

# Application of Low-Resolution Raman Spectroscopy to Online Monitoring of Miniemulsion Polymerization

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**ABSTRACT:** Raman spectroscopy has become a preferred technique for online monitoring of dispersion polymerization. Raman spectroscopy offers two specific advantages for these systems. First, it is insensitive to the presence of water, and the total amount of water in the emulsion has little to no influence. Second, it can use standard glass fiber conduits combined with a visible light excitation laser to allow use of a flexible remote sensor. A low-cost low-resolution Raman spectrometer (LRRS) was used to monitor emulsion polymerization, specifically batch miniemulsion polymerization.

Styrene was used as an internal reference to compensate for the effect of laser intensity fluctuation. A linear correlation between peak intensity ratio and monomer concentration was found. Probe fouling was controlled by using a protective film with minimal impact on measurement quality. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1507–1515, 2002

**Key words:** low-resolution Raman spectroscopy; emulsion polymerization; miniemulsion polymerization; internal reference; styrene; reaction monitoring

## INTRODUCTION

Emulsion polymerization is a domain of importance to industry. It is a process that allows the direct synthesis of polymers dispersed in water. This process has allowed the substitution of solvent-based paint by water-based paints, which has a critical environmental impact. Miniemulsion polymerization is typically performed in a semibatch process. Continuous stirred tank reactors are used to produce some large-volume products. About 20 years ago, John Vanderhoff and Mohamed El-Aasser discovered miniemulsion polymerization.<sup>1</sup> This process allows the introduction of hydrophilic molecules not readily transportable through water into the polymerizing droplets. The process also allows a direct control of the particle size, by controlling the amount of energy introduced in the system during emulsification, the surfactant type, and the concentration. Many parameters influence this process, such as temperature, nature and concentration of the surfactant(s), monomer(s) concentration, nature and concentration of the hydrophobe(s), initiator, and other various additives. For this process to become successfully commercialized, it is vital that it can yield high solid-concentration (40% and higher) polymers in a semicontinuous or continuous mode. To control polymerization properly in a continuous

mode, it is essential to have an analytical method allowing continuous monitoring of the polymerization. An easy and inexpensive method is described here that allows the monitoring of the polymerization of a miniemulsion polymerization. The method has been developed to monitor batch processes and semi-continuous processes but is particularly well suited for continuous polymerization, which is not the focus of this work.

Raman spectroscopy has been successfully used to monitor emulsion homopolymerizations<sup>2–4</sup> and, more recently, for to monitor the copolymerization of various systems.<sup>5–9</sup> Hegerth has published several reviews of Raman spectroscopy for emulsion polymerization.<sup>10</sup> Raman spectroscopy is an emission technique that is always in competition with fluorescence. To minimize this effect, long-excitation wavelengths are used, such as red and near infrared (typically ranging from 514 to 1064 nm). A Raman vibration is characterized as a shift from the excitation light. The data near the excitation wavelengths ( $0\text{ cm}^{-1}$ ) is characteristically very intense because of Rayleigh scattering; typically, a rejection filter is implemented to remove this band from the spectra. Raman spectrometry is sensitive to nonpolar molecular vibrations. Double, triple, and aromatic structures offer very strong emission peaks. Raman line intensities are proportional to the number of vibrating centers within the scattering volume. Particle size and optical properties of dispersed and continuous media do affect the line intensities. Water has a minimal presence in the spectra when shorter excitation wavelengths are used; some authors have reported using water as an internal ref-

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erence.<sup>3</sup> The application of Raman spectroscopy to monitor emulsion polymerization has found broader interest with the advancement of the instruments, including longer wavelength lasers and more sensitive charge-coupled device detectors at longer wavelengths. Unfortunately, these high-end instruments are expensive and are often limited to the research laboratory environment. Most of the advantages of Raman spectroscopy can be retained by using the most recent low-resolution spectrometer, which remains very affordable at typically one-tenth the price of the high-resolution instruments. Raman spectroscopy is readily recognized as a particularly efficient technique for monitoring emulsion polymerization. Because of the high cost associated with a high-resolution spectrometer, we focused on the newest generation of low-resolution Raman spectrometers (LRRS). These spectrometers offer some of the conventional advantages of Raman spectroscopy such as insensitivity to the presence of water molecules and the ability to use fiberoptics to conduct light in and out of the reactive media. The problems of laser intensity variations and of limited resolution were overcome by using an internal standard. It has been reported by other authors that the phenyl ring of styrene can be used as an internal reference.<sup>7,11-13</sup> This study used the phenyl ring of styrene as an internal reference.

Miniemulsion polymerization is a process standing between conventional emulsion polymerization and dispersion polymerization. In miniemulsion, the hydrophobe molecule is added to the solution of monomer(s), and that solution is mechanically dispersed to create a stable emulsion of particle size ranging from 30 to 300 nm. The particle size is established by controlling the shear source and the time under shear. Narrower size distributions are obtained with longer residence time. The choice of surfactant(s) is important to control stability, and its concentration will contribute to the particle size population characteristic. The presence of the hydrophobe molecule greatly reduces Oswald ripening. Those molecules, having no ability to transport through water, cannot diffuse from one droplet to another. Eventually, concentration variations in growing or shrinking droplets create disparities in chemical potential that limit (inhibit) the transport of monomer through the minimization of the total Gibbs energy. Finally, a water-soluble initiator is used to polymerize the monomer droplets. Many arguments remain on whether or not all droplets are polymerized. In most systems, a dominant fraction of the droplets are initiated, but renucleation does occur to a limited extent. Particle number is theoretically constant, but in most practical cases this number increases slightly at the beginning of the polymerization. In many cases of high solid content, limited coagulation is present and particle numbers decrease when reaching conversions higher than 50%. Several groups

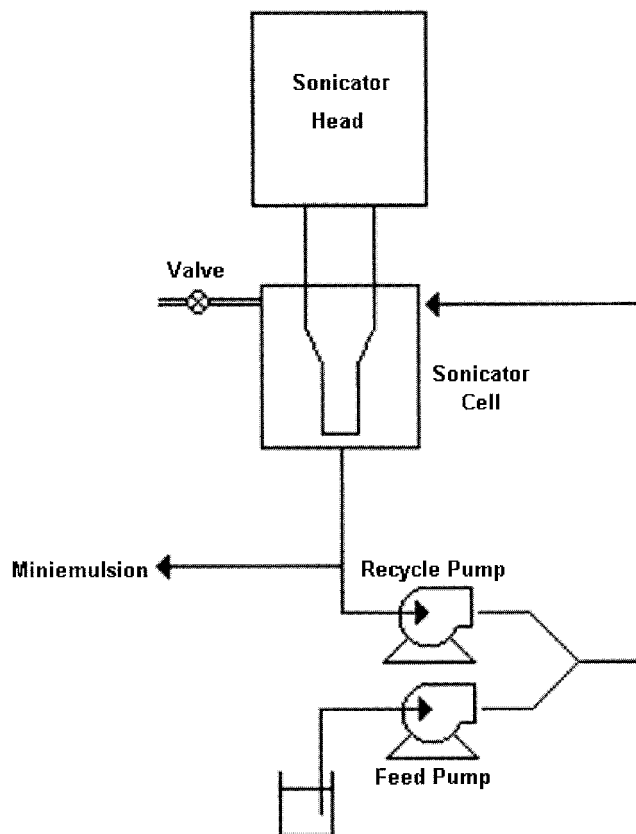


Figure 1 Sonicator flow sheet.

are successfully studying miniemulsion polymerization kinetics<sup>14-20</sup> and Raman spectroscopy as an additional tool for this task.

## EXPERIMENTAL

The following chemicals have been used in our various experiments: water was double distilled, deionized by resin exchange, and then degassed by hard-boiling while purging with nitrogen. High-purity water was degassed before use. Two surfactants were used: sodium dodecyl sulfate (SDS) and Di-octyl sulfosuccinate sodium (AMA 80). The monomers, styrene and butyl acrylate were stripped of their commercial inhibitor by passing the monomers through an alumina ( $\text{Al}_2\text{O}_3$ ) column. Hexadecane (HD) was used in all miniemulsions as a hydrophobe (or stabilizer). The initiator used was commercial sodium persulfate (NaPS) without further purification. All chemicals were purchased from Acros Organics (USA) with the exception of water and styrene. Styrene was purchased from Sigma Aldrich (St. Louis, MO).

The aqueous phase containing the water, SDS, and AMA-80 was mixed with the organic phase containing monomer and hexadecane to create a pre-emulsion. The mixture (under constant magnetic stirring) was transferred (using a fluid-metering pump) to a sonica-

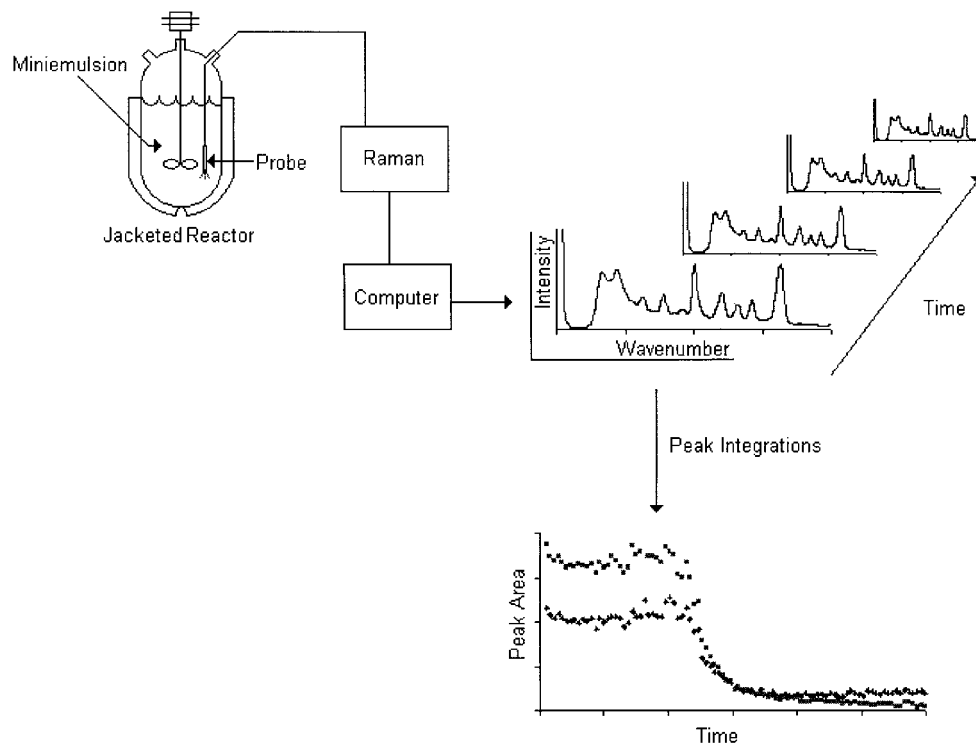


Figure 2 Raman system.

tor (Branson Ultra Sonifer 450; Branson Ultrasonics Corp., Danbury, CT) cell. This sonicator was equipped with a continuous cell adapter. This assembly was found to create a miniemulsion free of pooled organics and capable of creating a smaller average droplet size than the batch head originally used.

The effluent stream leaving the sonicator was split. Part of the effluent was taken as the product, while the other part was recycled back into the sonicator cell. The recycle stream was mixed with the mixture (pre-emulsion) stream and fed to the sonicator (Fig. 1). The recycle stream was added to decrease the instantaneous residence time from 15 min to 7.5 min while keeping the overall residence time to 15 min. This created a homogeneous and very stable miniemulsion that is free of pooled organics.

The reactor used for all miniemulsion polymerizations was a 250-mL jacketed reactor. A circulating water bath was connected to the reactor. All reactions were carried out at atmospheric pressure. The temperature in the reactor was measured by a thermocouple inserted into the reactor. Nitrogen was passed over the reaction mixture to create an inert environment. Mechanical stirring was used for the high-solid-content miniemulsions (40% and 50%). Magnetic stirring was used for the low-solid-content miniemulsions (30%). The Raman spectrometer probe was immersed directly in the emulsions for the measurement of spectra.

Ocean Optics<sup>21</sup> (Dunedin, FL) makes a LRRS under the product name R2000. The instrument consists of a

solid-state laser emitting at 785 nm. The excitation and the Raman scattered light is collected by a fiberoptic cable with a laser-line rejection filter. The Raman spectrum is collected by a CCD array. The spectral resolution is  $30 \text{ cm}^{-1}$ . Because the fiber optic probe is directly immersed into the miniemulsion, cleaning of the probe head is required to avoid excessive fouling and loss of signal.

The spectrometer is connected to a computer through a data acquisition card. The computer records the spectra automatically. The spectra can be gathered continuously at set time intervals and for set duration. The time interval signifies the time between when the spectra are recorded, and the duration signifies the time over which the spectra were collected. After the reaction is completed and all spectra have been recorded, they are then combined by a C program. Another program is used to integrate data over user-specified intervals. This program integrates defined peaks at various times and collects them into a single file. This algorithm is symbolized in Figure 2.

## Experiments

Table I provides the detailed reaction conditions used in this work. Styrene was present in all experiments run in this study. Experiments TRM-050 A-C and TRM-060 were homopolymerizations of styrene. Experiments TRM-049 and TRM-052 were copolymerizations of styrene and butyl acrylate. The styrene to

**TABLE I**  
Formulations Used for the Different Miniemulsions; Process Characteristics

Components (g)	TRM-049	TRM-050A	TRM-050B	TRM-050C	TRM-052	TRM-060
Monomer						
STY	40.4	57.6	76.9	96.1	17.3	76.9
BuA	17.3				40.4	
H <sub>2</sub> O	138.3	138.3	117.7	97.1	138.3	117.7
SDS	1.2	1.2	1.5	1.9	1.2	1.5
AMA-80	1.2	1.2	1.5	1.9	1.2	1.5
NaPS	0.06	0.06	0.08	0.10	0.06	0.08
Hexadecane	1.7	1.7	2.3	2.9	1.7	2.3
Final solid content (SC <sub>p</sub> )	32.5%	30.8%	39.9%	42.6%	28.7%	39.5%
Initial solid content (SC <sub>0</sub> )	1.1%	1.1%	1.5%	2.0%	1.1%	1.1%
Process conditions						
Temperature	70°C	70°C	70°C	Nonisothermal	70°C	70°C
Stirring	Magnetic	Magnetic	Mechanical	Mechanical	Magnetic	Magnetic
Conversion	0.95	1.0	1.0	0.82	0.96	0.98

butyl acrylate ratio was varied in these two experiments. For experiment TRM-049 the monomer used was 70% styrene and 30% butyl acrylate. TRM-052 used 30% styrene and 70% butyl acrylate.

The spectra for the experiments presented above were recorded for 10 sec. There was a delay of 66 sec between recordings. During these 66 sec, the laser was toggled on and off automatically by the spectrometer. The spectrometer was allowed to warm up for 20 sec before the recording of each spectrum. These 20 sec are included in the 66 sec between recording of spectra and the 45 sec during which the laser was turned off. There was a system lag of 1.8 sec. The total time between recording of spectra as reported in the time stamp file associated with each experiment was  $76.81 \pm 0.01$  sec.

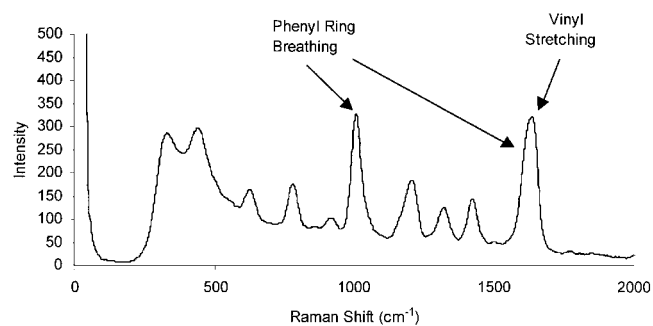
## Methodology

The Raman system previously described was used to continuously capture spectrum. A spectrum of pure styrene is shown in Figure 3. This spectrum has several significant peaks. The peaks of particular interest to this study are the peaks occurring at wavelengths 1000 and 1600  $\text{cm}^{-1}$ . The peak at 1000  $\text{cm}^{-1}$  represents the breathing (expansion/contraction) of the phenyl ring. The peak at 1600  $\text{cm}^{-1}$  represents the vinyl stretching that is present in all vinyl monomers. The phenyl ring contributes in part to the intensity of this peak. As the monomer is polymerized, the concentration of the vinyl bond decreases and the peak at 1600  $\text{cm}^{-1}$  decreases in intensity and integrated surface area. The vinyl bond contributes in part to this peak as well.

Experiment TRM-050B is presented to illustrate the manipulation of the data contained in each spectrum recorded. Experiment TRM-050B was a homopolymerization of styrene carried out at 70°C and atmo-

spheric pressure. The solids content of the experiment was 40% and required mechanical stirring. Figure 4 represents the integration of the peaks of the miniemulsion polymerization at 1000 and 1600  $\text{cm}^{-1}$ . The integration was carried out by the use of a C program. The program read all the data obtained from the spectrometer and prompted the user to define which wavelength interval to integrate. All spectra were integrated between these wavelengths. The integration carried out made use of the trapezoid rule because the points supplied by the spectrometer were not at constant intervals.

Use of the Raman spectrometer allowed monitoring of the emulsions during the heating stage. This was done to experiment TRM-050B as the mixture was heated to 70°C. It took 34 min to bring the mixture to 70°C from room temperature. Once this temperature was reached, the initiator was added. The polymerization started immediately, as can be seen from the drop in the peak integration values. Examination of the peaks at 1000 and 1600  $\text{cm}^{-1}$  shows the fast drop-off of peak intensity, which occurs as the polymerization proceeds, caused by stronger scattering. An internal standard technique was used to eliminate intensity



**Figure 3** Raman spectra of styrene.

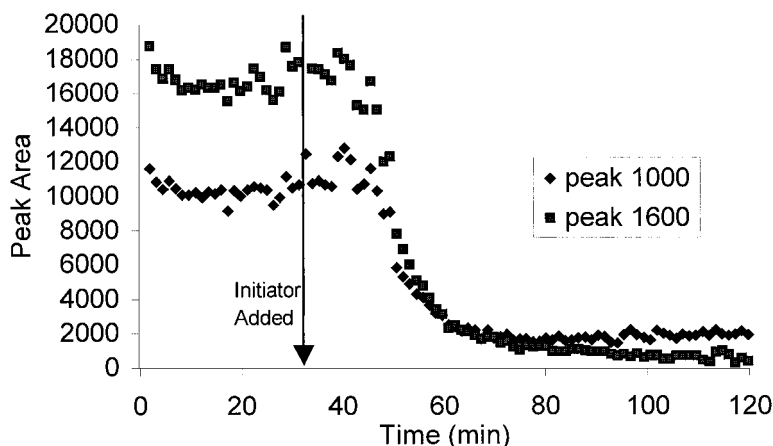


Figure 4 Miniemulsion polymerization of TRM-050B followed by Raman spectroscopy.

fluctuations resulting from peak intensity variation with the laser intensity. The peak ratio between the peak at  $1600\text{ cm}^{-1}$ , whose intensity is highly dependant on monomer concentration, and the peak at  $1000\text{ cm}^{-1}$ , of relative constant intensity, was calculated to interpret the data. Figure 5 shows the peak ratios from experiment TRM-050B. This figure shows that the ratio is unaffected by the laser intensity or the fouling of the probe, as it is constant until the initiator is introduced ( $t = 34\text{ min}$ ). The reduction in peak intensity after the addition of the initiator can be seen clearly in Figure 5.

The relationship between the peak ratio and the conversion was investigated by preparing samples of known monomer and polymer concentration. A latex of polystyrene was prepared by standard emulsion polymerization to yield an average particle size of  $74\text{ nm}$  at  $19.7\%$  solid content. A known amount of styrene monomer was added to the latex and allowed to swell overnight. The experiment was repeated with a second latex of significantly different particle size ( $125\text{ nm}$ ) and solid content ( $28.4\%$ ). Raman spectra of each sample were recorded at room temperature, and the ratio of the integrated peaks calculated. Each sample represents a latex of constant solid content and known equivalent conversion. Conversion was plotted as a function of peak ratio to obtain Figure 6. There is a

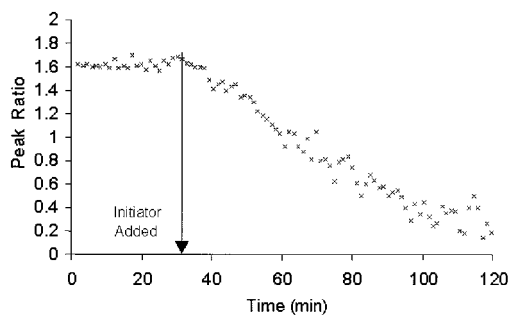


Figure 5 Peak ratio for TRM-050B.

clear linear relationship between the conversion and the peak ratio. This linear relation has been reported by other authors.<sup>7</sup>

The conversion can be determined from the peak ratio by relating the final peak ratio to the initial peak ratio. The average of the peak ratios before addition of the initiator is used as one of the constants. The average of the peak ratios at the end of the reaction when the polymerization has stopped is the other constant.

$$X_{\text{Raman}} = \left( \frac{R_t - \bar{R}_{t < 0}}{\bar{R}_{t > t} - \bar{R}_{t < 0}} \right) \times X_t$$

where  $X_{\text{Raman}}$  = conversion at time  $t$  determined from Raman,  $R_t$  = peak ratio  $1600/1000$  at time  $t$ ,  $\bar{R}_{t < 0}$  = average peak ratio before addition of initiator,  $\bar{R}_{t < t}$  = average peak ratio, and  $X_t$  = final conversion determined from gravimetry.

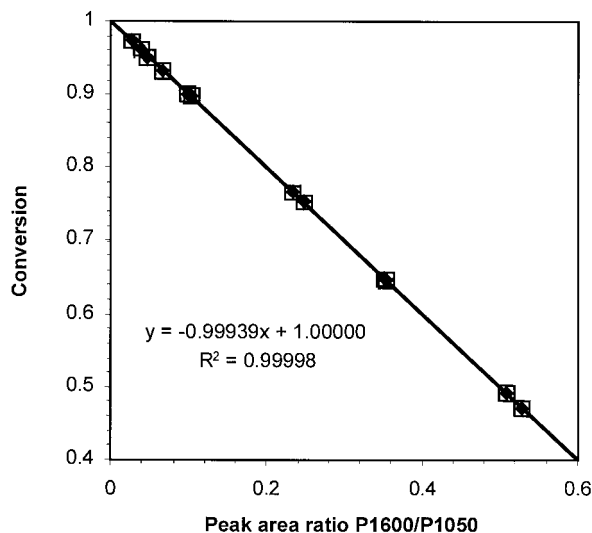
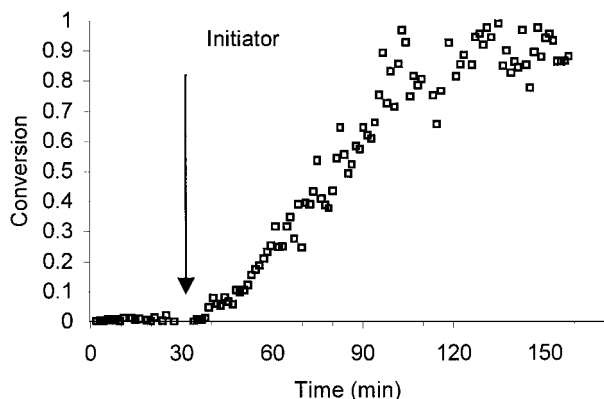


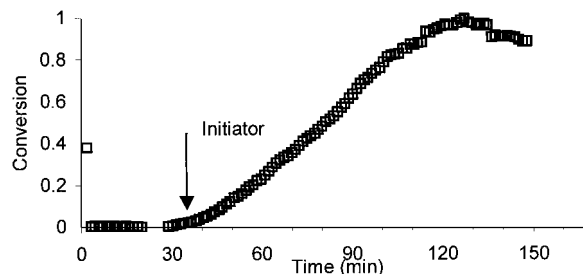
Figure 6 Conversion as a function of peak ratio.



**Figure 7** Conversion of TRM-050B as determined by Raman spectroscopy.

Using the formula described above, the conversion can be determined from the peak ratios. Finally, Figure 7 shows the conversion from Raman versus time for experiment TRM-50B and shows that the Raman handles the cases of low conversion accurately. Once higher conversions are reached, the accuracy of the Raman drops. As the reaction nears completion, the rate is slow and the Raman has trouble distinguishing between 95% conversion and 100% conversion. Calculating a moving average of the points smoothed the data presented in Figure 7. Examination of Figure 8 shows that smoothing has a beneficial effect at lower conversions but that at higher conversions the inability of the Raman is still shown. All the interpretations for experiments discussed in this study were done in this manner.

One of the major problems that occurred during the course of performing these experiments was probe fouling. The tip of the probe tends to develop a polymer buildup. When this occurs, the probe no longer sees what is happening inside the reaction mixture but rather the bulk built up on the outside of the tip. This leads to drastic drops in intensity as the probe goes from seeing a dynamic miniemulsion of relatively low conversion to a bulk polymer unrepresentative of the polymerization kinetics. One of the advantages of Raman technology is that certain probes can see through glass. As a first attempt at solving the probe fouling issue, another probe with a longer focus length was examined. It was found that the reactor walls were too



**Figure 8** Smoothed conversion of TRM050B as determined by Raman spectroscopy.

thick to allow the probe to be used externally. Other attempts were made by using of a thin piece of Teflon that was affixed to the tip of the probe. This effectively solved the probe fouling issue, but the line intensities were drastically reduced. After much trial and error, polyvinylidene (PVD) was tested. This particular coating applied to the tip of the laser ended the probe fouling problem and offered reasonable intensities. Table II shows the comparison between some of the different attempts to solve this problem.

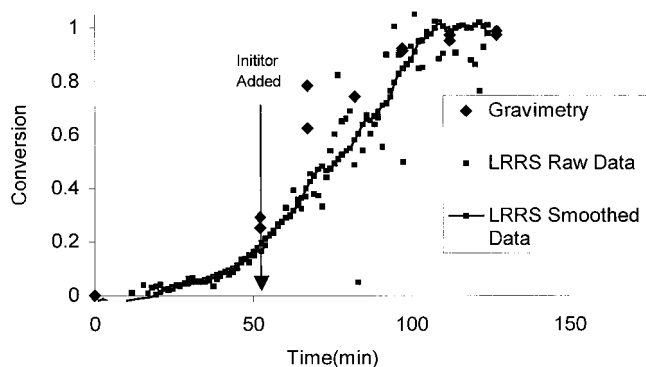
## RESULTS AND DISCUSSION

The Raman system was used to monitor several polymerization experiments. In several experiments, samples were taken to perform gravimetric analysis. The conversion was determined from the results of the gravimetric analysis. Hydroquinone inhibitor was added to the samples to quench the reaction. Considerable deviation was observed between the conversion determined from the Raman and the gravimetry. This deviation occurs because after the inhibitor is added, there is a lag before the reaction is quenched. The inhibitor was added to the vial before sampling. The sample is extracted from the reactor in a pipette and injected immediately into the vial containing inhibitor. The vial is then shaken to disperse the inhibitor in the sample. When the reaction rate is high, the inhibitor does not quench as effectively as with slow reaction rates.

During the middle of the polymerization when the reaction rate was highest, the largest deviation was noticed between the Raman and the gravimetric data. Experiment TRM-060 effectively demonstrates this

**TABLE II**  
Effect of Protective Film on Low-Resolution Raman Spectrometry Peak Intensity for Two Different Probes

	Long focal distance		Short focal distance			
	PTFE	PVD	Direct	PTFE	Fluo-Oil	PVD
Peak intensity (1000)	1000	3000	9000	1000	6500	6500
Peak ratio average	3.35	3.96	3.25	3.21	3.83	3.40
Standard deviation	2.20	1.24	0.19	1.42	0.28	0.20
Deviation (%)	66%	31%	6%	44%	7%	6%



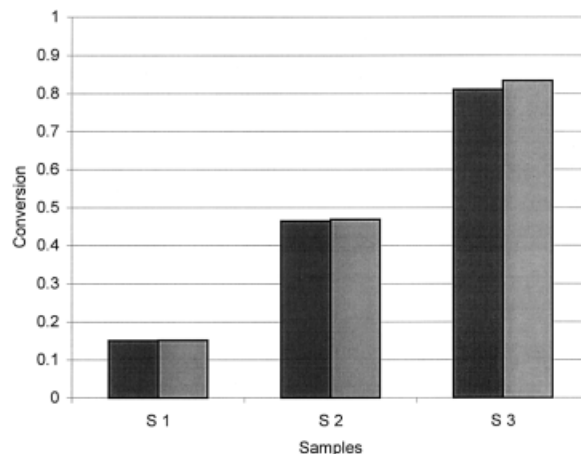
**Figure 9** Conversion determined by gravimetry and Raman spectroscopy for TRM-060.

phenomenon. This experiment was a polymerization of styrene with an overall solids content of 30%. It can be seen that there was a large deviation between the Raman and the gravimetric data. Examination of Figure 9 shows the deviation between the Raman and gravimetric data. The deviation is high during the middle of the polymerization and low near the end, when the conversion is high. The gravimetric data were obtained by taking the mass of each sample and then placing them in an oven to evaporate the remaining unreacted monomers, the excess water, and hexadecane. Once the polymer was dry, the mass of the dry polymer was taken. The conversion was then determined from the following equation:

$$X = \frac{M_s - M_0}{M_p - M_0'}$$

where  $X$  = conversion,  $M_s$  = mass of dry polymer in sample,  $M_0$  = mass of surfactants and initiator, and  $M_p$  = mass of dry polymer at 100% conversion.

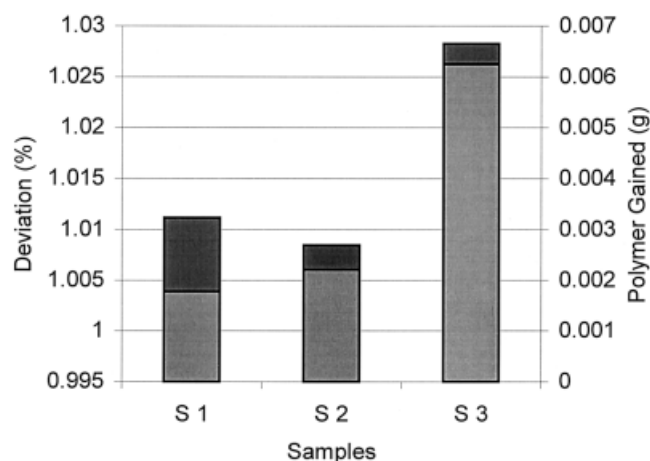
To ensure that the deviation between the Raman and gravimetric data was not the result of polymerization occurring in the oven, samples of known conversion were made and placed in the oven. The samples were made with conversions of S1 = 15%, S2 = 46%, and S3 = 80%. The samples were massed, and the temperature of the oven was recorded every 12 h for 72 total h. The polymerization that occurred in the oven was minimal, representing only a 1% deviation between the nominal conversion ( $X_{nom}$ ) and the experimental conversion ( $X_{exp}$ ). Figure 10 shows the deviation in conversion during the oven test. This minimal difference represents marginal gain in the amount of polymer present. Figure 11 represents the percent deviation and the polymer gained. The small gain caused by polymerization occurring in the oven does not account for the almost 10% deviation between the Raman and gravimetric data. The inability of the initiator to effectively quench the reaction is the only explanation for this deviation.



**Figure 10** Deviation in conversion during oven test.

Experiment TRM-060 and Figure 9 can be used to illustrate several other points. First, after each sample was taken there was a direct effect on the Raman monitoring. This was seen to happen on the 250-mL reactor but not on larger reactors. After each sample was taken, the conversion determined from the Raman increased slightly and then decreased. This is directly related to the size of the reactor. On the smaller reactors the sampling has a direct effect on the rate of reaction.

The other point that can be illustrated from this figure is the effectiveness of the Raman monitoring system. The miniemulsion was at room temperature when it was added to the reactor and the heating was started. The Raman began recording data at the beginning of the heating process. The reaction mixture was brought from approximately 25° to 70°C in 45 min. Once the reaction mixture reached 70°C, the sodium persulfate initiator was added and the reaction was started. It can be seen from the Raman data that the polymerization began before the addition of the initi-



**Figure 11** Error percentage and polymer gained during oven test.

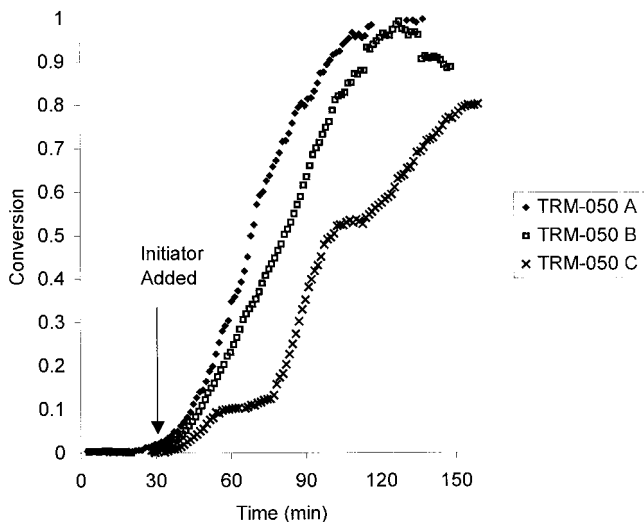


Figure 12 Reaction kinetics of TRM-050 A, B, and C.

ator. The conversion inside the reactor had reached 12.3% before initiator addition.

The Raman was used to monitor several other polymerization experiments, as noted in Table I. Experiments TRM-050 A, B, and C were the same miniemulsion. The miniemulsion was made to have a final solids content of 50%. TRM-050 A was a dilution to 30%, and TRM-050B was a dilution to 40% solids content. Figure 12 shows the data obtained by the Raman for experiments TRM-050 A, B, and C. Experiment TRM-050 C contained 50% desired final solids content. Because of the high solids content, on addition of the initiator, the temperature inside the reactor increased sharply. This reaction proceeded nonisothermally. The plateaus in Figure 12 represent the times when the cooling water was engaged and caused a drop in the reaction rate because of an overall drop in reactor temperature. The Raman monitoring

system worked well with this reaction. This further illustrates the Raman's capability to monitor systems that are erratic.

The Raman study was extended to copolymerizations of styrene and butyl acrylate. Differing proportions of styrene and butyl acrylate were investigated. All final solid contents were 30%. Although the butyl acrylate produced additional peaks in the spectra, the best ratio was found to be the 1000 to 1600  $\text{cm}^{-1}$  ratio. The Raman monitoring system accurately monitored the overall copolymerizations. Figure 13 shows the conversion as determined from the Raman. TRM-049 is a mixture of 70% styrene and 30% butyl acrylate in the organic phase. TRM-052 is a mixture of 30% styrene and 70% butyl acrylate in the organic phase. No deconvolution via chemometrics of the spectra was attempted. The intensity of the Raman peak at 1600  $\text{cm}^{-1}$  has a bias toward styrene, and the butyl acrylate vinyl stretch in that region is less intense. Further studies need to be done to further establish the potential of LRRS to track individual monomer reactivity in miniemulsion.

## CONCLUSION

It was established that LRRS can be successfully used to monitor miniemulsion polymerization kinetics. The use of a PVD film at the tip of the probe has efficiently reduced probe fouling. The phenyl ring of styrene/polystyrene was used as an internal reference and allowed the calculation of monomer conversion independent of changes in scattering intensity and laser excitation intensity. It was found that this technique was particularly useful to provide process information, which typically is difficult to obtain by gravimetric analysis. Finally, Raman Spectroscopy offers the potential of monitoring the conversion of individual

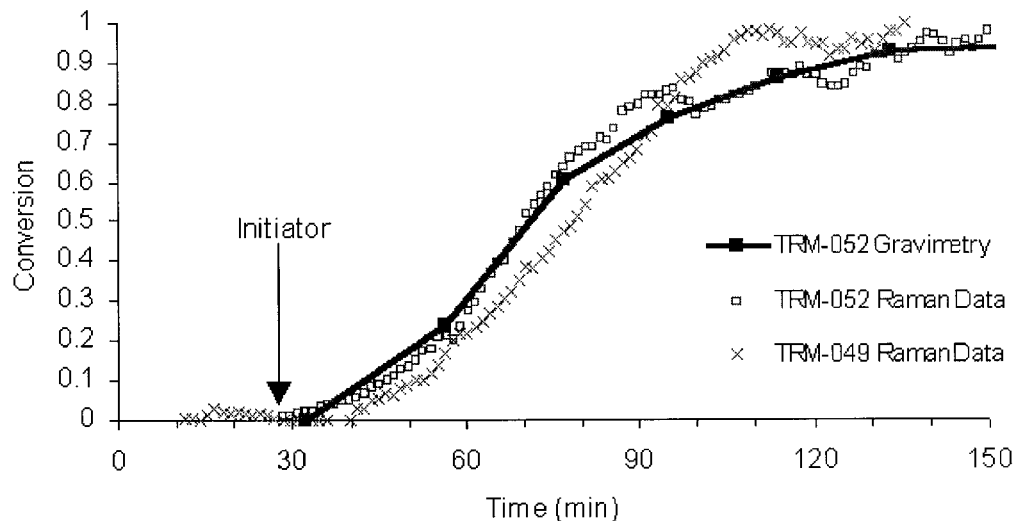


Figure 13 Reaction kinetics of TRM-049 and TRM-052.



monomers, as reported by van den Brink.<sup>8</sup> This is potentially feasible with LRRS when it is used with chemometrics.

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## References

1. Sudol, E. D.; El-Aasser, M. S. In *Emulsion Polymerization and Emulsion Polymers*; Lovel, P.A.; El-Aasser, M.S., Ed.; Wiley: New York, 1997; Chap 20.
2. Wang, C; Vickers, T. J.; Schlenoff, J. B.; Mann, C. K. *Appl Spectrosc* 1992, 46, 1729.
3. Wang, C; Vickers, T. J.; Mann, C. K. *Appl Spectrosc* 1993, 47, 928.
4. Oezpozen, T.; Schrader, B.; Keller, S. *Spectrochim Acta A* 1997, 53A, 1.
5. Dubois, E.; Amram, B.; Charmot, D.; Menardo, C.; Ridoux, J.-P. *Proc Intl Soc Opt Eng* 1993, 2089, 470.
6. Al-Khanbashi, A.; Dhamdhere, M.; Hansen, M. *Appl Spectrosc Rev* 1998, 33, 115.
7. Van den Brink, M.; Pepers, M.; Van Herk, A. M.; German, A. L. *Macromol Symp* 2000, 150, 121.
8. Agnely, M.; Amram, B.; Armitage, P. D.; Charmot, D.; Drochon, B.; Pere, E. *Appl Spectrosc* 2000, 41 pp. WO 2000049395 (2000).
9. Bauer, C.; Amram, B.; Agnely, M.; Charmot, D.; Sawatzki, J.; Dupuy, N.; Huvenne, J.-P. *Appl Spectrosc* 2000, 54, 528.
10. Hergeth, W.-D. In *Polymeric Dispersions: Principles and Applications*; NATO ASI Series E: Applied Sciences; Asua, J.M. Ed.; Kluwer: New York, 1997.
11. Gulari, E.; McKeigue, K.; Ng, K. Y. S. *Macromolecules* 1984, 17, 1822.
12. Sears, W. M; Hunt, J. L.; Strvens, J. R. *J Chem Phys* 1981, 335, 75, 1599.
13. Chu, B.; Fytas, G.; Zalczer, G. *Macromolecules* 1981, 14, 395.
14. Choi, Y. T.; El-Aasser, M. S.; Sudol, E. D.; Vanderhoff, J. W. *J Polym Sci Polym Chem Ed* 1985, 1985, 23, 2973.
15. Delgado, J.; El-Aasser, M. S.; Silebi, C. A.; Vanderhoff, J. W. *Polym Mater Sci Eng* 1987, 57, 976.
16. Elbing, E.; Parts, A. G.; Lyons, C. J.; Collier, B. A. W.; Wilson, I. R. *Aust J Chem* 1989, 42, 2085.
17. Blythe, P. J.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci A Polym Chem* 1997, 35, 807.
18. Samer, C. J.; Schork, F. J. *Ind Eng Chem Res* 1999, 38, 1792.
19. Aizpurua, I.; Amalvy, J. I.; Barandiaran, M. J. *Colloids Surf A* 2000, 166, 59.
20. Chern, C.-S.; Sheu, J.-C. *J Polym Sci A Polym Chem* 2000, 38, 3188.
21. <http://www.oceanoptics.com>