

Use of a Midrange Infrared Optical-Fiber Probe for the On-Line Monitoring of 2-Ethylhexyl Acrylate/Styrene Emulsion Copolymerization

E. G. CHATZI, O. KAMMONA, C. KIPARISSIDES

Chemical Engineering Department and Chemical Process Engineering Research Institute, Aristotle University of Thessaloniki, P.O. Box 1517, University City, 540 06 Thessaloniki, Greece

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ABSTRACT: A new versatile attenuated total reflectance (ATR) Fourier transform infrared (FTIR) technique has been developed for monitoring emulsion copolymerization reactions using midrange IR optical fibers. This probe was found to provide a novel opportunity for determining individual monomer conversions, as well as copolymer composition, for polymerizations carried out in aqueous media, even at a high solids content. Chalcogenide optical fibers were used to direct IR radiation from an FTIR spectrometer through an ATR probe immersed in a laboratory scale reactor and equipped with a two-reflection 45 degree ZnSe crystal. The utility of this technique for studying emulsion copolymerizations was demonstrated by monitoring a 2-ethylhexyl acrylate/styrene reaction at the azeotropic composition. Sufficient signal strength at the detector was achieved, resulting in IR spectra of high quality and resolution, while the short effective path length of the probe made it ideal for obtaining quantitative kinetic information from mid-range IR spectra in aqueous media. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 799–809, 1997

Key words: infrared spectroscopy; fiber optic; on-line monitoring; emulsion copolymerization

INTRODUCTION

The increasing demand for the production of polymers with prespecified properties has placed a large emphasis on the development of accurate and robust instruments for the on-line monitoring of the polymerization reactions. Although this task may seem to be simpler for emulsion polymerization systems, due to their lower viscosity, than for bulk and solution polymerizations, in practice, problems may arise due to coagulation of the latex particles causing clogging of the pipes, pumps, and valves of the sampling devices. The

recent development of fiber-optic probes suitable for remotely collecting infrared (IR) spectra via optical fibers has given rise to the possibility of making *in situ* measurements for a number of applications. Several remote fiber-optic chemical sensors have been reported in the literature¹ to have the capability of detecting more than one chemical component simultaneously and of providing results on the scene. However, most of them need to be accompanied by a separation technique, chemical reaction, and/or chemometrics; thus, a very limited number of applications have been reported on the real-time monitoring of polymerization processes.^{2–5}

The near-infrared (NIR) spectral region received some early attention for the development of on-line analyzers since it does not require complicated hardware or sampling techniques.^{6,7} A

Correspondence to: C. Kiparissides.

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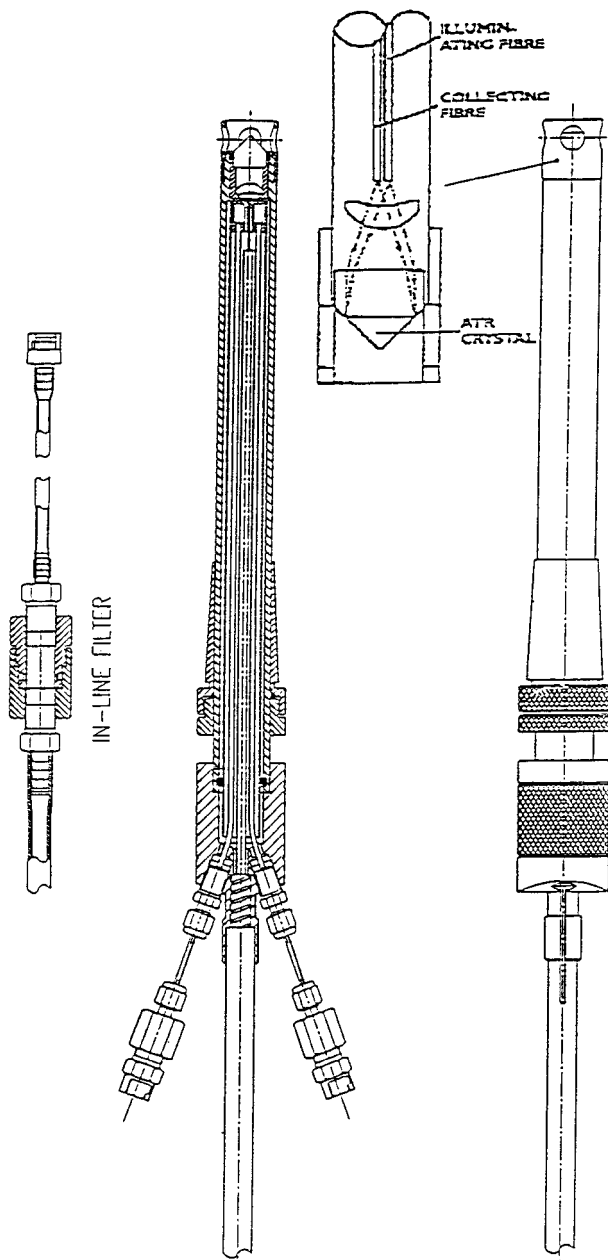


Figure 1 Schematic diagram of the MIR ATR fiber-optic probe.

fiber-optic probe can be simply inserted into an existing reactor system without time-consuming and expensive hardware modifications. The major drawback is that throughout this spectral region absorption peaks are very broad, overlapping, and nonspecific. Most NIR absorptions are overtones and combinations of the fundamental midinfrared molecular vibration bands and are typically weaker than their corresponding fundamental transitions. Consequently, they cannot be unabi-

guously assigned or used for minor component analysis. In latexes, this problem is compounded by the nonlinearities associated with light scattering in concentrated suspensions. Empirical, multivariate sensor calibration models have to be used in order to deal with this problem.⁴

On the other hand, research in the mid-infrared (MIR) spectral region has been sparse because of the lack of materials that can efficiently transmit radiation in this region and also be processed into fibers. MIR transmitting optical fibers in this region, such as chalcogenide and silver halide optical fibers, have become available only very recently.^{8,9} The MIR fiber-optic probe investigated in the present article, offers the possibility of continuous and accurate on-line monitoring of characteristic monomer and polymer vibrations in the MIR spectral region over a wide range of concentrations. It is especially suitable for obtaining quality spectra in aqueous media; thus, it can be used for the kinetic investigation of emulsion polymerization reactions. The objective of this research was to demonstrate the feasibility of estimating the individual monomer conversions and copolymer composition from the IR spectra collected using chalcogenide fibers as MIR transparent light guides through an attenuated total reflection (ATR) probe. It was shown that these quantities can be measured independently and in a straightforward manner from the recorded IR spectra after subtraction of the contribution of the aqueous phase.

THEORY

The principle of operation of the ATR probe used in the present investigation is similar to that of standard internal reflection spectroscopy (IRS). A unique aspect of IRS is the use of an optically dense prism, that is, an IR transparent material with a refractive index typically higher than 2.5, as an optical guide to obtain an IR spectrum. Typically, materials like Ge, ZnSe, Si, KRS-5, and sapphire are used because of their transparency in the wide range of the MIR region. The radiation passes through the prism and is totally reflected at the internal prism interface at incident angles θ larger than the critical θ_c ($=\sin^{-1}n_{21}$, where n_{21} is the refractive index ratio of the sample to the prism). The incoming light forms a standing wave pattern at the interface within the dense prism medium, which penetrates a finite distance d_p into the rare medium, i.e., in our case, the polymeriz-

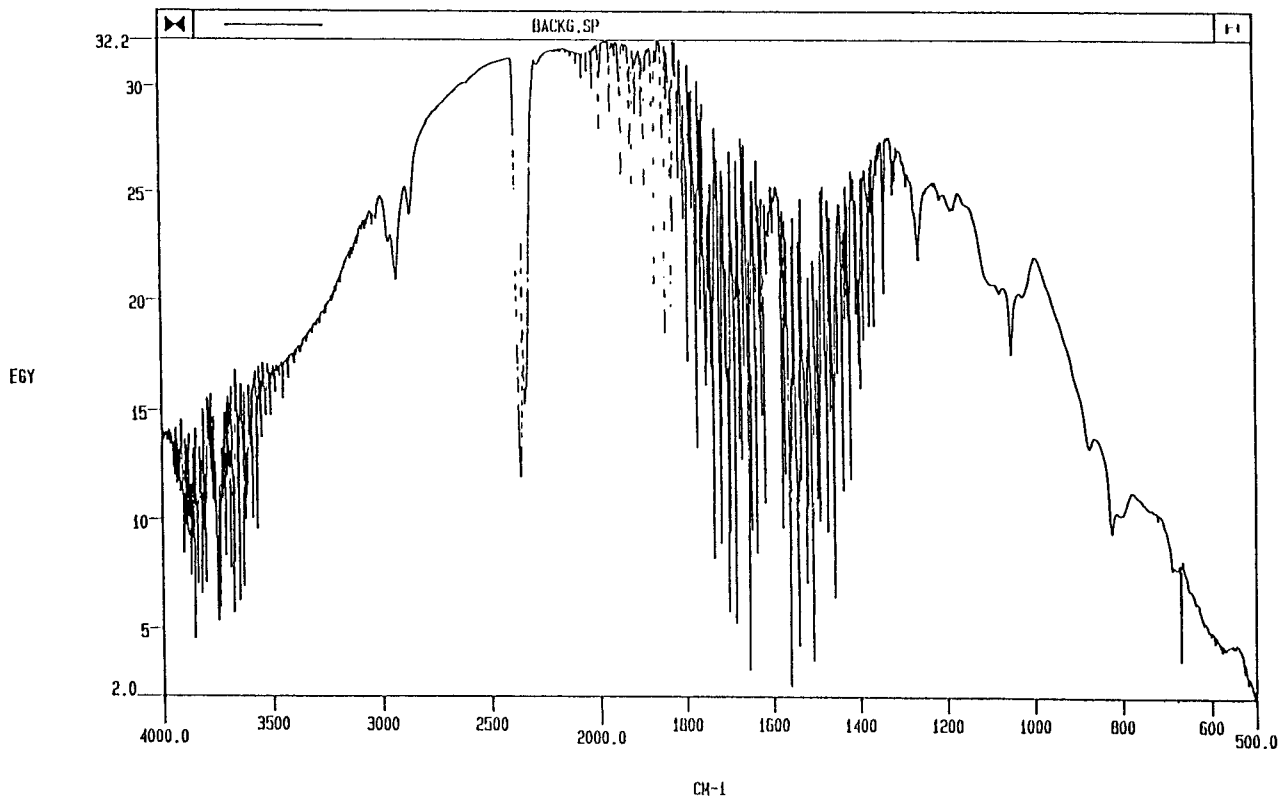


Figure 2 Background spectrum (64 scans, resolution 2 cm^{-1}) in transmission mode using a 14% energy throughput filter.

ing latex in optical contact with the prism. Since the rare medium exhibits absorption, the amplitude of the evanescent wave decays exponentially with the distance from the phase boundary, and, thus, the penetrating wave becomes attenuated so that the reflectance can be written as follows¹⁰:

$$R = 1 - kd_p$$

where d_p is the effective layer thickness or depth of penetration. The IR spectrum is obtained by detecting the absorbed radiation at the exit of the prism; thus, qualitatively, an IRS spectrum resembles a transmission spectrum. The resulting energy loss in the reflected wave is referred to as ATR.

The depth of penetration of the evanescent wave, i.e., the distance at which its intensity falls to $1/e$ of its initial value, can be expressed as

$$d_p = \frac{\lambda}{2\pi(\sin^2\theta - n_{21}^2)^{1/2}}$$

where λ is the wavelength of the IR light. Typical

penetration depths within polymeric samples in IRS range from a few tenths of a micron to a few microns, depending on the type of reflection element, the angle of incidence, and the wavelength of the infrared beam.

For constant angle of incidence and refractive index ratio, the depth of penetration and, thus, the corresponding absorption intensity at a certain frequency is proportional to the wavelength of incident light. As a consequence, there are two adverse effects arising from the wavelength dependence of IRS. First, the long wavelength side of an absorption band tends to be distorted; second, bands of longer wavelengths appear relatively stronger. Therefore, for quantitative analysis using IRS, the observed intensities in the IR spectrum should be corrected by multiplication to the wavenumber $\bar{\nu} = 1/\lambda$.

ATR offers an advantage for analyzing strongly absorbing materials, including aqueous solutions with concentrations of a fraction of a percent. Since the penetration depth is determined by the angle of incidence, the relative refractive index, and the IR frequency, the reproducibility of spec-

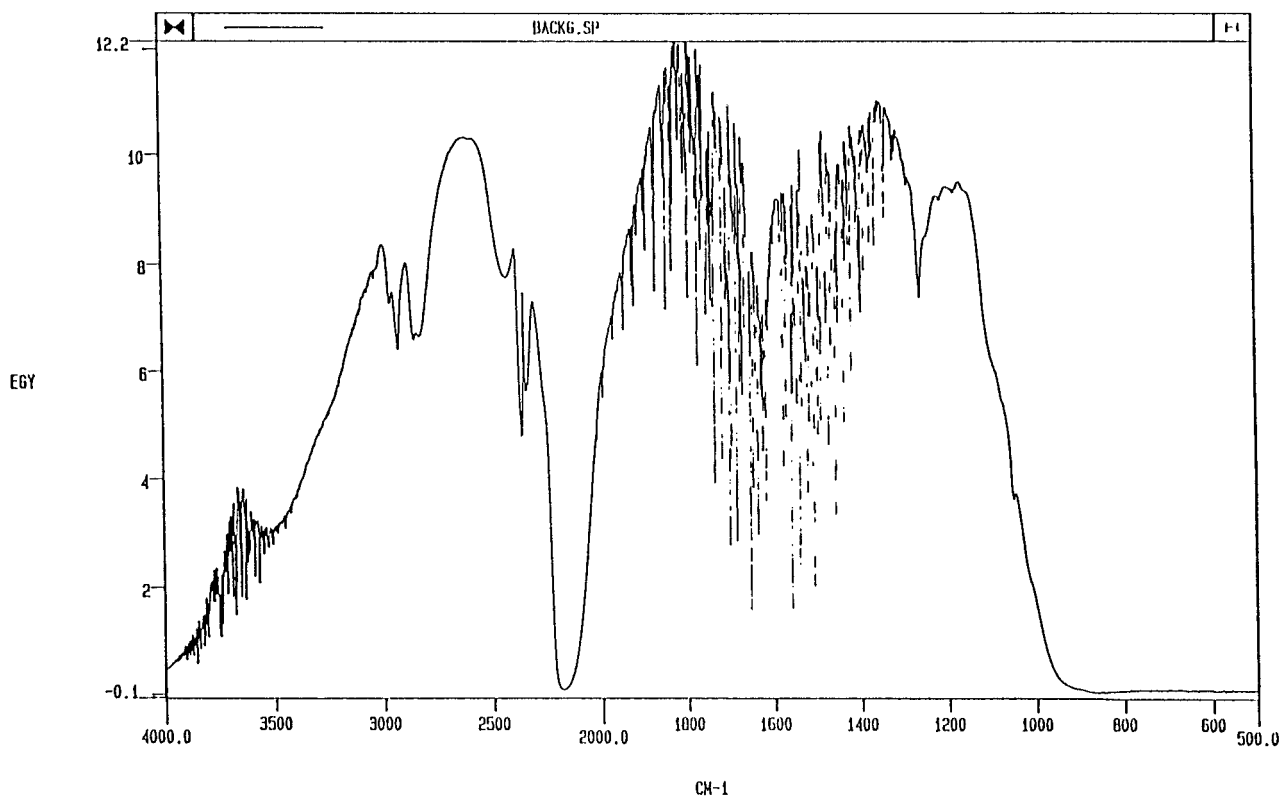


Figure 3 Background spectrum (64 scans, resolution 2 cm^{-1}) through the ATR fiberprobe without any energy filter.

tral intensity is good. In general, dilute solutions can be effectively studied using multiple reflections in order to increase the sensitivity of the ATR technique; whereas, if one desires to study concentrated solutions or the region of strong absorption, one can use single reflection ATR or a prism with a high refractive index.¹¹

EXPERIMENTAL

Fiber-Optic Sensor

The MIR optical fiber probe is schematically depicted in Figure 1. This high-temperature 2-Reflection ATR fiberprobe is manufactured by Graseby Specac, Inc., and is designed for use with a variety of FTIR spectrometers in laboratory, as well as in process control environments, in the temperature range of 20 to 200°C. It is an ATR probe with a 19 mm head diameter and uses a two-reflection 45 degree ZnSe crystal. It is equipped with 1.5 m of Chalcogenide optical fibers especially suitable for use in the MIR region (i.e., 4500–900 cm^{-1}). This standard length allows re-

mote sampling from either restricted access or hazardous areas (e.g., fume cupboard) and *in situ* measurements simply by immersion of the probe head into the bulk sample. The small size of the probe enables it to be used inside small containers and vessels, and the short effective pathlength makes it ideal for use in the MIR region, especially for obtaining spectra in aqueous media. It can be used over a wide range of concentrations, making use of the excellent signal-to-noise ratios of modern FTIR instruments to expand small absorption peaks.

The probe heads are prealigned to the fiber at the time of manufacture. An easy to align two-mirror/lens-interface system couples the fiber probe into the spectrometer sample compartment. The cladding of the optical fiber provides protection, ruggedness, and durability. It is made up of a spiral-wound stainless steel inner with a PVC outer sheath. Silicone rubber tubing between the fibers and the spiral-wound inner stainless steel gives further shock and abrasion protection.

An MCT instrument detector is preferred for use with this probe because of the relatively small

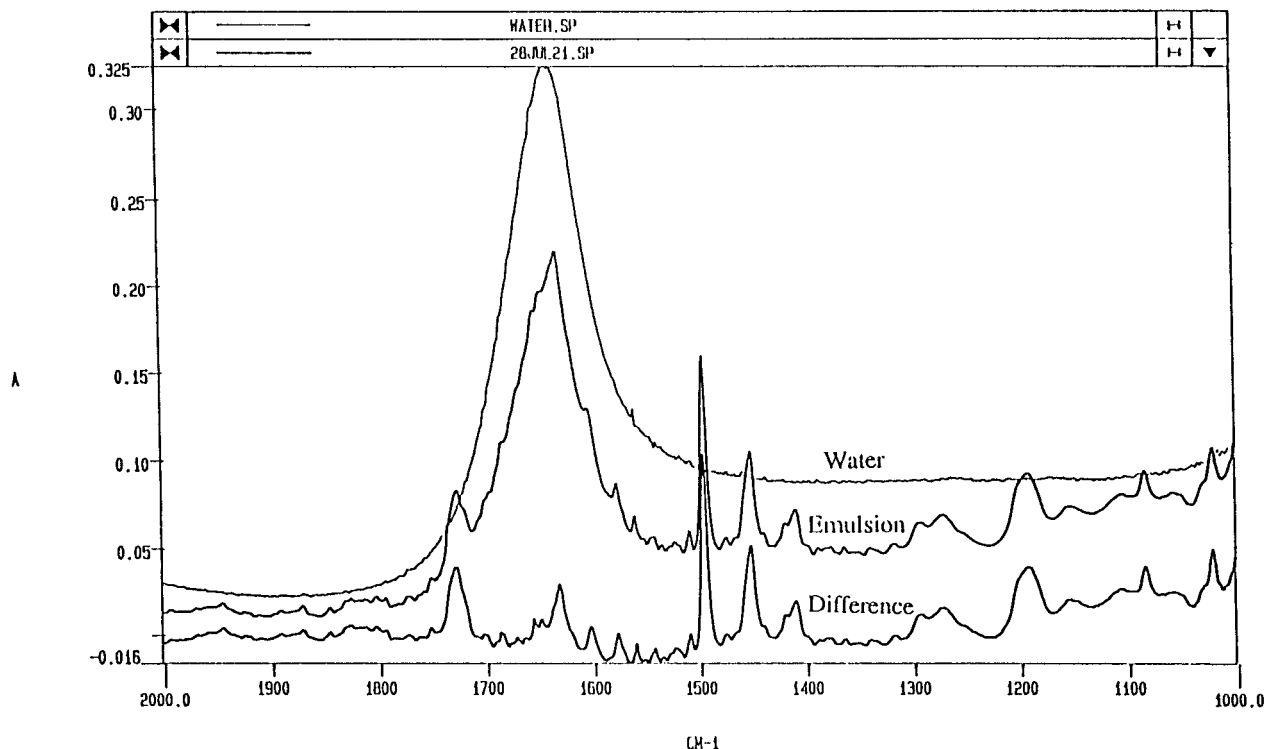


Figure 4 A typical example of the water subtraction procedure from the emulsion spectrum.

throughput of the fiber-optic systems as compared to conventional accessories. The total energy throughput may vary from 10 to less than 2%, depending on the type and length of fiber, wavelength region, and type of instrument. It is important to note that this particular fiber-optic probe uses the same principle of data collection as conventional reflection accessories. In general, the fiber-optic systems are not technique enhancement devices, and detection limits will not improve where conventional techniques fail.

IR Spectrophotometer

The MIR fiber-optic sensor was connected to a Perkin Elmer FTIR model 2000 spectrophotometer purged with nitrogen and equipped with a wide band MCT detector. The frequencies of the spectrometer were calibrated to an accuracy better than 0.15 cm^{-1} , and the S/N ratio was larger than 4000 : 1. ATR spectra were collected through the probe at the polymerization temperature, i.e., 70°C , in the range of $4000\text{--}900\text{ cm}^{-1}$, and two-hundred scans recorded at 15 min intervals were signal-averaged at a resolution of 2 or 4 cm^{-1} . The spectra were ratioed against a background

recorded in the open air before immersing the probe into the reactor. The background spectra (64 scans, resolution 2 cm^{-1}) in transmission mode, as well as through the ATR fiberprobe, are shown in Figures 2 and 3, respectively. The spectrum of distilled water was also recorded prior to the experiment in order to be used for subtraction of the water contribution from the spectra obtained during the course of the copolymerization reaction.

The transmission IR absorption spectrum of the purified and dried copolymer was collected at a resolution of 4 cm^{-1} in the form of KBr pellet, whereas the corresponding spectra of the two monomers were obtained by using the fiber-optic probe. Two-hundred scans were coadded in the range of $4000\text{--}450\text{ cm}^{-1}$ in order to improve the S/N ratio.

Experimental Procedure

Two free-radical batch emulsion copolymerization experiments of 2-ethylhexyl acrylate (2-EHA) and styrene (STY) monomers at the azeotropic composition (i.e., 90 wt % styrene) were carried out according to the following experimental proce-

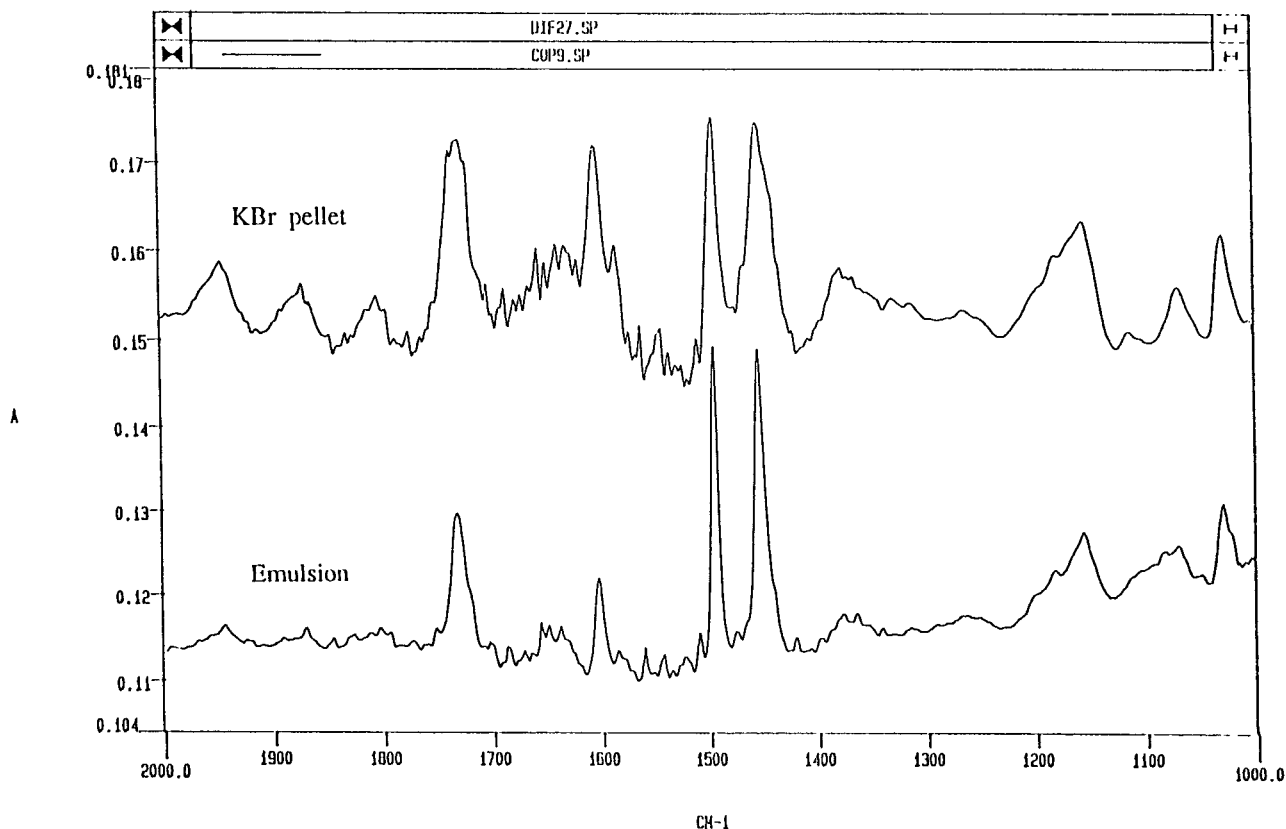


Figure 5 Comparison between the emulsion ATR difference spectrum close to reaction completion and the spectrum of dried reprecipitated copolymer obtained as a KBr pellet at the same resolution.

ture. A predetermined amount of emulsifier (8 wt % on total monomers) dissolved in water was added into a 500 mL water-jacketed glass reactor, followed by styrene and, subsequently, 2-EHA. The reactor was purged with nitrogen while the emulsion was being heated to 70°C at a rate of 3.5°C/min. When the temperature reached the prespecified level, the initiator (0.6 wt % on total monomers) in the form of a small quantity of concentrated aqueous solution was added into the reaction mixture, whereas the nitrogen flow was stopped 15 min after the addition of the initiator. The MIR sensor was immersed into the reaction mixture immediately after loading the monomers and was being cooled during the experiment by means of a controlled flow of filtered water. IR spectra were collected at fifteen minute intervals starting from the time of addition of the initiator ($t = 0$ min). The IR spectra were measured in the range 4000–900 cm^{-1} at a resolution of 2 and 4 cm^{-1} for the first and second experiments, respectively. The total monomer conversion was monitored during polymerization by conventional gra-

vimetry as well as by thermogravimetric analysis (TGA). After completion of the reaction, the polymerization mixture was poured into a ten-fold volume of methanol, and the copolymer was recovered by precipitation. The polymer was purified by successive reprecipitations from dichloromethane and dried at room temperature for at least three days.

RESULTS AND DISCUSSION

The successful use of an on-line spectroscopic optical-fiber sensor for monitoring copolymerization reactions presupposes the existence of characteristic absorbance bands for the two monomers and the individual structural units in the copolymer. Another important criterion is the ability to subtract the solvent absorbances in order to facilitate monomer conversion analysis. The MIR spectroscopic monitoring of latexes suspended in water is very difficult using conventional transmission techniques, due to the intense absorption of water

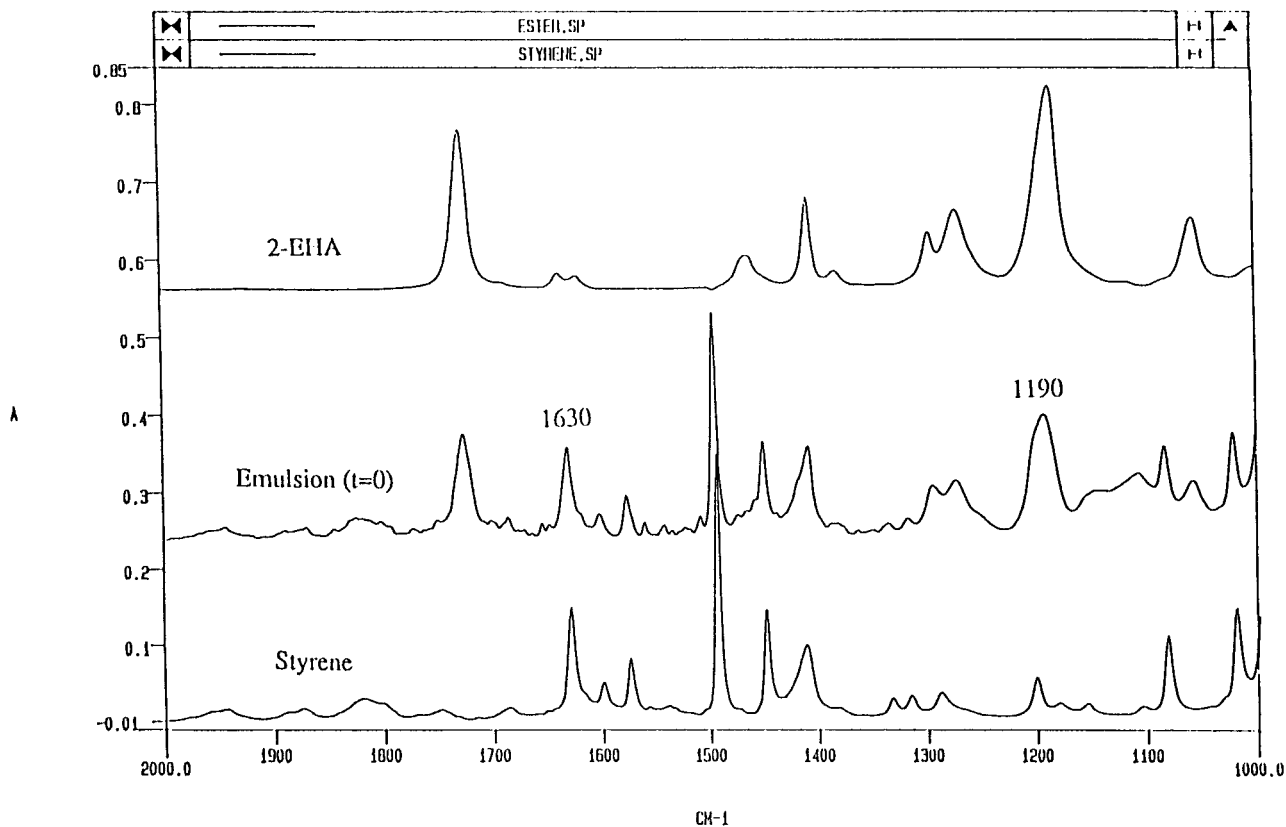


Figure 6 Comparison between the ATR difference spectrum obtained for the emulsion at reaction time $t = 0$ and the corresponding ATR spectra of styrene and 2-EHA pure monomers.

covering the major part of the normal analytical IR region, i.e., $4000\text{--}200\text{ cm}^{-1}$, even at relatively short pathlengths, thus yielding almost total absorption especially around 3400 and 1640 cm^{-1} . Even if thin capillary films are prepared, the absorption peaks due to the emulsified latex components are quite weak and very difficult to observe, especially if they underlie the strong water absorptions. Severe experimental difficulties exist, associated with performing difference or compensated spectroscopy using capillary films whose thicknesses are nonreproducible and probably impossible to match. On the other hand, the maximum practical pathlength necessary to obtain adequate transmission through an aqueous solution in a conventional liquid cell is around 0.015 mm , which poses a practical problem both for filling with moderately viscous materials and for efficient cleaning. Another problem associated with these pathlengths is the interference fringes observed with the required high refractive index materials, such as zinc selenide, which are relatively inert and not readily attacked by aqueous solu-

tions. The large reflection losses due to high refractive indices or the restricted range of IR transparency due to absorption impose additional problems in handling aqueous latexes in the MIR range. These problems may be overcome by using internal reflection spectroscopy. A cylindrical multiple internal reflectance cell, known as the CIRCLE cell, composed of a rod of a high refractive index material with conical ends, has been used in the literature for the quantitative characterization of aqueous latex systems.¹² For standard off-line analysis, the rod is mounted in a multipurpose sample chamber, which can be tailored to serve a number of functions, e.g., a sampling boat, a flow cell, an *in situ* reactor, etc. In all cases, the liquid sample surrounds the internal reflectance element (the rod), and the ends of the rod protrude beyond the sample chamber, which is situated within a small optical bench. A ZnSe cylindrical internal reflectance crystal embedded within a laboratory scale reactor has been also used for the *in situ* monitoring of simple nonaqueous chemical reactions at stoichiometric condi-

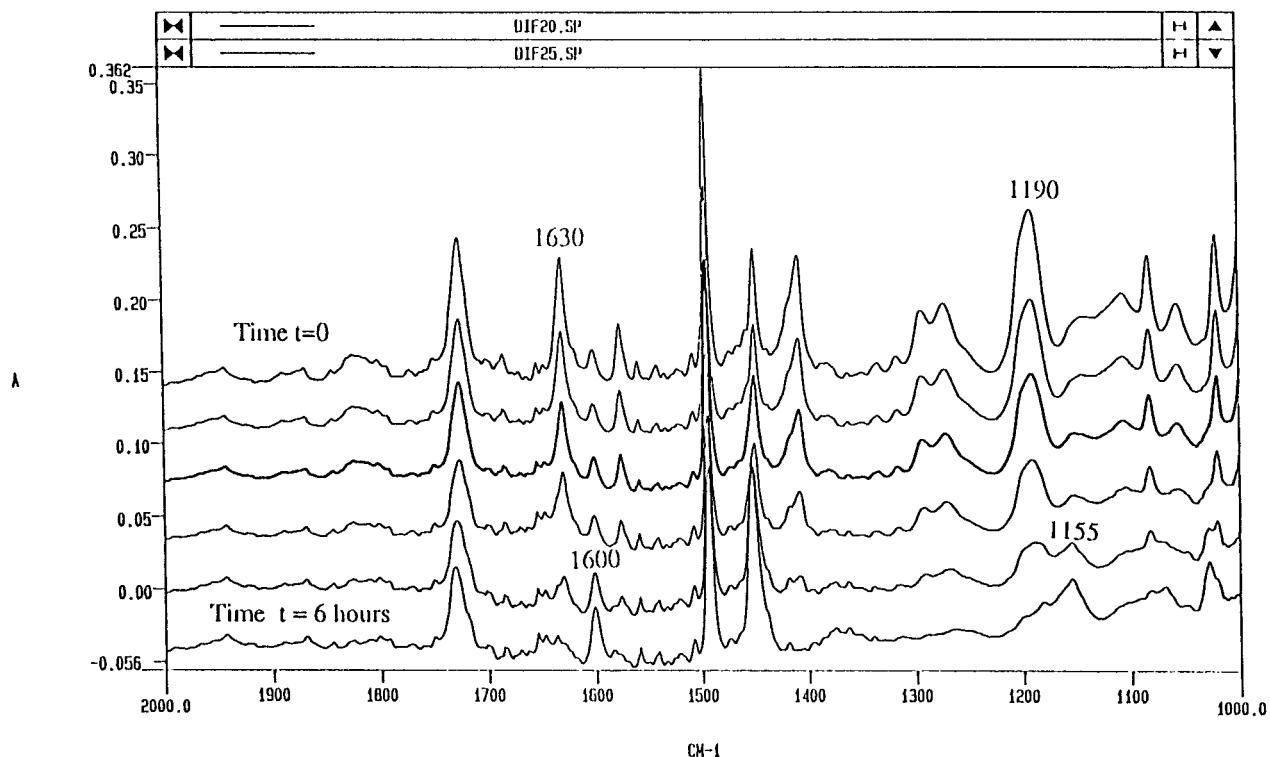


Figure 7 Indicative copolymer difference spectra (emulsion-water) measured at different degrees of conversion at a resolution of 4 cm^{-1} .

tions through coupling with midrange chalcogenide optical fibers.⁸ The present investigation is the first successful attempt for the on-line chemical reaction monitoring in an aqueous phase, using a two-reflection ATR crystal, coupled with chalcogenide midrange optical fibers immersed in a laboratory reactor.

The single beam spectrum in Figure 3 shows the spectral response for the complete system with the internal reflection probe and the 1.5 m of chalcogenide fibers. This spectrum contains wavelength-dependent features from the spectrometer, similar to the ones presented in the single beam spectrum of Figure 2, from the transfer optics and the optical fibers, as well as spectral features caused by the presence of carbon dioxide and water vapor in the room air. The percentage of transmittance spectrum resulting from ratioing the single-beam spectrum from the spectrometer with the probe and the optical fiber to an open-beam spectrum from the spectrometer showed that about 5% of the open-beam energy is transmitted through the accessory and the 1.5 m chalcogenide optical cable. It can be also observed from the response profile of Figure 3 that the chalcogenide glass optical fiber does not transmit en-

ergy below 900 cm^{-1} , thus offering a good IR transparency between 4000 and 900 cm^{-1} .

A representative example of the quality of spectra obtained is shown in Figure 4. It can be observed that the spectra of the emulsion have the monomers and copolymer bands superimposed on the basic contours of the water spectrum (Fig. 4). Therefore, computer-subtracted difference spectra have been used for further analysis, generated using the interactive difference command. It has been demonstrated well that, due to the short effective pathlength, the water contribution can be effectively subtracted from the spectra, thus making the ATR probe ideal for obtaining spectra in aqueous media. The corresponding factor selection was made on the basis of "best" flat baseline and the elimination of negative absorbance peaks. As illustrated in Figure 5, the spectrum generated by computer subtraction close to reaction completion compares favorably with the spectrum of the isolated reprecipitated copolymer obtained as a KBr pellet. Minor deviations can be attributed to the wavelength dependence of the IRS technique, giving rise to a slight distortion of the long wavelength side of the absorption bands, as well as to relatively stronger bands at longer wavelengths.

For all further quantitative analysis, the observed intensities in the IR spectrum have been corrected by multiplication to the wavenumber $\bar{\nu} = 1/\lambda$.

Figure 6 shows a comparison between the obtained difference spectrum of the emulsion at the start of the reaction and the ATR spectra of pure styrene and 2-EHA monomers. Characteristic absorbance bands are easily identifiable for the two monomers, such as the skeletal ring breathing vibration at 1630 cm^{-1} for styrene monomer and the C—O stretching vibration of the saturated ester group at 1190 cm^{-1} for 2-EHA monomer. The corresponding vibrations of the two monomeric structural units in the produced copolymer appear at 1600 and 1155 cm^{-1} , respectively, and their intensities are representative of the overall copolymer composition.¹³ Figure 7 shows indicative emulsion spectra measured at different degrees of conversion at a resolution of 4 cm^{-1} , after subtraction of the water spectrum. Distinct spectral changes are observed as a consequence of the polymerization reaction. More specifically, the 1630 cm^{-1} styrene, as well as the 1190 cm^{-1} ester monomer characteristic peak, diminish with increasing reaction time, whereas the corresponding bands in the copolymer (i.e., at 1600 cm^{-1} and 1155 cm^{-1}) increase with time. In fact, as shown in Figure 5, the emulsion difference spectrum at a reaction time of 6 h is almost identical to that of the dried copolymer obtained as a KBr pellet at the same resolution, which indicates almost complete conversion.

A quantitative estimate of the individual degrees of conversion for both monomers can be made by calculating the ratio of the absorbances (peak heights after baseline correction) of the 1630 and 1190 cm^{-1} characteristic absorption

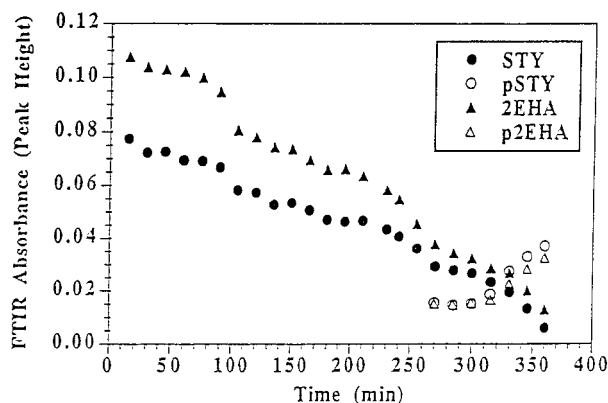


Figure 8 Variation of monomer and polymer characteristic peak intensities with reaction time.

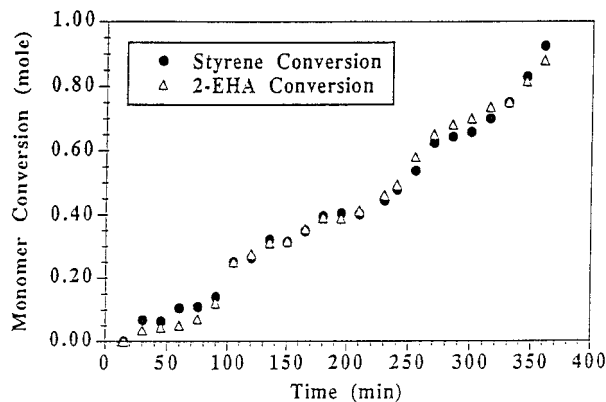


Figure 9 Estimated individual monomer degrees of conversion (mole) for styrene and 2-EHA as a function of reaction time.

bands at reaction time t to those at the start of the copolymerization reaction ($t = 0$), according to the following equations:

$$x_{\text{STY}}(\text{mole}) = 1 - \frac{A_{1630}(t)}{A_{1630}(t=0)}$$

$$x_{2\text{-EHA}}(\text{mole}) = 1 - \frac{A_{1190}(t)}{A_{1190}(t=0)}$$

The overall conversion (wt) can be subsequently calculated as

$$X(\text{wt}) = \frac{w_1}{w_1 + w_2} x_{\text{STY}} + \frac{w_2}{w_1 + w_2} x_{2\text{-EHA}}$$

where $w_1/(w_1 + w_2)$ and $w_2/(w_1 + w_2)$ are the weight fractions of monomers 1 and 2, respectively, fed into the reactor at time $t = 0$.

The variation of monomer and polymer characteristic peak intensities with reaction time are depicted in Figure 8 for a resolution of 4 cm^{-1} . The absorption intensities were calculated as peak heights after baseline correction of the characteristic absorption bands of styrene and 2-EHA units in the monomer and copolymer. The corresponding estimated individual degrees of conversion for the two monomers are plotted in Figure 9 and are essentially identical, in agreement to the azeotropic copolymerization conditions. The overall conversion (wt) estimated from the spectra obtained by using the ATR fiberprobe has been successfully compared to the conversion values obtained by TGA and conventional gravimetry measurements, as shown in Figure 10.

The reproducibility of the results has been

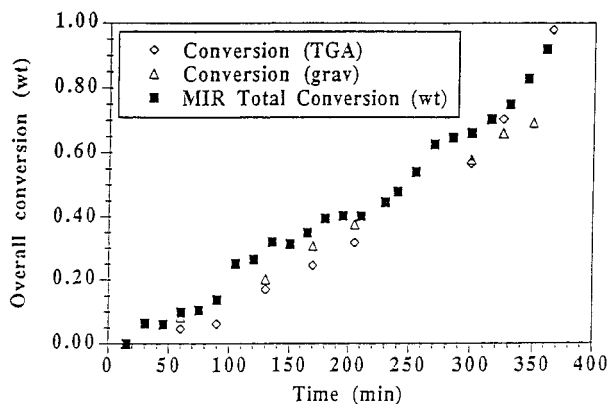


Figure 10 Comparison of the overall conversion (wt) estimated from spectra obtained by using the ATR fiberprobe to the conversion values obtained by TGA and gravimetry.

tested by means of a second batch copolymerization experiment carried out under identical conditions, except that the spectra were collected at a resolution of 2 cm^{-1} . The calculated conversion profile for the ester monomer is not influenced by the resolution used for collecting the IR spectra (Fig. 11). The lower conversion values calculated for styrene from the spectra obtained at a 2 cm^{-1} resolution at high reaction times (Fig. 12) can be attributed to the increased amount of noise due to the water vapor evident in the background spectrum. This water vapor contribution in the region of $1700\text{--}1500\text{ cm}^{-1}$ is thus almost exclusively affecting the estimation of the styrene monomer characteristic absorption intensities. The effect is also evident in the calculated overall conversion values (Fig. 13). Therefore, a lower resolution of 4 cm^{-1} may be preferred in order to

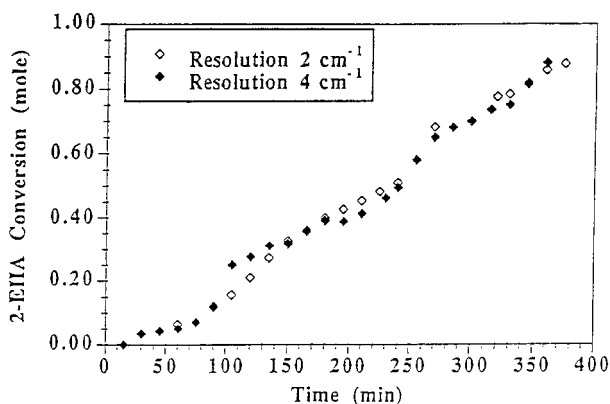


Figure 11 Comparison of the 2-EHA conversion values calculated from spectra obtained using a resolution of 2 and 4 cm^{-1} .

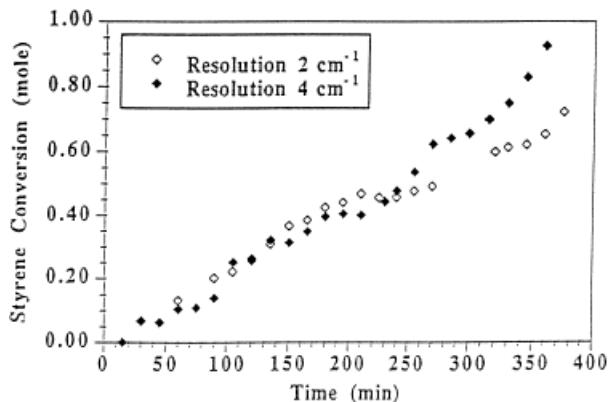


Figure 12 Comparison of the styrene conversion values calculated from spectra obtained using a resolution of 2 and 4 cm^{-1} .

assure optimum measurement conditions using the MIR fiber-optic sensor.

The estimation of the evolution of the cumulative copolymer composition from IR spectroscopic measurements in copolymerization systems with different reactivity ratios would be a more severe test of the on-line monitoring approach investigated in the present article. Therefore, the absorbances of two sequence-independent bands, namely, the skeletal ring breathing vibration at 1600 cm^{-1} of the styrene units in the copolymer and the C—O stretching vibration at 1155 cm^{-1} of the 2-EHA units, have been determined as peak heights after baseline correction from the ATR difference spectra of the emulsion obtained during the last two hours of the polymerization. A universal calibration curve¹³ was used for obtaining the ratio of the mole fractions of the structural units in the copolymer from the corresponding ratio of

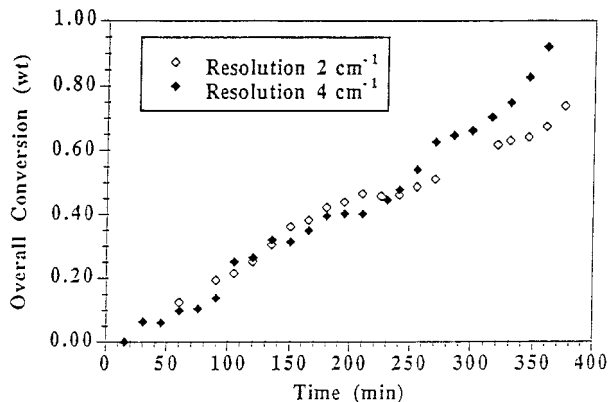


Figure 13 Comparison of the overall conversion values calculated from spectra obtained using a resolution of 2 and 4 cm^{-1} .

absorbances of these peaks after correcting for the variation of the depth of penetration with the wavelength of IR radiation. The estimated mole fraction of styrene in the copolymer assumed an essentially constant value of 0.91 throughout the last two hours of the copolymerization reaction, as expected for these azeotropic conditions. This value is in good agreement to the expected value of 0.94 estimated^{14,15} in terms of the residual monomer mole fractions and literature values^{16,17} of the reactivity ratios (i.e., $r_{\text{STY}} = 0.94$ and $r_{2\text{-EHA}} = 0.26$).

Although our initial goal was to detect only monomer conversion with time, the real-time monitoring of copolymer composition also was shown to be both possible and potentially useful. In particular, information related to the emulsion copolymerization mechanism may be obtained by monitoring conversion and copolymer composition as a function of time, especially for nonazeotropic conditions. From the data presented, it is clear that the new fiber-optic-based MIR sensor is a valuable tool for the spectroscopic investigation of emulsion polymerization processes.

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