ATR-UV Monitoring of Methyl Methacrylate Miniemulsion Polymerization for Determination of Monomer Conversion

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ABSTRACT: Attenuated Total Reflection (ATR) UV spectroscopy has been used to monitor monomer conversion in methyl methacrylate miniemulsion polymerization. It was found that the vinylic groups of methyl methacrylate strongly absorb the UV light with a maximum absorption at 225 nm. This absorption peak decreases as monomer is converted to polymer. The polymer has a strong absorption at a lower UV region. The results from this feasibility study indicate that ATR-UV sensor technique has a great potential to be used for on-line or in-line process monitoring in emulsion and miniemulsion polymerization. With a partial least square (PLS) calibration model, very good prediction the monomer conversion was obtained. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1471–1475, 2006

Key words: ATR; UV; spectroscopy; methyl methacrylate; miniemulsion; polymerization; monomer conversion

INTRODUCTION

Emulsion polymerization is an important industrial process. Miniemulsion polymerization is a rapidly emerging technology. Conversion of monomer to polymer (monomer conversion) is one of the most important process variables in batch or semibatch polymerization. It can be determined off-line by gravimetry or gas chromatography. Gas chromatography (GC) has been widely used for monomer quantification, since most of the monomer compounds are highly volatile.[1] Both gavimetry and GC analysis are tedious and time consuming, which cannot meet the needs for process monitoring. There are many other methods available such as densitometry,[2] ultrasound velocity,[3] and calorimetry,[4] which can be applied for on-line analysis. All three of these methods are recipe specific (i.e., the contents of the reactor at the start of the polymerization must be known accurately), and they are unable to discriminate between monomers in a copolymerization. More recently, advanced analytical techniques such as Fourier transform infrared[5] and Raman[6] spectroscopy have been developed for on-line or in-line monitoring of emulsion and miniemulsion polymerization processes. The major backward of the near-infrared (NIR) spectroscopic application is that the absorption peak in this region is nonspecific and,

in addition, most NIR absorption are overtones and combinations of the fundamental mid-infrared (MIR) molecular vibration bands and are typically weaker than their corresponding fundamental transition. In an emulsion or miniemulsion, the problem is compounded by the nonlinearities associated with light scattering in concentrated suspensions. Mid-infrared spectroscopy via attenuated total reflectance (ATR) or internal reflection is most widely used of the spectroscopic sensors for these types of polymerizations. In this approach, the so-called evanescent wave, probing the medium outside the probe, is utilized. Thus, the intense absorption of water that covers the major part of the normal analytical region in the conventional MIR spectroscopy can be minimized, which makes it possible to record the MIR spectra of monomer/polymer emulsions. However, the signal-to-noise ratios are relatively low, which makes the poor precision in the spectroscopic measurements. Although Raman spectroscopy was regarded as a very promising technique in emulsion applications because of its noninvasive, scattering measurement features as well as low water interference, like IR, its signal-to-noise ratios are rather low. The low signal-to-noise ratios lead to a poor precision in the spectroscopic measurements.

The UV-Visible range has found less use for a direct process analysis. Spectra in this range are broader and less informative, but the main obstacle is probably highly absorptive over short path lengths. Typically, most existing applications of UV-Vis for process analysis involve measurements of components such as H_2S

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or SO_2 in the gas phase.[7] At the high concentrations of the measured species often found in liquid process streams, this leads to extremely high absorbances when using normal optical path lengths. With the introduction of an ATR probe for UV-Vis range, new possibilities for measurements on optically thick solutions have arisen. In the UV-Vis range, the effective optical path length for ATR can be reduced to 1–2 μm per reflection. By varying the length of the probe, one can change the number of reflections and thus the sensitivity. On-line or in-line ATR probes for UV-Vis measurements are available commercially. Because of the low cost and ease of maintenance, the ATR-UV technique may provide a better alternative to ATR-NIR or -FTIR methods. Chai[8,9] has demonstrated the feasibility of analyzing sodium hydroxide and sulfide concentrations simultaneously in synthetic kraft white liquor by ATR at the UV-Vis range. Later, Chai et al.[10–13] successfully performed in-line simultaneous monitoring of sulfide and polysulfide in modified kraft white liquor, hydroxide, sulfide, and carbonate in kraft white liquor, and dissolved lignin, hydroxide, and sulfide in kraft pulping liquors.

The objective of the presented work is to evaluate ATR-UV spectroscopy as a method for monitoring emulsion and miniemulsion polymerization, and demonstrate its feasibility for online estimation of monomer conversion in these systems.

EXPERIMENTAL

Chemicals

Methyl methacrylate (MMA) was obtained from Aldrich. MMA was passed through an ion exchange column to remove inhibitors. The surfactant was sodium dodecyl sulfate (SDS), the costabilizer was hexadecane (HD), and the initiator was potassium persulfate (KPS). SDS was supplied by ICN Biomedicals Inc, while HD and KPS were supplied by Aldrich; all three were used as received. Hydroquinone, for quenching, was supplied by Fisher and the water used throughout the work was deionized.

Miniemulsion preparation

HD was dissolved in the MMA. The organic phase was added to a solution of SDS in de-ionized water under vigorous stirring and then stirred for 45 min in an ice water bath, after which the emulsion was sonicated (Fisher Sonic Dismembrator) at 70% output (maximum output of 300 W) for durations of 25 min. During sonication, the miniemulsion was immersed in the water bath to keep its temperature below 20°C. The miniemulsion was then transferred into a round-bottom glass reactor equipped with reflux cooler and a magnetic stirrer, then nitrogen was purged for 30 min. After 30 min, a solution of KPS (initiator) was

TABLE I
Polymerization Recipe

	Weight (%)	Mass (g)
Monomer mix		
MMA	29.81	75.00
Hexadecane	0.60	1.52
Total	30.41	76.52
Aqueous phase		
Water	69.56	175.02
SDS	0.36	0.91
Total	69.91	175.93
Initiator		
KPS	0.04	0.10
% Solids	29.85	29.84
Total (after initiator)	100.00	251.64

injected into the reactor and the whole system was immersed in a water bath held at the reaction temperature (60°C). Polymerization was carried out under nitrogen atmosphere. At regular time intervals of 15 min, samples were taken for conversion measurement, particle size distribution analysis, and off-line UV analysis. Analysis samples were inhibited with a 0.5M hydroquinone solution in water. The recipe is given in Table I.

ATR-UV analysis

All measurements were conducted in a laboratory ATR-UV system. The system consists of an ATR-UV flow cell with one path (reflection) (Axiom, model TNL-120H23–3, Irvine, CA) for on-line analysis; a peristaltic pump (RP-1, Rainin, Emeryville, CA); a 25-mL beaker, tubing, and connectors; and a UV/Vis spectrophotometer (UV-8452, Hewlett–Packard, now Agilent Technologies, Palo Alto, CA, USA). The ATR cell consists of an ATR probe made of a quartz rod and a housing unit. The miniemulsion sample is delivered to ATR flow cell by a peristaltic pump. The UV/Vis spectrum of the sample was recorded by the spectrophotometer equipped with an HP ChemStation software.

Reference methods and method calibrations

Monomer conversion was determined through gravimetric analysis. The accuracy was ±1% on monomer conversion. Latex particle sizes and polydispersities were analyzed using quasi-elastic light scattering (QELS, Protein Solutions DynaPro99 with DynaPro DCS v 5.26 software). Commercial chemometric software, SMICA (Umetrics AB, Sweden) was used in multivariate calibration.

RESULTS AND DISCUSSION

Application of ATR-UV to aqueous emulsions

A detailed description of the ATR principle has been given by Harrick.[14] In this method, a transparent
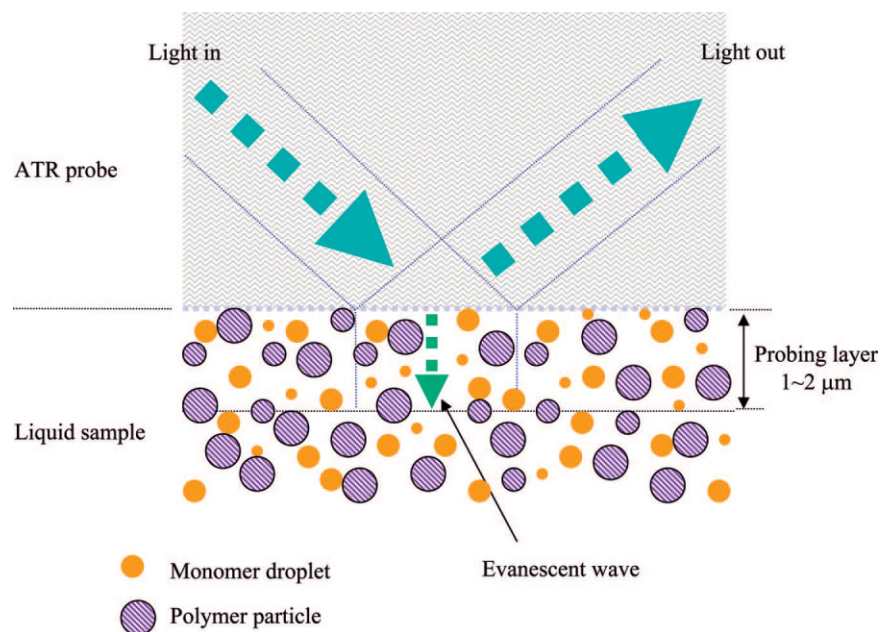
Figure 1 Schematic of an ATR-probe on measuring an emulsion. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

probe of high refractive index (n_p) is brought into contact with a sample that must have a lower refractive index (n_s). Light is introduced to the probe at an incident angle, θ, toward the interface between the probe boundary and the sample. If the angle of incidence (θ) is greater than the critical angle θ_c (given by Snell's law: $\sin\theta_c = n_s/n_p$), total reflection will occur when the light hits the probe boundary. At the reflection point, the light will extend into the medium (sample) in the form of an evanescent wave and is absorbed by the sample. Therefore, the light reflected back to the probe carries the spectral information about the physical properties of the sample and can be recorded by a spectrometer.

Figure 1 shows the schematic of an ATR-probe for use with an aqueous emulsion that contains both monomer droplets and polymer particles. In a miniemulsion, the sizes of both the monomer droplets and the polymer particles formed during the process are much smaller than the optical path-length, i.e., the penetrating distance by the evanescent light. When a UV light source is used, the double bonds in monomer molecules can absorb UV-evanescent light. As polymerization proceeds, monomeric double bonds are eliminated; the polymer formed absorbs the UV light in at shorter wavelengths as shown in Figure 3.

Following the definition of absorbance in conventional absorption spectroscopy, we can express absorbance in ATR spectroscopy with z reflections as

$$a^z_{ATR} = z \cdot \varepsilon \cdot C \cdot b_{eff} \tag{1}$$

where z is the reflection number of the probe, ε is the absorption coefficient, and C is the molar concentration

of the substance to be analyzed. b_{eff} is the effective absorption path length of a single pass, and a is the absorbance of one pass. As mentioned above, the optical path length per reflection, b_{eff}, is about 1–2 μm, which depends on the refractive index of the medium. One can change the number of reflections and thus the sensitivity of an ATR system by varying the length of the ATR probe.

Equation (1) indicates that the absorbance in ATR spectroscopy is linearly proportional to the molar concentration (C) of the species to be analyzed, even when a multi-pass ATR probe is used. With a miniemulsion as the medium, the effective absorption path length b_{eff} can be regarded as constant.

ATR-UV spectra of the samples from MMA miniemulsion polymerization

Figure 2 shows the monomer conversion (measured by gravimetry) and the average particle size (measured by QELS) of 13 samples at the different process times in MMA miniemulsion polymerization. Note that the monomer conversion goes only to 80%, most likely due to the fact that the polymerization was run below the glass transition temperature of PMMA. (That is, the glass transition temperature of the PMMA/MMA solution at 80% conversion is ~60°C.) Note that also the average particle size goes up with conversion. This is counter to the concept of a miniemulsion in which the droplets become polymer particles. The resolution of this apparent discrepancy lies in the fact that samples for QELS analysis are highly diluted with water. During the dilutions process, residual MMA, which is reasonably soluble in water, is
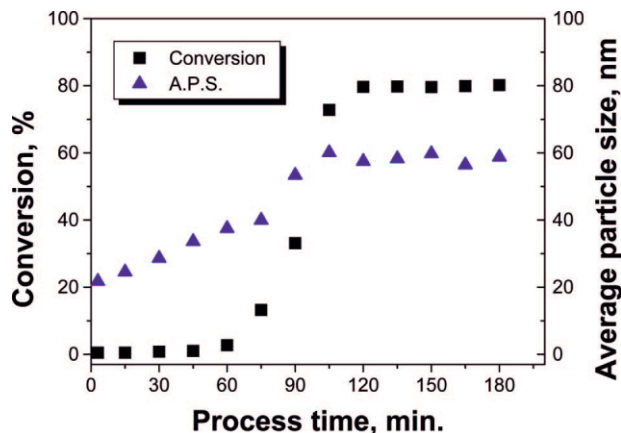
Figure 2 Monomer conversion and particle radius profiles during miniemulsion polymerization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

stripped out of the particles, leaving only the polymer. Figure 3 shows the corresponded ATR-UV spectra of these samples. Spectra were taken from samples drawn during polymerization, and run immediately after the polymerization.

The spectral peak with a maximum absorption around 225 nm results from the double bond in MMA monomer. With more MMA being converted into PMMA, the spectral intensity at this wavelength decreases and the strong PMMA maximum absorption peak appears at a shorter wavelength. In Figure 3, it may be seen that 200 nm is a possible isosbestic point, i.e., both MMA and PMMA have an identical absorptivity at this isosbestic point wavelength.

Monomer conversion determination by linear calibration

For the miniemulsion samples, the refractive index of the aqueous phase remains essentially constant.
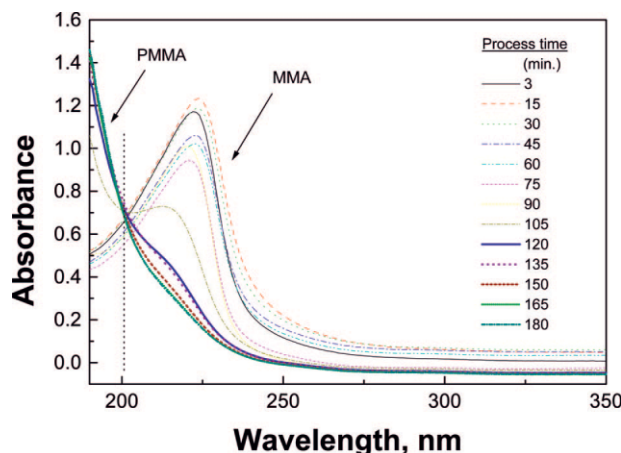

Figure 3 ATR-UV spectra of the miniemulsion samples as a function of polymerization time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
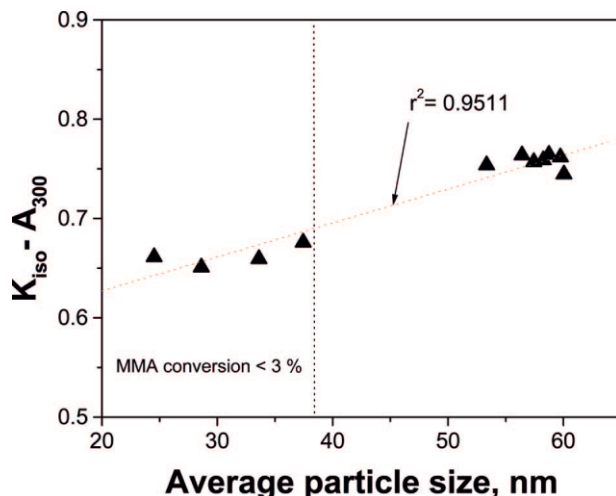

Figure 4 Relationship between the relative absorption at 300 nm and the average particle radius measured by QELS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Therefore, the effective optical path-length, b_{eff}, in eq. (1) can be regarded as a constant. However, changes in monomer/polymer particle size affect their UV absorption as shown in Figure 3. The spectral absorption at the wavelengths above 300 nm is essentially independent on the monomer and polymer absorption; thus, we can estimate the particle size effect using the spectral information from such a wavelength range. Figure 4 shows the empirical relationship between a relative absorption change at 300 nm and the particle size, which can be simply expressed as

$$P = \frac{K_{lso} - A_{300} - 0.559}{0.0034} \qquad (2)$$

where A_{300} is the absorption at 300 nm and K_{iso} is the absorbance at the isosbestic point. P represents the average particle size.

Equation (3) then may be used to predict the monomer conversion rate. The results based on this model are shown in Figure 5.

$$\text{Conversion (\%)} = k_1[(A_{200} - A_{234}) - k_2 P] \qquad (3)$$

where A_{200} and A_{234} are the absorptions at 200 and 234 nm, respectively. k_1 and k_2 are adjustable parameters.

It can be seen that the results match well with gravimetry results.

Multivariate calibration

To extract the maximum information from the ATR-UV spectra of emulsion, a chemometric technique was used for the calibration. Chemometrics[15,16] is well-developed and widely used in the process of analyti-

cal chemistry, and various software packages are commercially available. Multivariate partial least square (PLS) analysis is one of the most frequently used techniques in chemometrics. PLS allows the use of the entire spectrum for the prediction of monomer conversion. Once a model is established, prediction of monomer conversion can be made from any given set of measured spectral intensity data.

In the present work, the set of miniemulsion samples (13) from the process were used. The monomer conversion data for 11 of the 13 samples and their corresponding ATR-UV spectra (from 190–300 nm) were used for training the calibration model, that is, to determine the parameters for the predictive model. The model was validated by the two samples not included in the model training, and the results are shown in Figure 6. As expected, better prediction of monomer conversion is obtained than with the linear calibration method mentioned earlier. The prediction errors for monomer conversion are within 3%. This correlation includes the particle radius data by QELS, but removing it does not appreciably reduce the predictive ability of the method.

CONCLUSIONS

ATR-UV characterization of samples from MMA miniemulsion polymerization was performed. MMA has a strong UV absorption with a maximum value at a wavelength of 225 nm, while PMMA absorbs at a lower wavelength. ATR-UV spectroscopy has been shown to be effective in monitoring monomer conversion because of the change in absorption caused by the loss of the double bond of MMA on polymerization. Good agreement between ATR-UV spectroscopy and gravimetry has been demonstrated, both for a linear
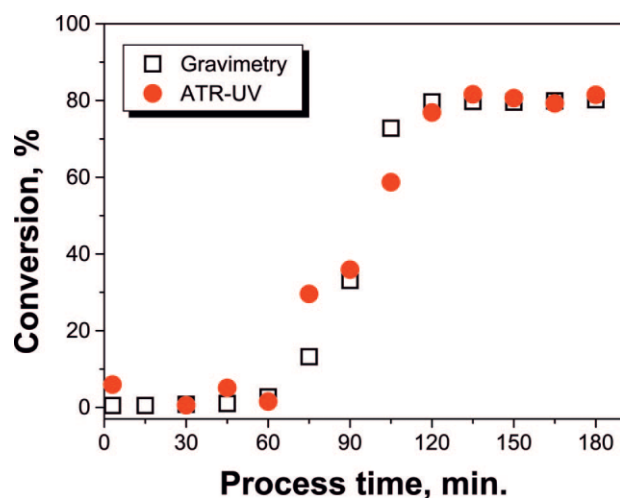

Figure 6 Conversion profile obtained by multivariate calibration (PLS) method and comparison with gravimetry. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

calibration and a PLS model. ATR-UV spectroscopy appears to be a simple and low cost method for monitoring monomer conversion during emulsion and miniemulsion polymerization.

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Figure 5 Conversion profile obtained from ATR-UV with a linear calibration. [Color figure can be viewed in the online issue, which is availa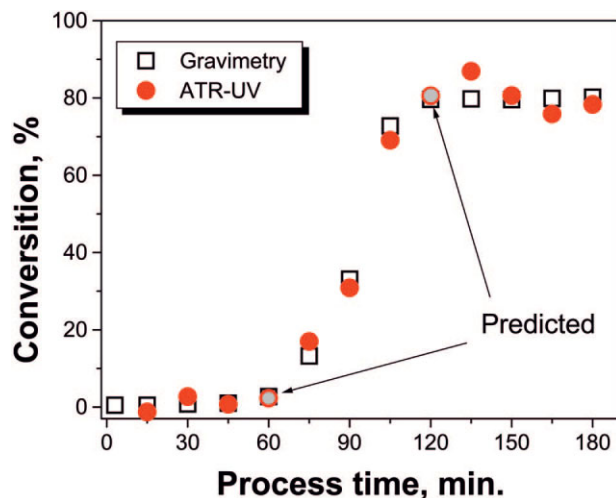ble at www.interscience.wiley.com.]