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Polymer 44 (2003) 6123–6128

polymer

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Polymer Communication

Evidences of correlation between polymer particle size and Raman scattering

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Received 20 March 2003; received in revised form 15 July 2003; accepted 18 July 2003

Abstract

This work describes evidences of correlation between polymer particle size and Raman scattering and shows that it is possible to use Raman scattering to monitor the evolution of average particle size during emulsion polymerization reactions. The main focus is the estimation of the average polymer particle diameter from spectra collected in a short acquisition time and consequently low signal-to-noise ratio. Finally, a multivariate linear model, (Partial Least Square-PLS), is fitted from the reaction data and a good linearity between spectra and average polymer particle diameter is found. It is shown that despite varying monomer and polymer concentrations it is possible to monitor average particle sizes during emulsion polymerization reactions using Raman spectroscopy.

Keywords: Raman spectroscopy; Average polymer particle diameter; Emulsion polymerization

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1. Introduction

Emulsion polymerization is a free radical polymerization performed in a heterogeneous reaction system, yielding submicron solid polymer particles dispersed in an aqueous medium. Emulsion polymerization is a widely used industrial process for the production of synthetic polymer colloids or latexes of several different types of polymers, which are used in a wide variety of applications: synthetic rubber, coatings, paints, adhesives and binders.

In emulsion polymerization, particle size distribution (PSD) is one of the most important characteristics of the latex, as it may affect the reaction rate and the final properties of the latex, such as film formation, latex stability, etc. The final PSD is determined by the particle nucleation and the growth of polymer particles. There is still a great deal of controversy regarding the dominant mode of particle formation in emulsion polymerization (micellar, homogeneous, coagulative and droplet nucleation). However, it is commonly accepted that in conventional emulsion polymerization one mechanism generally dominates particle formation depending on, for example, the surfactant concentration or the monomer solubility in the aqueous phase. The size and the number of resulting particles depend on the operative mechanism of particle formation and affect the rate of reaction directly. The growth of particle size is due to radical propagation inside polymer particles. However, in several systems the particle aggregation may also affect the size and number of particles during the reaction process.

Despite the large volume of research in the field of emulsion polymerization some aspects of the process, such as the mechanisms that affect the PSD, are still not fully understood. The on-line monitoring of particle size during the polymerization reaction, especially in industry, would bring very important information about particle formation and growth rate leading to a better control of the final PSD [1–3].

Real time monitoring and control of average particle diameter during emulsion polymerization reactions remains a challenge since most available measurement techniques are either quite time consuming (e.g. Transmission Electronic Microscopy—TEM) and/or require sample dilution (e.g. Capillary Hydrodynamic Fractionation—CHDF, Dynamic Light Scattering—DLS). Also, all these techniques require sampling from the reactor what may not be feasible in an industrial reactor during the reaction. With

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doi:10.1016/S0032-3861(03)00669-4

Table 1
Formulation used in reaction 1—semicontinuous styrene emulsion polymerization reaction at $T = 75$ °C and feed period = 220 min

Reactant	Initial charge (g)	Monomer feed stream (g)	Aqueous phase feed stream (g)
St	–	254.566	–
AA	–	7.234	–
Water	190.05	–	77.971
SLS	–	–	0.866
$Na_2S_2O_8$	0.452	–	0.173
Na_2CO_3	0.152	–	0.390
Seed[a]	10.175	–	–

[a] Polystyrene seed with $D_p = 33$ nm and 30% of solids content.

the development of fiber optics based techniques, Raman spectroscopy, which is an established technique for the analysis of polymers in laboratory scale, has also become promising for polymerization process monitoring allowing sophisticated spectroscopic process measurements in otherwise inaccessible environments [4–7].

The present work describes evidences of correlation between polymer particle size and Raman scattering and shows that it is possible to use Raman scattering to monitor the evolution of average particle size during emulsion polymerization reactions. The evidence of correlation between polymer particle size and Raman scattering was recently reported by Ito et al. [8] and by van den Brink et al. [9], nevertheless in none of these two works the evolution of the particle size was estimated during emulsion polymerization reactions. In the work of Ito et al. [8] all tests were performed with mixtures of different commercial water-based emulsions (styrene-butadiene rubber, poly(methyl methacrylate) and polyacrylonitrile) varying only the amounts of each different polymer, therefore, the solids content was always constant, no monomer was present in the samples and particle size changed with polymer composition. van den Brink et al. [9] analyzed samples of the final latexes produced in several different reactions in a cuvette placed on a motorized XY table in order to measure the evolution of the intensity as a function of sample position (focal depth profiles) and the authors correlated the intensity ratio at two different focal depths to particle size and/or particle concentration. Nevertheless, during emulsion polymerization reactions, not only monomer and polymer are present at varying concentrations, but another different phase, monomer droplets, in addition to the polymer particles and the aqueous phase, may also be present. Therefore, in the present work tests are performed with samples taken during styrene emulsion polymerization reactions in order to verify if, despite all those 'interferences' (varying monomer concentration and solids content), it is possible to measure the average particle size during emulsion polymerization reactions using Raman scattering. The main focus of the present work is the estimation of the average polymer particle diameter from spectra collected in a short acquisition time and consequently low signal-to-noise ratio. These operation conditions are necessary for in-line applications where the reaction medium changes significantly during the process. Finally, a multivariate linear model (Partial Least Square—PLS) is fitted from the data of the reactions and a good linearity between spectra and average polymer particle diameters is found.

2. Methodology and experimental

The main objective of the present work is to verify the possibility of estimating the polymer particle size during emulsion polymerization using Raman spectroscopy. An important characteristic of the emulsion polymerization process is the heterogeneous medium (monomer droplets, polymer particles, etc.). Since the spectroscopic measurements are influenced by the heterogeneity and variability of the medium, this characteristic must be taken into account during the fitting of models to be used for the estimation of properties during emulsion polymerizations (e.g. monomer

Table 2
Formulation used in reaction 2—semicontinuous styrene emulsion polymerization reaction at $T = 80$ °C and feed period = 165 min

Reactant	Initial charge (g)	Monomer feed stream (g)	Aqueous phase feed stream (g)
St	–	267.986	–
AA	–	7.614	–
Water	190.088	–	70.955
SLS	0.050	–	1.181
$Na_2S_2O_8$	0.604	–	0.189
Na_2CO_3	0.152	–	0.475
Seed[b]	10.047	–	–

[a] Polystyrene seed with $D_p = 33$ nm and 30% of solids content.

concentration, polymer content, polymer particle size, etc.). Thus, the data used on the model fitting must describe all stages of the reaction. In order to obtain a data set with this characteristic, two reactions were performed.

2.1. Reaction conditions and latex characterization

Reactions were carried out in semicontinuous conditions with formulations shown in Tables 1 and 2. All reactants, styrene (St), acrylic acid (AA), sodium lauryl sulfate (SLS), sodium persulfate ($Na_2S_2O_8$) and sodium carbonate (Na_2CO_3), were used as received in order to approach industrial reaction conditions. The initial charges were purged with nitrogen during a period of 60 min and nitrogen feeding to the reactor was maintained during the whole reactions.

The Raman spectra were collected in a FRA 106/S FT-Raman accessory attached to a IFS 28/N spectrometer from Bruker, equipped with a quartz beamsplitter. Each spectrum is an average of 32 scans with resolution of 8 cm^{-1}, which takes ~45 s as acquisition time. The laser frequency is 1064 nm. Laser power was set to 450 mW. Glass tubes with a diameter equal to 6 mm were used to measure the spectra at room temperature (~25 °C). In all analyses a constant focal depth was used.

Photon correlation spectroscopy (Coulter N4-Plus) was used as reference technique for the average particle diameters. Gas chromatography (Shimadzu GC 17-A) and gravimetry were used, respectively, to measure monomer concentration and polymer content in the samples.

2.2. Selection of calibration sample set

In order to assure that the model is able to track particle size independently of the solids content (since usually during batch and semicontinuous reactions these two variables increase together) two different types of sample sets were chosen to be used during the model fitting procedure. Sample Set 1 was composed of samples of reaction 1 that were diluted in order to have always the same solids content (~7.2 wt%) and, thus, making the main difference among samples be due to the particle size (Table 3). For each sample of this set three spectra were collected. On the other hand, sample Set 2 was composed of samples collected during reaction 2 that were analyzed directly. Two

Table 3
First set of samples, derived from reaction 1, diluted to make the polymer content similar among the samples

Sample	Average particle size (nm)	Monomer concentration (wt%)	Polymer content (wt%)
1[a]	54.7	0.82373	7.17
2	72.6	0.43661	7.12
3[a]	85.8	0.34601	7.18
4	93.3	0.23593	7.07
5	101.8	0.26494	7.20
6[a]	107.2	0.21763	7.21
7	116.1	0.15244	7.32
8[a]	121.1	0.21799	7.21
9[a]	125.1	0.06323	7.55
10[a]	129.0	0.18465	7.14
11	134.5	0.38470	7.30

[a] Samples used for the model fitting.

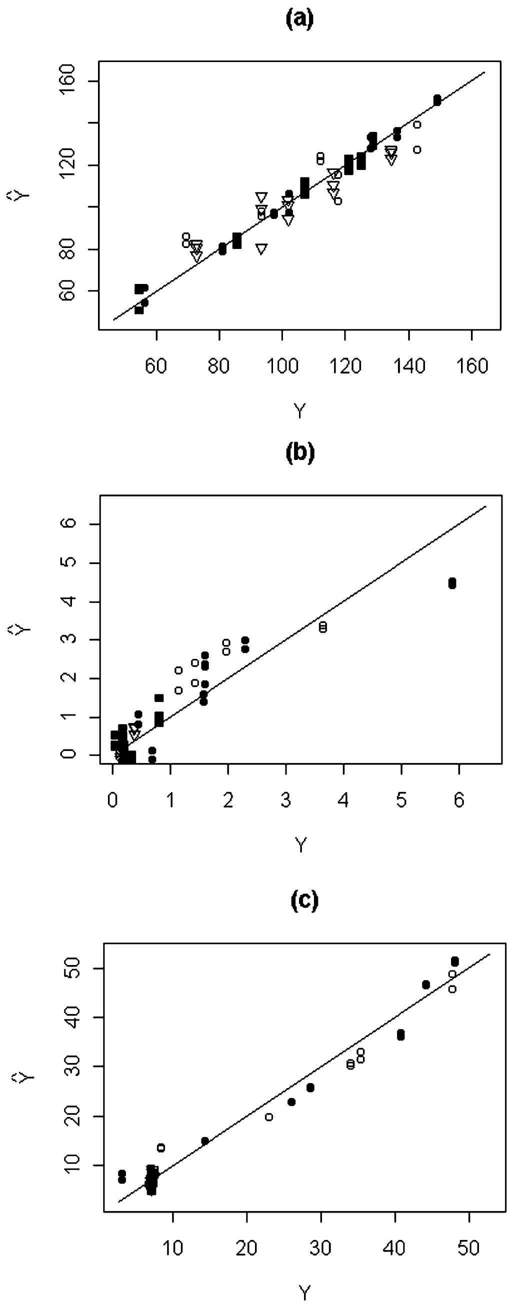

Fig. 1. Predictions of PLS models. '*Y*' denotes the expected value, '$\hat{Y}$', the predicted value for the average polymer particle diameter (nm) in (a), monomer concentration (wt%) in (b) and polymer content (wt%) in (c). Full squares and circles correspond to samples of the model fitting data set (denoted by superscript 'a' in Tables 3 and 4, respectively) and open triangles and circles correspond to samples for test data set.

Table 4
Second set of samples collected during polymerization 2

Sample	Average particle size (nm)	Monomer concentration (wt%)	Polymer content (wt%)	Reaction time (min)
1[a]	56.4	1.62068	3.2400	10
2	69.6	3.65722	8.5700	20
3[a]	81.2	5.89481	14.5000	30
4	93.7	1.97602	23.0600	40
5[a]	97.5	0.46913	26.2100	60
6[a]	102.3	1.59093	28.6100	90
7	112.3	1.58399	34.0400	105
8	117.8	1.43272	35.4100	120
9[a]	128.4	2.30227	40.8900	135
10[a]	136.4	1.61893	44.2400	150
11	143.1	1.14964	47.8100	165
12[a]	149.5	0.71373	48.0858	195

[a] Samples used for the model fitting.

spectra were collected for each sample of Set 2. In this case particle size increases together with the solids content as in a usual batch or semicontinuous emulsion polymerization reaction without particle renucleation and/or coalescence (Table 4).

2.3. Model development

A PLS model [10,11] was fitted with both sets of samples using the full spectral region (from 400 to 4000 cm^{-1}) since preliminary studies using narrower spectral regions resulted

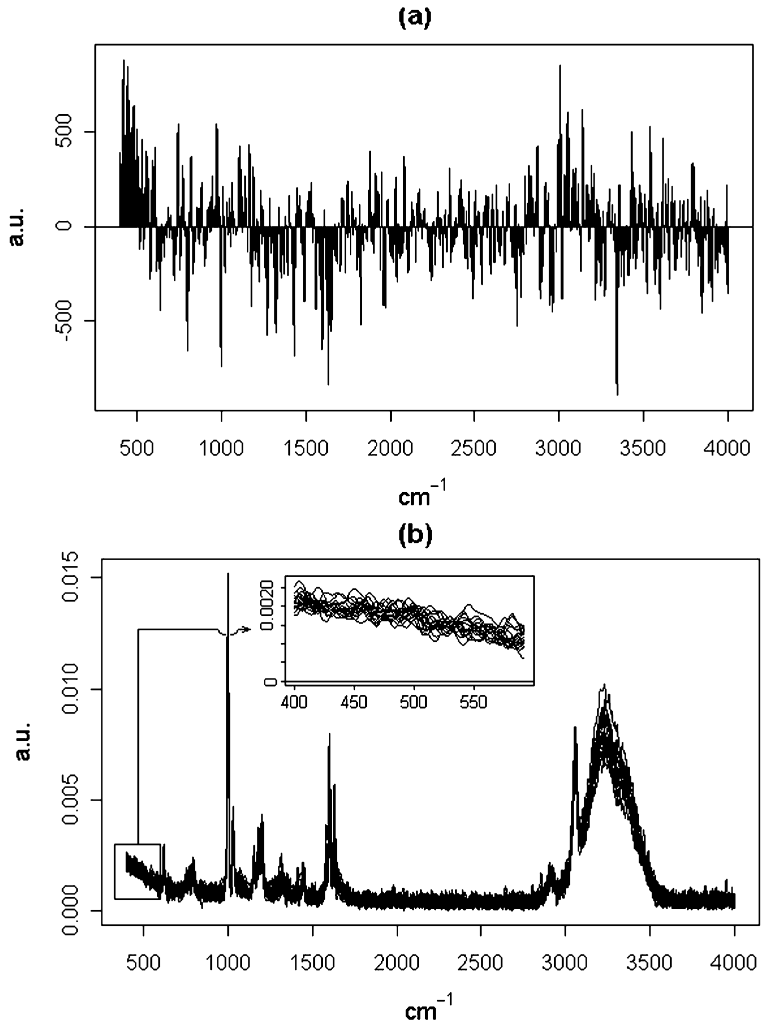

Fig. 2. (a) Regression coefficients for particle size estimation. (b) Raman spectra for the samples denoted with ‘a’ in Table 3.

in models that required a higher number of latent variables and that lead to poorer predictions. Sample Sets 1 and 2 were divided in two new sets (as described in Tables 3 and 4), one for the calibration step (the data used to fit the model, samples denoted by the superscript 'a' in Tables 3 and 4) and another for the predictions (to test the model). Five latent variables were used in the model [10], [11]. Besides particle size, this model was also used to predict other properties, namely, styrene concentration and polymer content.

All computations were performed using programme R (http://www.r-language.org).

3. Results

Fig. (1) shows the results of the model for both, the sample set used for model fitting and sample set used for model testing. Predictions of the average polymer particle diameter, Fig. 1(a), are quite satisfactory, showing that there exists a correlation between Raman spectra and average particle size and, furthermore, that it is possible to estimate the polymer particle size from Raman spectra during an emulsion polymerization.

On the other hand, predictions for monomer concentration and polymer content, Fig. 1(b) and (c), respectively, are not good, indicating that the model for the estimation of polymer particle size really describes the variation due to polymer particle size and not due to another correlated property. These results are interesting since they show that polymer particle size may interfere on the model predictions of other variables like monomer concentrations or polymer content. Nevertheless, it is important to point out that better predictions of these variables can be achieved if either the behavior of the evolution of average particle size is the same in all reactions used to build and test the model (i.e. if more complete data sets are used for model fitting), or pretreatment (like spectra normalization) can be applied to reduce the influence of polymer particle size on estimating monomer concentration and polymer content [5–7,12].

The relationship between polymer particle size and Raman spectra is not yet fully understood. It has been suggested for styrene-butadiene polymer particles produced by emulsion copolymerization that the larger particles tend to have a larger crystal region and a lower density amorphous region than the smaller particles, and that this crystal region should be observed on low frequency ($<400\ \mathrm{cm}^{-1}$) vibrations [8]. In the present work the spectral region does not comprise the region under $400\ \mathrm{cm}^{-1}$ and the studied system is composed of amorphous polymer particles.

The regression coefficient is usually used to interpret the influence of the estimated property on the spectra [8]. In the present work, the regression coefficient corresponding to particle size estimation is difficult to be interpreted due to the strong fluctuations as can be seen in Fig. 2(a). Nonetheless, in the spectral region between 400 and $500\ \mathrm{cm}^{-1}$ the regression coefficient for particle size presents only positive values, an indication that this spectral region is correlated with the polymer particle size. In other words, the increase of polymer particle size results in an increase of the intensities in region between 400 and $500\ \mathrm{cm}^{-1}$. A similar observation has been made by van den Brink et al. [9] who attributed the intensities on this region to the influence of the spectrum of the cuvette glass. In the work of van den Brink the increase of the influence of the glass spectrum over the latex spectra is related to the polymer particle size by means of the signal loss due to the elastic light scattering [9]. It is important to emphasize that the spectroscopic setup used in the present work to collect Raman spectra was arranged to provide a fast spectra acquisition resulting in a low signal-to-noise ratio. On one hand, this low ratio makes the interpretation of the intensities in the region between 400 and $500\ \mathrm{cm}^{-1}$ difficult to be performed as can be observed in Fig. 2(b). On the other hand, the fast spectra acquisition allows the fast estimation of polymer particle size during emulsion polymerization reactions. This fast estimation of particle size is very important when mechanisms with fast dynamics like particle nucleation and/or coalescence are involved.

4. Conclusions

The results presented here show that it is possible to estimate the average polymer particle diameter from Raman spectra under realistic conditions (samples collected during a polymerization reaction and spectra collected with short acquisition time) in a simple feasible experimental setup. This approach is different of those described in the literature (i.e. using a large number of scans on the spectra acquisition [8] of prepared samples or in a more complex experimental approach using different focal depths [9]). This observation is quite relevant since the rapid estimation of polymer particle size will allow the implementation of closed-loop control strategies of this very important latex property. Also, the fast and reliable tracking of particle size evolution might help to put some light on very important but still not fully understood mechanisms such as particle nucleation and coalescence.

Acknowledgements

The PROFIX fellowship of CNPq-Brazil for P.H.H. Araujo and the financial support from CNPq and FAPESP (grant number 01/13017-1) are gratefully appreciated.

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