Analysis of Near Infrared Spectra during Methyl methacrylate (MMA) Suspension Polymerizations

Jorge G.F. Santos Jr.,[1] *Débora V. Way,*[1] *Príamo A. Melo,*[1] *Márcio Nele,*[2] *José Carlos Pinto**[1]

Summary: Near infrared spectroscopy (NIRS) provides means for real-time monitoring of polymerization reactors. Previous experimental studies report successful implementations of NIR-based monitoring techniques for styrene, vinyl chloride and acrylic acid / vinyl acetate suspension polymerizations; however, no information is available in the literature for methyl methacrylate (MMA) polymerizations. For this reason, the main objective of this paper was analyzing the NIR spectra obtained in-line and *in situ* during MMA suspension polymerizations and observing whether NIR spectra may be used for in-line monitoring and control of the average particle size in these systems. Particularly, NIR spectral responses to changes of the average particle size were analyzed in poly(vinyl chloride), polystyrene and PMMA suspensions, showing that the NIR spectra of distinct reacting systems respond differently to modification of the suspended particle sizes. Finally, it was observed that the control of average particle sizes and particle size distributions in MMA suspension polymerizations requires that control actions be taken at the initial polymerization stages, when monomer conversion is below 30 wt%.

Keywords: near infrared spectroscopy; NIRS; polymerization; poly(methyl methacrylate); PMMA; suspension

Introduction

Suspension polymerization processes are used to produce a large number of important commercial resins, such as polystyrene (PS), poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), among others.[1,2] In a typical suspension polymerization system, a mixture of monomers and initiators is dispersed in a continuous aqueous phase through combination of agitation and use of suspending agents (stabilizers).[3] As reaction evolves, monomer droplets are converted into a viscous dispersion and finally into solid polymer particles of size in the range 10–1000 μm.[4,5]

One of the most important issues in suspension technologies is the monitoring and control of the final average particle sizes and particle size distributions (PSD).[4] The initial size distribution of monomer droplets does not remain constant along the reaction time, as monomer droplets/polymer particles are subject to both coalescence and breakage, which depend on the operation conditions and on the spatial coordinates (breakage occurs primarily near the agitation zone, while the rate of coalescence is higher near the stagnant zones).[6] The proper characterization and control of particle sizes is of fundamental importance because the PSD (and average bead sizes) are related to important quality parameters of the final resin. As discussed by Santos *et al.*,[7] the production of small particles may lead to significant losses during the post-reaction treatment of the polymer beads, while production of large particles can make

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[1] Programa de Engenharia Química / COPPE, Universidade Federal do Rio de Janeiro, Cidade Universitária, CP 68502, Rio de Janeiro 21945-970, Brazil
E-mail: pinto@peq.coppe.ufrj.br

[2] Escola de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, CP 68502, Rio de Janeiro 21945-970, Brazil

processing of the final polymer resin difficult.

The lack of instruments that are able to measure and monitor the quality of polymer resins has been recognized as the most important problem in the field of polymerization reactor control.[8–10] This is particularly true when in-line monitoring of particle size distributions in heterogeneous polymerization reactions is considered. However, development and implementation of monitoring techniques based on near infrared spectroscopy (NIRS) is changing this field considerably.[8–12] For instance, it has been shown that the NIR signal is sensitive to changes of the morphological properties of suspended particles in suspension polymerization reactors, allowing for monitoring of particle sizes and other morphological aspects of the produced beads.[8–13] Besides, the NIR-based techniques can also be used to monitor and control compositions during suspension copolymerizations.[14]

NIR monitoring of suspension polymerization reactions is possible because the obtained signal is a complex combination of the distinct physical phenomena that take place when the reaction medium is illuminated by the light emitter, such as light absorption, reflectance, scattering, etc. The relative importance of each phenomenon depends on the composition of the reacting mixture, as the optical properties of the system depend on the chemical composition of the medium and of the interface between the aqueous and organic phases. As a consequence, it is not possible to conclude that NIR-based monitoring techniques can be implemented successfully in all suspension reacting systems. Previous experimental studies report successful implementations of NIR-based monitoring techniques for styrene, vinyl chloride and acrylic acid / vinyl acetate suspension polymerizations;[8–14] however, no information is available in the literature for methyl methacrylate (MMA) polymerizations. Despite that, monitoring and control of average particle sizes in MMA suspension polymerizations is of fundamental importance during production of resins intended for use as bone cements.[15]

Based on the previous remarks, the main objective of this paper is evaluating the influence of PMMA particle size upon NIR spectra obtained in-line and observing whether NIR spectra may be used for in-line monitoring and control of the average particle size. Particularly, NIR spectral responses to changes of the average particle size are analyzed in PVC, PS and PMMA suspensions, showing that the NIR spectra of distinct reacting systems respond differently to modification of the suspended particle sizes. As shown in the manuscript, the control of average particle sizes and particle size distributions in MMA suspension polymerizations is possible, but requires that control actions be taken at the initial polymerization stages, when monomer conversion is below 30 wt%.

Experimental Part

Materials

MMA was supplied by Sigma-Aldrich (St. Louis, USA) with purity of 99.9%. The initiator. benzoyl peroxide (BPO), was supplied by Fluka (Seelze, Germany) with purity of 99%. The suspending agent, poly(vinyl alcohol) (PVA), with weight-average molecular weight of 78000 Da, degree of hydrolysis of 85% and purity of 99%, was supplied by Vetec Química Fina (Rio de Janeiro, Brazil). Distilled water was used as the suspending medium in all experiments. Anti-fouling Noxol WSW, manufactured by Akzo Nobel Polymer Chemicals, was kindly provided by Braskem. The PVC powder (commercial grade) was provided by Braskem. PS particles were synthesized in the lab, as described in previous works.[7,12] Unless stated otherwise, chemicals were used as received without further purification.

Experimental Procedure

Experiments were monitored *in situ* with the help of an NIR spectrophotometer

(Monochromator model 6500 supplied by NIRSystems, Inc. Silver Spring, MD, USA). Spectra were collected with a stainless steel transflectance probe with length of 30 cm and diameter of ¾ in, using a sampling window of 6 mm. Sampling times were equal to 3 min and recorded spectra were averages of 32 scans obtained in the range 450 – 2800 nm. Second derivatives of the crude spectra were used for analyses, for removal of baseline shifts and magnification of small spectral changes.[8]

The first set of experiments consisted in measuring NIR spectra of MMA-water dispersions under different agitation speeds (from 200 rpm to 2200 rpm, by increment of 200 rpm) in order to characterize the sensitivity of the NIR spectra to changes of the suspended droplet sizes. Measurements were made at room temperature to avoid spontaneous thermal polymerization. Different organic loads (4.75, 13.05 and 25 wt% of MMA) were analyzed.

The second set of experiments consisted in measuring NIR spectra during two distinct MMA suspension polymerizations, as described in Table 1, in order to observe how NIR spectra change during real polymerizations when the droplet sizes are different. Reactions were carried out in a 1-liter stirred jacketed glass reactor. Initially, the aqueous PVA solution was fed into the reactor; after temperature stabilization at 85°C, a solution containing BPO and MMA was added. The organic load was equal to 25 wt%.

Preliminary analyses indicated that the probe had to be treated with an anti-fouling product, in order to prevent the agglomeration of polymer in the sampling window. It is important to emphasize that previous publications did not report the necessary use of anti-fouling products for installation of the NIR-equipment, which probably means that MMA polymerizations are more likely to induce the agglomeration of polymer material in the sampling window than styrene, vinyl chloride and vinyl acetate polymerizations. Anti-fouling agents are normally utilized at plant sites to prevent fouling of reactor walls, stirrer, heat exchange surfaces, etc; however, the use of anti-fouling agents is not usual at lab-scale facilities, probably because the smaller reactors can be cleaned more easily. As observed experimentally, successful spectral analysis of MMA reactions was not possible without anti-fouling treatment, given the massive coagulation of polymer material in the sampling window of the NIR probe.

Table 1.
Recipes for the polymerization reactions.

Reaction	MMA (g)	PVA Solution (g/L)	BPO (g)	Agitation (rpm)
PMMA 1	150	2	4	850
PMMA 2	150	1	4	500

The third series of experiments consisted in suspending PMMA, PS and PVC powders of two different diameters in water and measuring the NIR spectra of the suspensions, in order to compare the sensitivity of the NIR spectra to changes of particle diameters for different resins. Before performing the trials, polymer powders were sieved and classified; therefore, it could be assumed that particle sizes were essentially uniform. Given the much lower amounts of classified polymer samples available to perform the experiments, the organic loads used in these experiments were equal to 10 wt%. Analyzed particle diameters are shown in Table 2.

Characterization

Particle size distributions were determined through optical microscopy, using a Nikon SMZ 800 stereomicroscope (Nikon, USA) and a software for image analyses (Particle Size Distribution Analyzer, PSDA).[16] A minimum of 300 particles were used for

Table 2.
Polymer particles used in the third set of experiments.

Polymer	$Dp_{small} \pm SD$	$Dp_{large} \pm SD$
PMMA	110 ± 16	225 ± 36
PS	82 ± 15	412 ± 84
PVC	112 ± 20	149 ± 21

- Dp: Average particle diameter
- SD: Standard Deviation

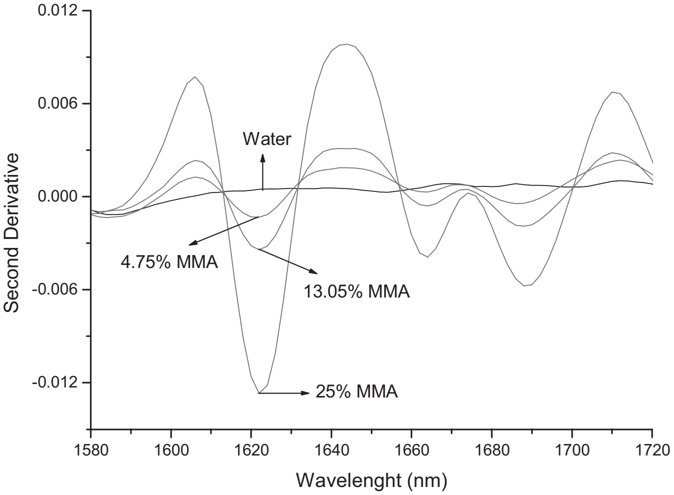

Figure 1.
Second derivatives of the NIR spectra of MMA-water suspensions presenting different MMA contents. Agitation of 1000 rpm.

evaluation of the average particle sizes. Monomer conversion was determined through gravimetry.

Results and Discussion

Figure 1 shows the second derivatives of the original NIR spectra of stirred MMA-water suspensions presenting different organic loads, at constant agitation. As one might already expect, NIR spectra are sensitive to changes of the organic load.

Figure 2 shows that the NIR spectra of MMA–water dispersions are also sensitive to changes of the agitation speed, indicating that the NIR spectra are sensitive to changes of the morphology of the MMA droplets suspended in the aqueous phase, as observed previously for styrene-water suspensions.[7]

It is well known that variations of both suspending agent concentrations and agitation

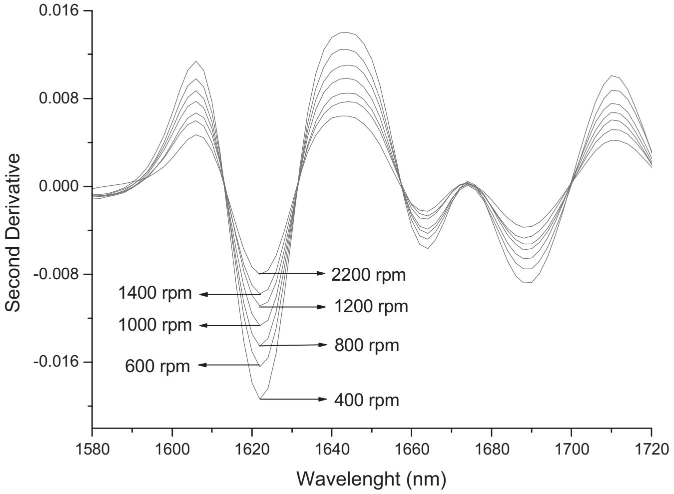

Figure 2.
Second derivatives of the NIR spectra of MMA-water suspension (25 wt% MMA) for different agitation speeds.

speeds promote significant modifications of the obtained particle size distributions. For this reason, different amounts of PVA and different agitation speeds were used in some of the designed experiments. Figure 3 shows NIR spectra collected along the two reactions described in Table 1. One can observe that the obtained spectra changed along the reaction course and that spectra collected at the two distinct experiments were different (although similar), indicating that the NIR spectra are sensitive to changes of the morphology of the produced polymer powders. Changes were particularly intense between 1600 and 1750 nm, as observed previously by Santos *et al.*[8] It is important to observe that the spectra in both experiments changed suddenly after 30 minutes of reaction and remained approximately constant after that, as discussed in the following paragraphs. Figure 4 presents the particle size distributions of the polymer particles obtained in runs PMMA 1 and PMMA 2. Significant differences could be observed, as one might already expect. Run PMMA 2 led to polymer powders with larger average particle diameter and standard deviation (when compared to run PMMA 1), due to the smaller amount of PVA and to the lower agitation speed used in this trial. Figure 5 presents the NIR spectra of the final PMMA 1

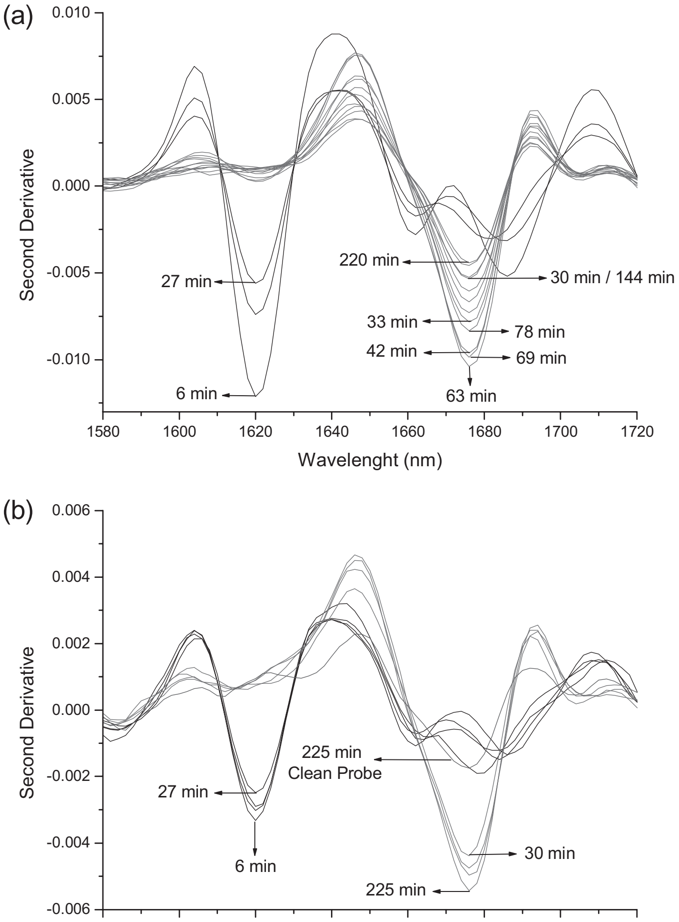

Figure 3.
Second derivatives of the NIR spectra during the polymerization experiments: PMMA 1 (a) and 2 (b).

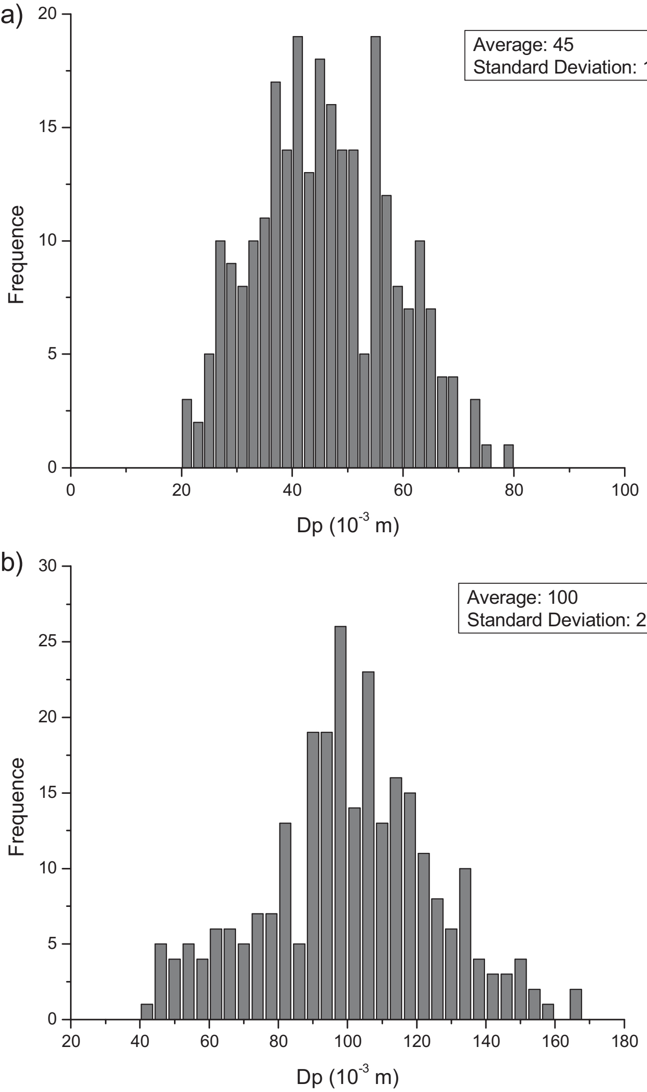

Figure 4.
Particle size distributions of polymer powders obtained in polymerization experiments: PMMA 1 (a) and 2 (b).

and PMMA 2 suspensions, where one can observe the significant differences between the two sets of results, indicating that NIR spectra are sensitive to the morphology of the produced polymer powders.

Table 3 shows how monomer conversion and average particle diameter change along the reaction time. One can clearly observe that dramatic conversion changes occur around 30 minutes of reaction, due to the well-known strong gel effect of MMA polymerizations. As shown in Table 3, average particle diameters increase (due to coalescence) until 30 minutes and afterwards remain essentially constant (the reduction of particle sizes after 30 minutes is related to the increasing monomer conversion and the larger density of the polymer). These sudden changes of monomer conversion and average particle sizes explain the simultaneous changes observed in the collected NIR spectra. These results

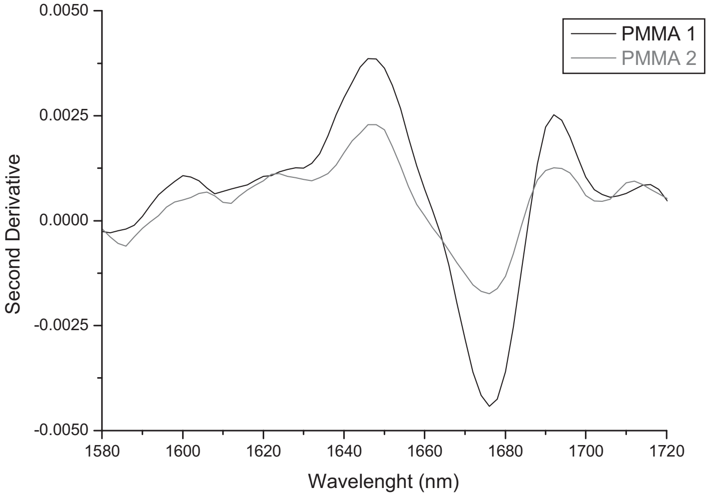

Figure 5.
Second derivatives of the NIR spectra of the PMMA-water suspensions at the end of experiments 1 and 2.

Table 3.
Average particle diameters and conversion along suspension polymerizations.

PMMA 1			PMMA 2		
Time (min)	Conversion (%)	Dp ± SD (μm)	Time (min)	Conversion (%)	Dp ± SD (μm)
5	10	19 ± 7	5	11	48 ± 13
10	19	28 ± 8	10	20	72 ± 17
25	40	58 ± 18	25	38	127 ± 26
30	84	50 ± 11	30	80	114 ± 19
240	93	45 ± 12	240	92	100 ± 25

- Dp: Average particle diameter
- SD: Standard Deviation

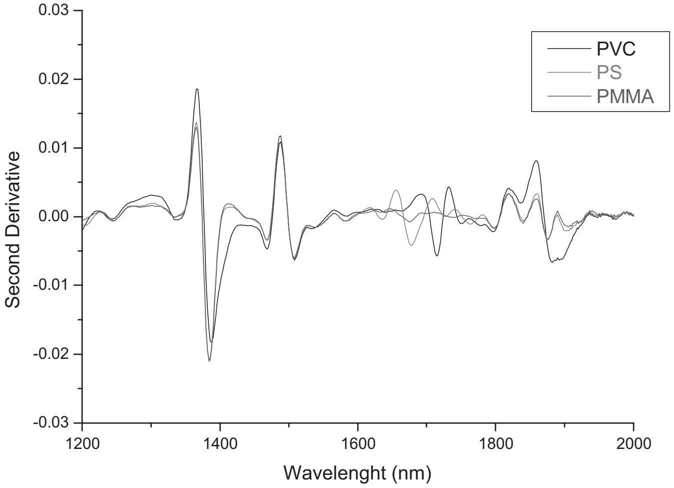

Figure 6.
Second derivatives of the NIR spectra of PVC, PS and PMMA polymer particles suspended in water.

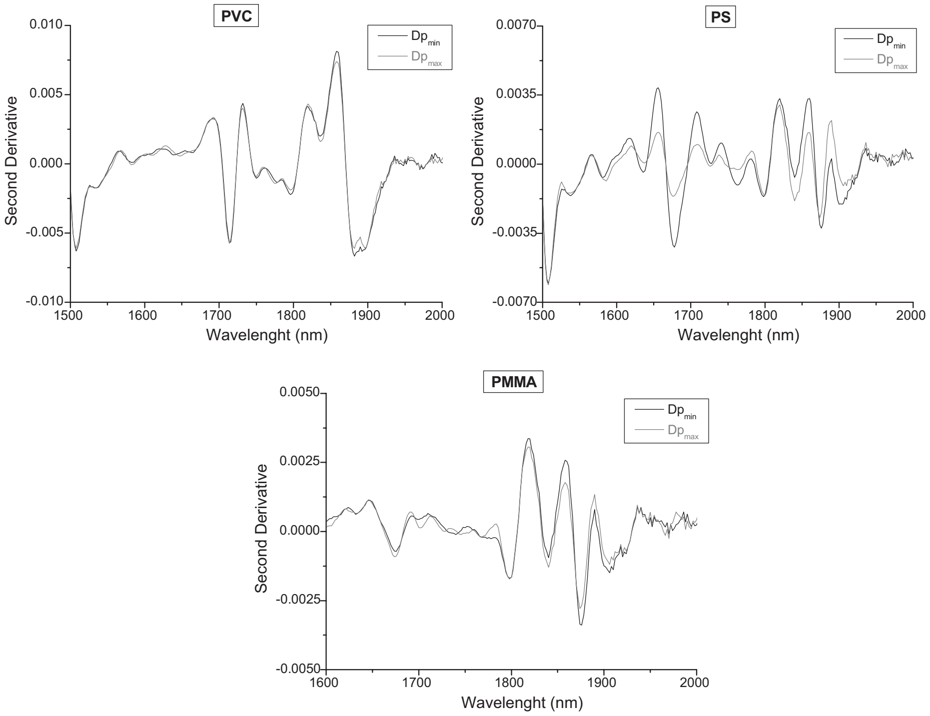

Figure 7.
Second derivatives of the NIR spectra of PVC, PS and PMMA particles of different average sizes suspended in water.

also indicate that control actions must be taken during the early stages of the MMA suspension polymerization, if one is interested in controlling the final average particle sizes and particle size distributions. After the onset of the characteristic MMA gel effect acceleration, control of particle morphology becomes impossible, as particle reach the particle identification point.

Figure 6 shows the NIR spectra of aqueous suspensions of PVC, PS and PMMA particles, indicating that spectra are different mainly in the range of 1600–1800 nm, as also observed previously by Santos *et al.*[8]. Figure 7 shows the NIR spectra of aqueous suspensions of PVC, PS and PMMA particles of different average sizes, as described in Table 2. It can be observed that spectral changes are different in the three cases, which means that spectral sensitivity to changes of particle diameter depends on the particularly analyzed polymer material. The lowest spectral sensitivity was observed for PVC (although particle sizes did not change considerably in this case), while the largest spectral sensitivity was observed for PS. It is also very interesting to observe that the largest spectral sensitivity to changes of the average size of PMMA particles was observed in the range 1800–1900 nm, while Santos *et al.*[8] reported the largest spectral sensitivity in the range 1600–1700 nm for polystyrene particles.

Conclusion

Based on results obtained in this work, it can be concluded that NIRS is sensitive to changes of the average droplet size in aqueous MMA and PMMA suspensions, especially in the spectral range from 1500 to 1800 nm. It was also observed that spectral sensitivities to changes of the average particle sizes depend on the polymer material, meaning that monitoring and control capabilities of NIR-based techniques depend on the particular analyzed chemical system. Finally, it was observed that the control of average particle sizes and particle size distributions in MMA suspension polymerizations require that control actions be taken at the initial polymerization stages, because of the onset of the very strong and characteristic gel effect of MMA polymerizations, which lead to the very fast stabilization of the particle morphology when conversion rises above 30%.

Acknowledgements: The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) for providing scholarships and supporting our work.

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