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# Emulsion (Co) Polymerization of Styrene and Butyl Acrylate Monitored by On-line Raman Spectroscopy

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SUMMARY: The homo- and copolymerizations of styrene and n-butyl acrylate were studied by on-line in-situ Raman spectroscopy. Results from the solution (homo)polymerizations proved to be very useful in the quantification of the Raman data from the emulsion homopolymerization. From the homopolymerization data it was possible to successfully calculate the partial monomer conversions for the emulsion copolymerization of these monomers.

## Introduction

Recent developments in detector technology and advances in spectrometers are responsible for the greatly enhanced sensitivity of Raman spectrometers$^{1)}$. Since light in the visible light region is used, the application of fiber optics makes remote control accessible for industrial processes$^{2)}$. Furthermore, as the Raman technique is especially sensitive to highly polarizable molecular bonds, vinyl bonds are the most prominent bands in the spectrum, while water shows only low intensities in the region below 3200 cm$^{-1}$ $^{3)}$. This makes Raman spectroscopy a particularly good candidate for the on-line monitoring of emulsion polymerizations, a field where appropriate alternatives for on-line sensors are only scarcely found$^{4)}$.

The on-line monitoring by Raman spectroscopy has been reported for the emulsion (homo)polymerizations of styrene$^{5)}$, methyl methacrylate$^{6)}$ and vinyl acetate$^{7)}$, and the copolymerizations of styrene - butadiene - acrylic acid$^{8)}$ and styrene - butylacrylate$^{9)}$. An overview of the possibilities and problems which can be encountered using Raman spectroscopy in the study of polymer latexes is given by Hergeth$^{10)}$.

The quantification of the Raman data can give rise to problems. As the Raman technique is a scattering technique, no direct relation between the absolute intensity and monomer concentration can be made$^{11)}$. For this purpose, spectra need to be scaled (i.e. normalized) in such a way that concentrations can be determined from the relative intensities. In order to do

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this, a few different approaches are found in the literature. The first approach is to add an additional component to the reacting mixture as an internal standard$^{5)}$. Although this approach works well, it is not preferred to add an extra component to the reaction mixture because the additive may interfere with the polymerization process. Another approach is to use bands of non-reactive components such as the solvent$^{12)}$ or dispersant$^{6)}$ as an internal standard. Also, bands of the monomer may be used as the internal standard$^{9)}$, assuming that these bands do not change during the polymerization. It should be noted, however, that most monomer peaks change during polymerization, as will be shown in the next section. The final approach is by applying multivariate calibration techniques (principle component analysis)$^{9,13)}$. Here, concentrations are obtained by calibration, such that there is no necessity to normalize the spectra.

In this paper, the emulsion homo- and copolymerization of butyl acrylate and styrene are studied. This is done by first monitoring the solution (homo-)polymerizations of the individual monomers. The results of these solution polymerizations are subsequently used to study the emulsion homopolymerizations of both monomers. The advantage of studying solution polymerization reactions is that the solvent can be used as an internal standard, and spectra are scaled to a solvent peak. Characteristic bands of the monomer can then easily be monitored during the polymerization. Moreover, the results were used to calculate monomer concentrations during the emulsion copolymerization of styrene and butyl acrylate. In this case, assessment of the monomer concentrations from the individual monomer bands is not possible, as these bands are completely overlapping in the spectrum. For this reason, alternative peaks in the spectrum are to be used for determination of the styrene and butyl acrylate concentration.

## Experimental

Styrene (Sty, Merck) and n-butyl acrylate (BA, Merck) were passed through an inhibitor remover column (Dehibit 200, PolySciences), in order to remove t-butyl catechol (present in Sty) or hydroquinone (present in BA). Apart from the monomers, all chemicals were used as received. For the emulsion polymerizations sodium persulphate (SPS, Merck) was used as the thermal initiator (1 mM) and sodium dodecylsulphate (SDS, Merck) was used as the surfactant (10 mM). Water was deionized using Super Q ultra filtration (Millipore). All emulsion polymerizations were performed to obtain 30 % weight polymer at full conversion. The emulsion copolymerization was performed at a molar styrene fraction of $f_S$=0.20. The emulsion polymerization of BA was performed at 40°C, the styrene and copolymerization reaction at 50°C, all under batch conditions.

The solution polymerizations were all performed in Dioxane (Merck). Azobis-isobutyronitrile (AIBN, Fluka) was used as the thermal initiator (10mM). The solution polymerizations were performed at 70°C, with 35 wt% monomer in the initial solution.

The set-up and data processing are described in detail elsewhere14). For the solution polymerization, the probe head was equipped with a 40 mm macrolens, focussing the laser light into the reactor through a glass wall and collecting the scattered light into the probe head. For the emulsion polymerizations, the head was equipped with a 20× magnification long working distance (LWD) objective (Union Optics), allowing to work at approximately 1 cm away from the glass window. The Superhead was placed on a (manual) XY table to optimize the position of the probe to the reactor wall in the µm range accuracy. Acquisition times were 30 seconds to 1 minute to obtain a spectrum.

## Results and discussion

The normalized Raman data for the solution polymerizations of Sty and BA are shown in Figure 1. The vinyl peak shows the most prominent change with polymerization and decreases linearly with conversion. However, it can be seen that more monomer peaks change with conversion. For instance , the aromatic ring vibration near 1000 cm$^{-1}$ for styrene clearly decreases with increasing conversion, this in contrast to previous measurements9) for the Sty/BA system.

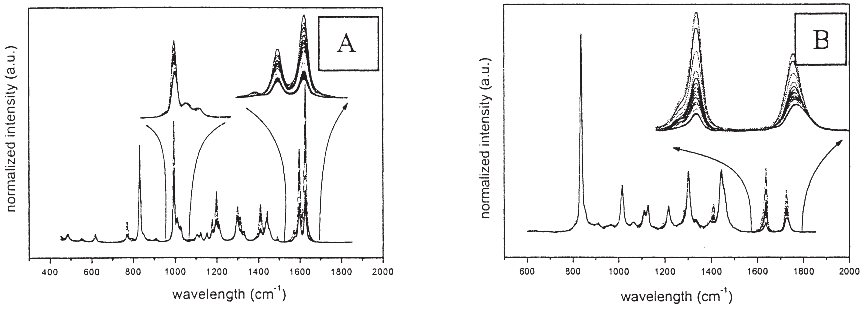

Figure. 1: Raman spectra for recorded during the solution polymerization of styrene (A) and butyl acrylate (B)

The decrease was also observed by Chu et al15) during the bulk polymerization of styrene. From the data it was established that for the monomers bands, other than the vinyl band, a linear relation with conversion exists. Figure 3 shows the intensities for the aromatic bands at 1600 cm$^{-1}$ and 1000 cm$^{-1}$ for styrene, and the carbonyl band at 1730 cm$^{-1}$ for BA, divided by the intensities at zero conversion. All lines shown in figure 3 give a high correlation coefficient ($R^2$>0.999) when fitted by linear regression. The fits can be used for predicting monomer concentrations during the emulsion polymerization of both monomers.

The changing intensities may be accounted for by either the changing symmetry of the molecule, intramolecular interactions in the polymer, or by changing solvent interactions when monomer is converted into polymer. However, if the last hypothesis were to be true, changes may be expected in the solvent bands as well. Nevertheless, Figure 1 shows that the solvent bands at 830, 1300 and 1430 remain constant throughout polymerization.

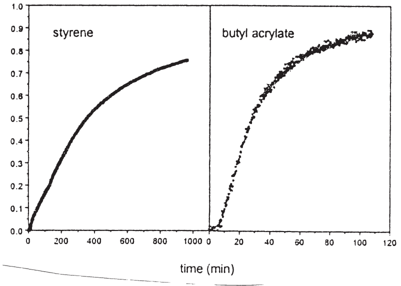

Figure 2: conversion -time curves for the solution polymerizations of styrene and butyl acrylate. Conversion was calculated using the scaled vinyl band.

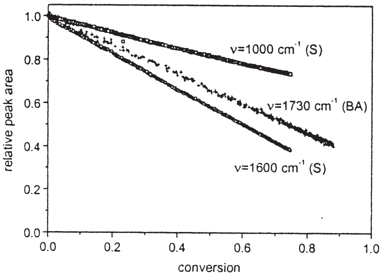

Figure 3: Relative peak areas [A(X)/A(0)] as a function of conversion for the solution polymerizations of styrene and butyl acrylate

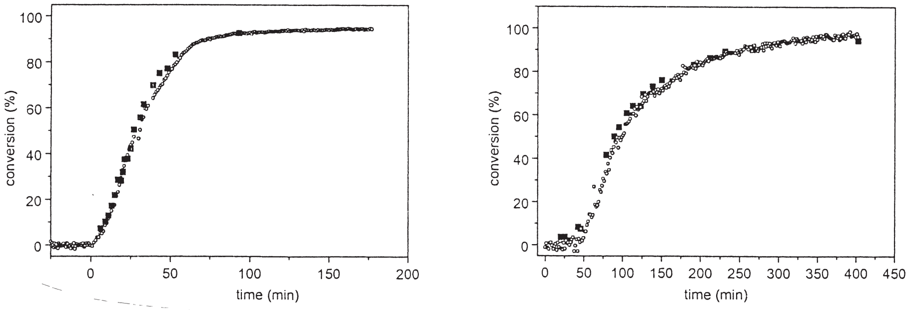

Figure 4: conversion versus time for the emulsion polymerizations of styrene (left) and butyl acrylate (right). ■: gravimetric data; o: Raman data

Figure 4 shows the results for conversion versus time for the emulsion polymerizations. In the absence of a proper internal standard, the conversions were calculated from the ratio between area of the vinyl peak and the carbonyl peak 1730 cm$^{-1}$ for BA and the vinyl to aromatic ($\nu$=1610 cm$^{-1}$) ratio Sty. The conversions thus obtained were found to be in good agreement with gravimetric data (see Fig. 4).

The Raman data for the emulsion copolymerization are shown in Figure 5. It can be seen that, although there is a higher BA content (BA:Sty=4:1), the spectra are dominated by Sty (see also Fig. 1). Further, the vinyl bands of Sty ($\nu$=1631 cm$^{-1}$) and BA ($\nu$=1638 cm$^{-1}$) show a total overlap. Therefore, the vinyl band (Fig. 5) can not be used directly for determining the monomer concentrations.

The decrease in intensity, starting at approximately 75 minutes, is the result of two factors: the first being the onset of polymerization, the second one is that less light is collected by the collecting optics due to light scattering by the formation and growth of the polymer particles.

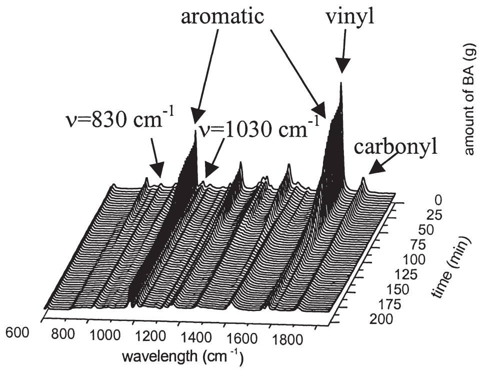

Figure 5: Raman data for the copolymerization of styrene - butyl acrylate

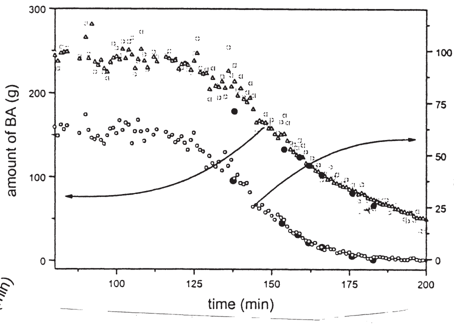

Figure 6: Results for the emulsion copolymerization of styrene - butyl acrylate (●: GC results; ▫:BA, carbonyl; Δ: BA (calculated from Sty); o:Sty, aromatic)

For BA, the peak at 830 cm$^{-1}$ was found to be a suitable internal standard, staying almost constant throughout the reaction. For Sty, the peak at 1030 cm$^{-1}$ was found to be an appropriate internal standard. These internal standards were established both from the solution and emulsion polymerizations. In the latter case, Raman data were compared with off-line gravimetric data. Next, the changes in the maximum (normalized) intensity of the aromatic peak near 1600 cm$^{-1}$ and the integrated area of the carbonyl peak near 1730 cm$^{-1}$ were used for calculating monomer concentrations. The results for Sty show little scatter due to the good signal to noise ratio (see Fig. 6). However, the calculated concentrations for BA resulted in more scatter. For this reason, the results for BA were calculated in an alternative way$^{9)}$: Using the previously calculated Sty concentrations, the contribution of Sty to the vinyl peak was obtained. This contribution was subtracted from the total vinyl peak and the difference was assumed to be the contribution of BA to the vinyl band. The results thus obtained are also shown in figure 6 and it can be seen that estimation of the BA concentration is significantly improved.

## Conclusion

It has been shown that both the solution and emulsion polymerization of n-butyl acrylate and styrene can be successfully monitored by remote on-line Raman spectroscopy. The solution polymerizations proved useful in the quantitative assessment of the emulsion polymerizations, where no internal standards can be designated a priori. Using the results of the homopolymerizations, it was also possible to predict monomer concentrations during the emulsion copolymerization of styrene - butyl acrylate under batch conditions.

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