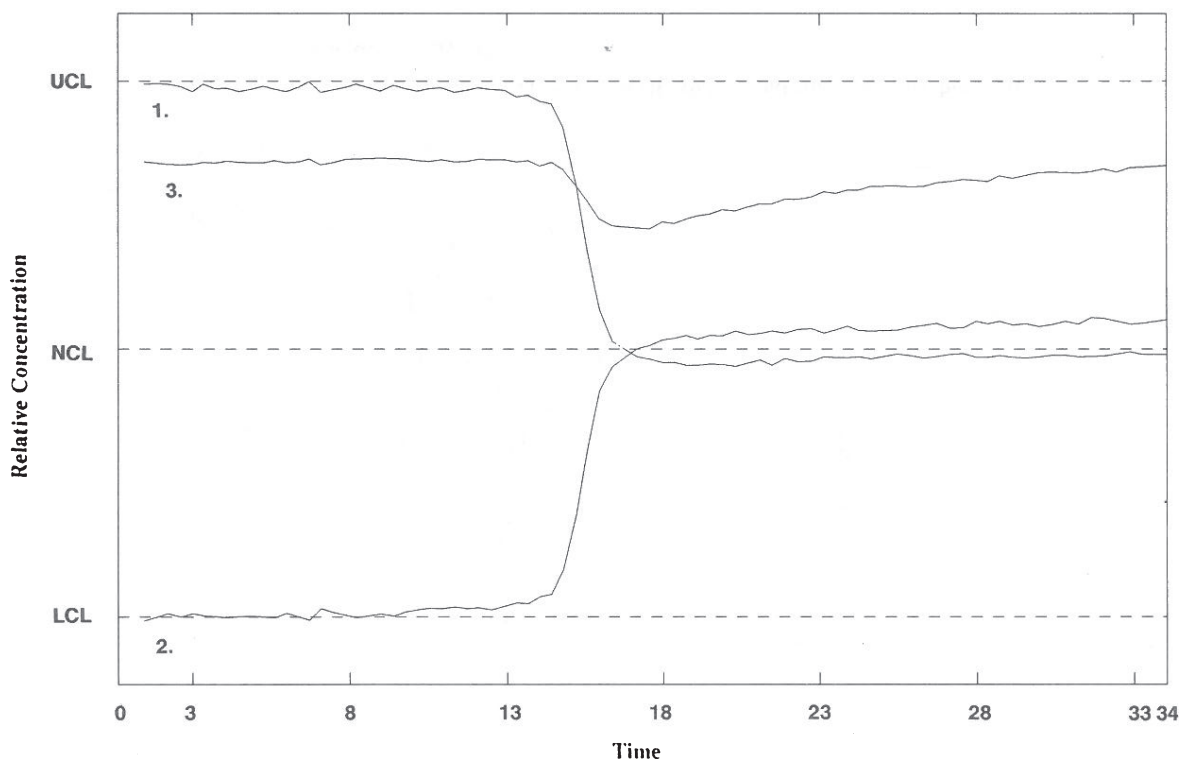

Figure 5: Concentration versus time of (1) styrene, (2) Polystyrene, and (3) toluene in the acid-catalyzed polymerization process.

data. In doing this, the program will automatically compensate for any impurities that are present, as long as a full range of possible impurity values are included in the calibration set. This feature proved useful in the work discussed below by enabling us to compensate for various temperature dependent effects.

5. Monitoring of Selected Polymerization Reactions

To illustrate the capabilities of the FTIR immersion approach to process monitoring, we carried out a series of laboratory scale polymerization experiments. These included the acid-catalyzed polymerization of styrene, the free radical polymerization of both styrene and methyl methacrylate, and the formation of a copolymer of styrene and methyl methacrylate. The acid-catalyzed process was carried out at room temperature while the free radical experiments were carried out under reflex conditions using the apparatus illustrated in Figure 2.

Spectra were obtained using the spectrometer's automatic collection mode at a rate of about one spectrum every 30 seconds during each of the polymerization runs. For our experiments, we saved all of the spectra and "replayed" them later using multiple component analysis software to obtain plots of the concentration of each species versus time. In a practical situation, a laboratory experiment such as this would be used to select the correct parameters and methods for data analysis. On-line, the data analysis would be run simultaneously with the data collection so as to provide an essentially real time

read-out of the concentrations.

6. Acid Catalyzed Polymerization

In developing a methodology for monitoring a specific process using FTIR, the first step is to select a set of spectral bands that are representative of the various chemical species present. This can be done automatically by using chemometric software. However, for the work reported here, we simply examined the spectra and selected bands having minimum overlap with those of the other species.

In Figure 3, the upper trace (A) is spectrum of a 20% solution of the styrene monomer in toluene, 3B is toluene alone, and 3C is the spectrum of styrene obtained by subtracting the toluene spectrum from the mixture. This figure illustrates one of the powers of mid-IR spectroscopy - the ability to positively identify an unknown component of a mixture by sequentially stripping away the spectra of the know components. This is a result of the sharpness and stability of the mid-IR spectral bands and of the high degree of linearity and precision of the FTIR spectrometers.

Figure 4A is a spectrum of the reaction mixture about 25 minutes after adding the catalyst. Figures 4B and 4C are the results of sequentially subtracting the toluene spectrum (3A) and the styrene solution spectrum (3B) from this spectrum. The final result can be easily identified as polystyrene.

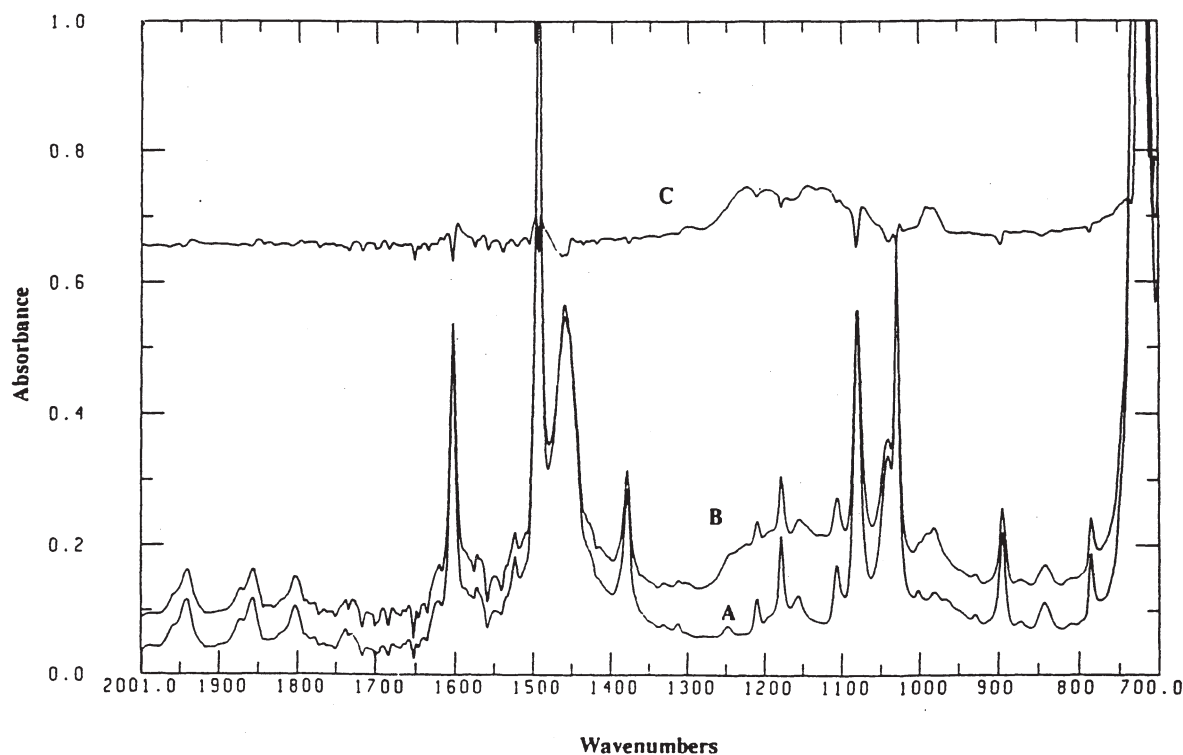By examining the various spectra of figures 3 and 4, we were

Figure 6: Spectra of toluene at (A) 25°C and (B) 100°C, and the difference between these two spectra (C).
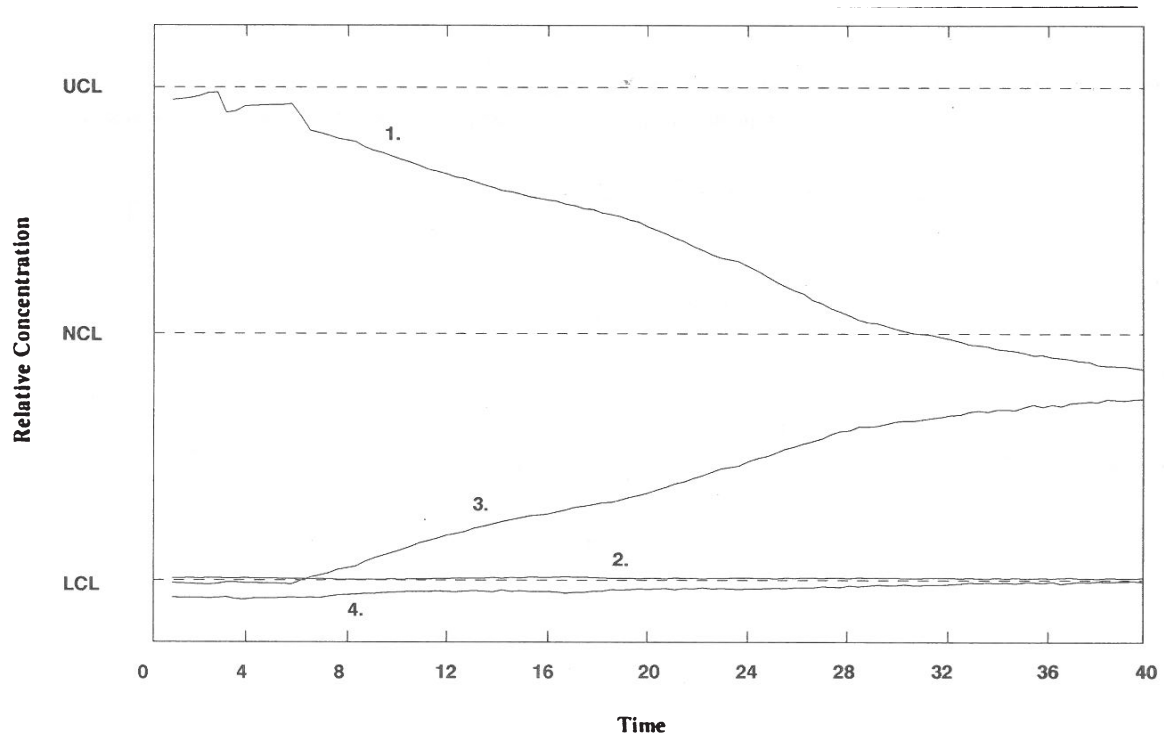
Figure 7: Indicated concentration versus time of (1) styrene, (2) methyl methacrylate, (3) polystyrene, and (4) PMMA during the free radical polystyrene polymerization process.
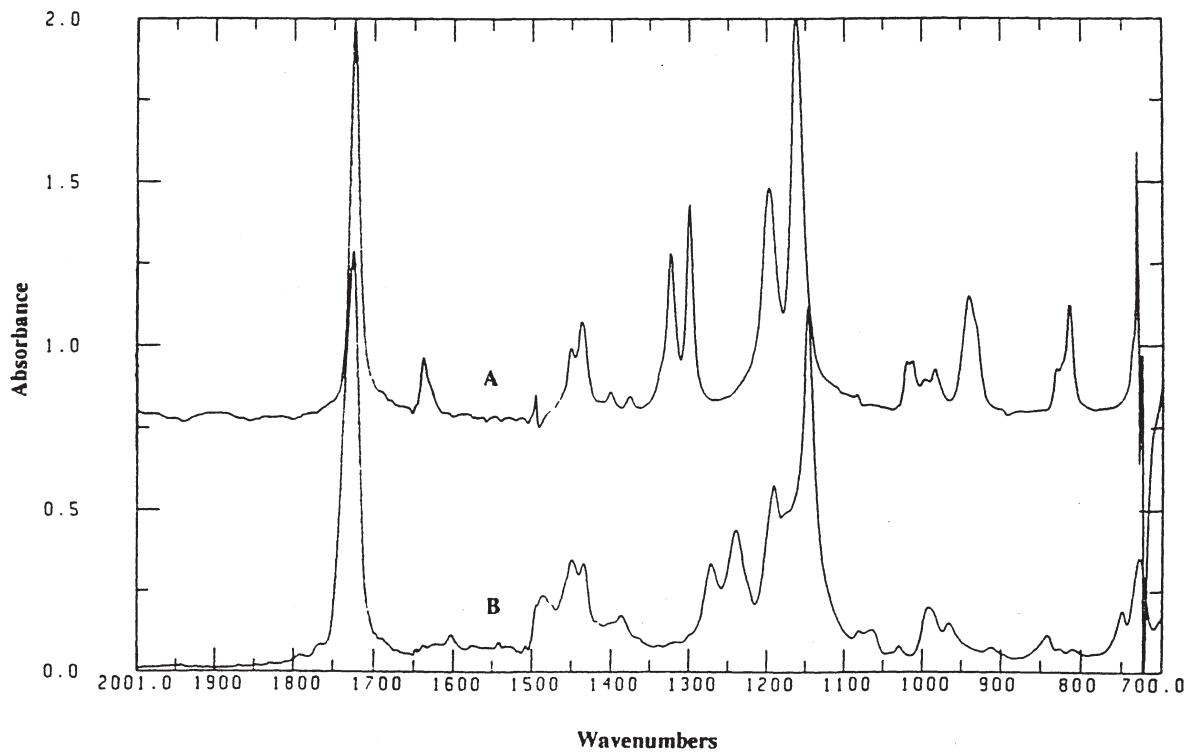

Figure 8: A - Spectrum of methyl methacrylate after subtracting toluene.
B - The final reaction product (PMMA) after subtracting spectra of toluene and methyl Methacrylate.

able to select a convenient set of spectral bands for use in the quantitative analysis program. These are indicated by the letters T (toluene), S (styrene), and P (polystyrene) in the two figures. It is not necessary for the bands of the various species to be completely non-overlapping. The computer program solves the simultaneous equations to obtain the concentrations of the individual constituents. The spectra of Figures 3B, 3C, and 4C were used as standards in setting up the analysis program.

Figure 5 is a plot of concentration versus time for the three constituents of the acid catalyzed reaction. As the figure shows, this process has a long initiation period followed by a short reaction time. This type of behavior illustrates the utility of the immersion probe technique in accurately determining when a reaction is complete so that the process can be terminated at the optimum point. The dip in the toluene concentration may be due to a temporary inhomogeneity caused by preferential polymerization in the vicinity of the probe.

7. Free Radical Polymerization

The free radical polymerization runs were initiated at room temperature and then brought up to the reflux temperature of approximately 109°C. This introduced two new factors into the analysis, the temperature dependence of the spectral bands of the various process constituents and that of the Chemraz "O" rings used in the probe. These effects are il-

lustrated in Figure 6, which consists of toluene spectra at 25°C and 100°C and the difference. The broad features in the difference spectrum are due to the temperature dependence of the "O" ring spectrum. The sharp negative peaks are due to the fact that the toluene bands become weaker and broader at elevated temperature.

In the case of the process constituents, the temperature artifacts were eliminated by obtaining high temperature calibration spectra of toluene and the two monomer solutions and by using the final reaction product spectra (after the appropriate subtractions) as the polymer standards. In addition, toluene spectra taken at various temperatures were included in the calibration set to minimize the dependence of the analysis on the characteristics of both toluene and Chemraz. In this set of experiments, although toluene and Chemraz were included implicitly in the calibration, their concentrations were not displayed.

Figure 7 is a time history of the free radical styrene polymerization run, revealing a much different time dependence than the acid catalyzed run of Figure 5. The process is generally much more gradual, taking place under diffusion controlled conditions.

Note that Figure 7 includes curves for all four of the variables, styrene, polystyrene, MMA, and PMMA even though only two of these constituents were present for each run. This was done to validate the method for later use in the copolymerization experiment.
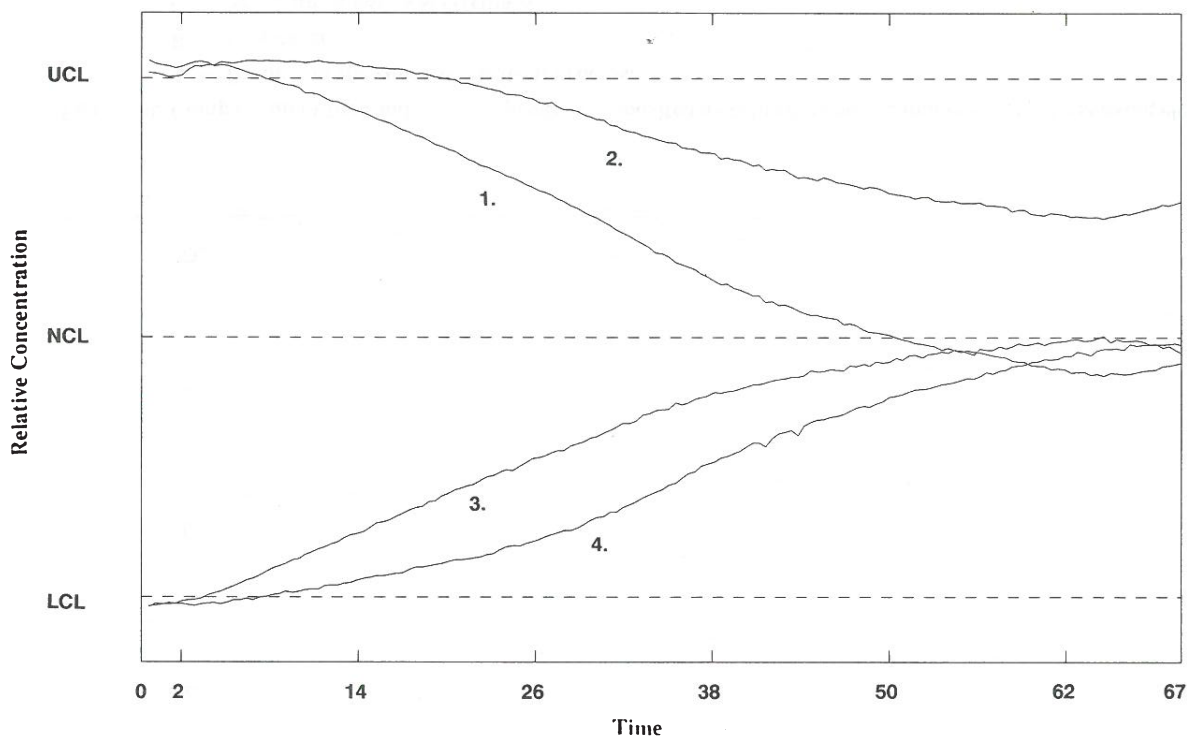

Figure 9: Indicated concentration versus time of (1) styrene, (2) methyl methacrylate, (3) polystyrene, and (4) PMMA during the free radical copolymerization process.

A free radical polymerization run of methyl methacrylate gave results similar to those of Figure 7, but with an even slower reaction rate. The time required for consumption of one half of the monomer was about 66 minutes as opposed to 33 minutes for styrene polymerization. The bands used for this run and for copolymerization run discussed below are indicated in Figure 8. This includes the spectra of dissolved methyl methacrylate (A) and of the final product, polymethyl methacrylate (B). In both cases, we decided to use the strong carbonyl band in the vicinity of 1730 cm^{-1} for the analysis since it does not overlap any strong bands of toluene, styrene, or polystyrene. Of course, the carbonyl band is present in both the monomer (MMA) and the polymer (PMMA), but it is sufficiently shifted to higher frequency in the polymer to provide adequate separation.

At this point, a comment is in order about the methods used in doing the calibration for the quantitative analyses. In the case of the monomers, we had initial spectra of solutions with known concentrations. However, in the case of the polymers, we used the final spectra of the reaction mixtures for calibration. Although, in principle, the concentrations of the polymers can be inferred from the change in monomer concentrations, we did not take this step. Thus, the polymer concentration scale is arbitrary.

8. Copolymerization of Styrene and Methyl Methacrylate

The free radical copolymerization was carried out starting with a solution of ten percent styrene and ten percent MMA in toluene. In this case, the P-matrix calculation involved a total of four explicit variable constituents, the two monomers and two polymers, plus three implicit variable, toluene, Chemraz, and temperature. The concentrations of the four components of interest are shown in Figure 9.

In interpreting the data of Figure 9, we can interpret the vertical scale between the lower control limit (LCL) and the upper control limit (UCL) as running from 0 to 100% concentration. This is meaningful in the case of monomers, suggesting the process consumed about twice as much styrene monomer as MMA. Since the polymer scale is arbitrary, we can not draw such an overall conclusion about the final polymer values reached. However, it is apparent that polystyrene was being formed preferentially during the early stages of the process, with PMMA formation accelerating after 15 or 20 minutes.

As Figure 9 illustrates, the use of the IR immersion probe makes it possible to precisely monitor the degree of polymerization at any point during a reaction. This capability could prove very useful in cases such as the production of glues and resins in which the correct degree of partial polymerization is
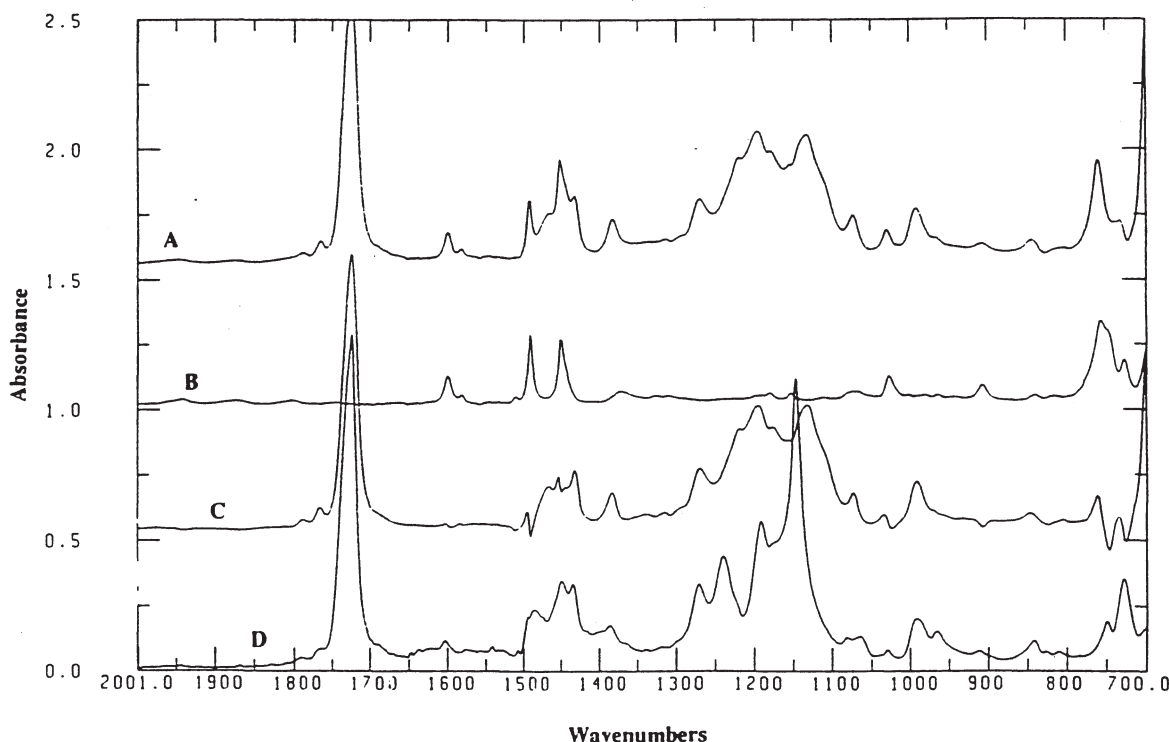

Figure 10: Comparison of the final reaction products deposited as thin films on the immersion probe sensing element.
A - Product of the copolymerization process.
B - Polystyrene.
C - Spectrum A minus spectrum B.
D - PMMA.

crucial to the quality of the product. In addition, the ability to closely monitor the balance between the various constituents in a reaction creates the opportunity not only to optimize reaction conditions but also to tailor the properties of the final product to meet a specific need.

Since free radical polymerization takes place under diffusion controlled conditions, one would expect the final product to exhibit a random sequence of styrene and MMA units. Its characteristics should thus approximate those of an ideal copolymer rather than a mixture of two individual polymers. This assumption can be tested by doing an infrared analysis of the final product.

To obtain samples of the final products of our experiments, we simply removed the probe from the reaction vessel while the mixture was still hot. When this is done, the solvent immediately evaporates, leaving a uniform polymer film on the probe structure and ATR element. The results are given in Figure 10. It is clear that, while the copolymer spectrum has some features in common with both polystyrene and PMMA, there are also significant difference. On subtracting the polystyrene spectrum from the copolymer, we found that the bands of the former were present but were shifted to higher frequency. Comparing this result with PMMA, we find that the strong carbonyl band has been relatively unaffected by copolymerization but that the bending modes between 1100 and 1300 wavenumbers had been substantially altered. The degree of alteration suggests that the great majority of MMA units are bordered by at least one styrene unit.

This final step is not only useful in testing the degree of copolymerization but can be used to validate the choice of bands used for P-matrix analysis. Clearly, the choice of the carbonyl band as an indicator of PMMA concentration is probably not as accurate due to the band shifts. However, the accuracy could be improved by averaging over a range of frequencies encompassing the extent of the shift.

9. Conclusion

The experiments reported above illustrate the fact that the use of an IR immersion probe with a modern FTIR spectrometer can yield an intimate view of chemical reaction, making it possible to optimize all of the parameters and to terminate the reaction at any desired degree of completion. Experiments carried out on a laboratory scale can be used to fine-tune the parameters of a process scale reaction. In addition, the monitoring technique itself can be scaled up, making it possible to obtain continuous on-line data which is fully consistent with the data obtained in the lab.

References

1. Doyle, W.M. and Jennings, N.A., "Fourier Transform-Infrared Chemical Reaction Monitoring Using an In Situ Deep Immersion Probe", Spectroscopy, Vol. 5, No. 1, Jan. 1990, p.34.
2. Archibald, D.D., Lin, L.T., and Honigs, D.E., "Remote Near-IR Spectroscopy Over an Optical Fiber with a Modified FT Spectrometer", Applied Spectroscopy, Vol. 42, No. 3, 1988, p. 468.
3. Harrick, N.J., Internal Reflection Spectroscopy, John Wiley, New York, 1967.
4. Doyle, W.M., "Absorbance Linearity and Repeatability in Cylindrical Internal Reflectance FT-IR Spectroscopy of Liquids", Applied Spectroscopy, Vol. 44, No. 1, 1990, p. 50.
5. Crocombe, R.A., Olsen, M.L., and Hill, S.L., "Quantitative Fourier Transform Infrared Methods for Real Complex Samples", Computerized Quantitative Infrared Analysis, ASTM STP 934, G.L. McClure, Ed., American Society for Testing and Materials, Philadelphia, 1987, p. 95.