

## MD-CT-1

### MONOMER CONCENTRATION MEASUREMENT IN EMULSION POLYMERIZATION REACTIONS USING RAMAN SPECTROSCOPY

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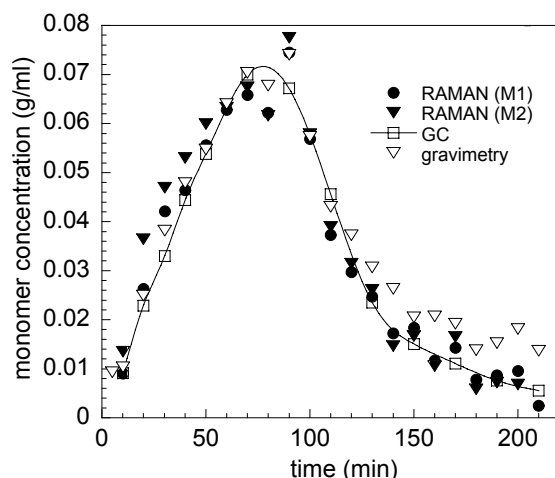
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Emulsion polymerization, which has as principle the conversion by free-radical polymerization of monomer(s) in an aqueous dispersion into stable dispersion polymer particles, has a wide industrial application field, ranging from concrete additives to drug delivery systems. As the end-user properties depend on the polymer structure the emulsion process control has received a lot of attention in the last decades. In such instance, the development of sensors for on-line monitoring of polymerization reactors, to measure the monomer and polymer concentration for example, has become a challenge in the engineering process<sup>[1, 2]</sup>. In parallel with such need there is the development of analytical spectroscopic techniques based on fiber optics. Although spectroscopic techniques have been largely used in the polymer field in laboratory scale their uses in the hazardous industrial ambient is still limited. With the development of fiber optics based techniques these limitations are being overcome allowing sophisticated spectroscopic process measurements in inaccessible environments. Thus, the Raman spectroscopy, which is an established technique for the analysis of polymers in laboratory scale, has become promising for polymerization process monitoring<sup>[3, 4, 5]</sup>. In terms of the emulsion process, Raman spectroscopy has as additional advantages the weak Raman scattering of the water and the stronger scattering of vinyl bands, common in most of the monomers used in emulsion polymerization. Besides the instrumental developments, the process monitoring by spectroscopic techniques requires the development of calibration models to correlate the sensor measurements with the desired properties. In this instance the process variability, i.e. temperature variation, heterogeneous medium, different particle sizes, etc., takes place as an important problem to be overcome. Thus, this work presents successful results on building calibration models for off-line measurements (the process sample is extracted and the spectrum is immediately collected) for semi-batch polymerization process for two different homopolymers, derived from vinyl acetate and butyl acrylate. Two different approaches (M1 and M2) on reducing the effect of process variability on the spectra are tested. The results are compared with reference methods, i.e. gravimetry and gas chromatography. The recipe for semi-batch polymerizations is shown in Table 1. Reaction temperature was 60°C and feed streams 1 and 2 were continuously added during 90 minutes.

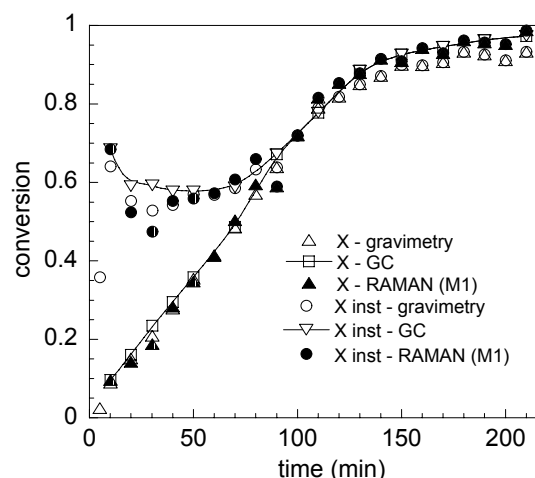
**Table 1** - Formulation of the reaction.

	BuA (g)	AA (g)	Water (g)	SLS (g)	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (g)	Na <sub>2</sub> CO <sub>3</sub> (g)
Initial charge	—	—	420	2.00	—	0.50
Feed stream 1	110.00	1.10	—	—	—	—
Feed stream 2	—	—	30	—	1.00	—

The results for the acrylate monitoring process are shown in Figure 1 and 2. Figure 1 shows the evolution of monomer concentration along the reaction as it is measured by Raman with correlation method M1 presenting a slightly better result than M2. Results for instantaneous and global conversion (Figure 2) obtained by Raman are equivalent to that obtained by gravimetry and gas chromatography (GC). The results for vinyl acetate homopolymerization are analogous to these results confirming that Raman Spectroscopy is an promising technique to monitoring emulsion polymerization process.



**Figure 1:** Evolution of monomer concentration during the reaction given by different analytical methods.



**Figure 2:** Evolution of global conversion (X) and instantaneous conversion (X inst) given by different analytical methods.

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### References

- [1] Chien, D. C. H.; Penlidis, A. 1990, J.M.S – Rev. Macromol. Chem. Phys., 30(1), pp. 1-42.
- [2] Kammona, O.; Chatzi, E. G.; Kiparissides, C. 1999, J.M.S – Rev. Macromol. Chem. Phys., 39(1), pp. 57-134.
- [3] Al-Khanbashi, A.; Hansen, M.G.; Wachter, E.A. Appl. Spect. 1996, 50, pp. 1089.
- [4] Özpozan, T.; Schrader, B.; Keller, S. 1997, Spect. Acta, 53, pp. 1.
- [5] Van den Brink, M.; Hansen, J.F.; Peinder, P.; Van Herk, A.M.; German, A.L. 2000, J. Appl. Polym. Sci., 79, pp. 426.