Institute for Polymer Research
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Symposium documents for

J.R. Leiza

Abstract

Presentation

Monitoring emulsion polymerization reactors: Calorimetry *vs.* Raman Spectroscopy

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Introduction

Emulsion polymers are *products-by-process*, which means that the final product properties and quality are defined during the polymerization. Therefore, efficient polymerization process control is needed to produce high-performance polymers. This requires the availability of on-line measurements. An adequate online sensor must be able to provide continuous (or at least frequent) measurements, must be accurate enough and has to operate over long periods of time in environments often physically and chemically aggressive.

In the last three decades significant effort has been devoted both by academic and industrial research groups to the development of suitable, accurate and robust monitoring techniques for polymerization reactors. The monitoring of emulsion polymerization reactors might a priori seem easier than the homogeneous counterpart reactors because of the lower viscosity of the reaction medium, but it turned out to be much more complex[1,2] Sensors for the monitoring of several properties (e.g., conversion, polymer composition, molecular weights, particle size …..) have been developed and assessed in polymerization reactors. Not all the reported techniques were accurate or robust enough as to be implemented in industrial environments. Excellent reviews about the development and applications of online sensors developed in the last three decades have been published[3-6]. The current trend is to use noninvasive techniques in order to avoid the complexity of manipulating viscous or reaction mediums prone to suffer coagulation. Reaction calorimetry and Raman spectroscopy are two of the most promising noninvasive techniques to monitoring emulsion polymerization reactors because of the advantages they have in comparison with other techniques.

In reaction calorimetry, the measurement is noninvasive, rapid, robust, relatively simple and cheap because it is based on temperature measurements. As a consequence, it is one of the techniques that most easily can be implemented in industrial environments. Among the different spectroscopies techniques that have been applied to monitor emulsion polymerization reactors, Raman spectroscopy offers several advantages in comparison with the absorption based spectroscopies: Near-Infrared (NIR) and Mid-Range Infrared (MIR). Thus, water has a very weak signal in Raman spectroscopy and functional groups that are inactive or very weak in absorption present a strong Raman scattering, i.e., carbon-carbon double bonds. Furthermore, for industrial implementation Raman spectroscopy offers the

possibility of using silica fibers (that have a low cost) with a length of up to 100 m, to transmit the radiation to and from the sample.

In this work, the performance of the noninvasive techniques (calorimetry and Raman spectroscopy) to monitoring semibatch high solids content emulsion polymerizations for two different monomer systems (vinyl acetate/butyl acrylate, VAc/BA, and butyl acrylate/ methyl methacrylate, BA/MMA) is compared. Overall and instantaneous conversions, as well as free monomer concentrations were measured. The polymerizations were carried out under starved conditions (high instantaneous conversions) for the BA/MMA system, and under non-starved conditions for the VAc/BA system.

Results and Discussion

Figure 1 shows the evolution of the instantaneous conversions (as calculated by gravimetry) for the seeded semibatch experiments carried out for each comonomer system. It can be seen that the trend was similar in both cases; namely, there was an accumulation of monomer during the first stages of the process, and then the conversions were roughly steady up to the end of the feeding period. Beyond this point, the conversions increased as the process proceeded batchwise. The conversions reached during the plateau were greater than 80% for BA/MMA and under 70% for VAc/BA. The former corresponded to starved conditions, whereas the latter did not.

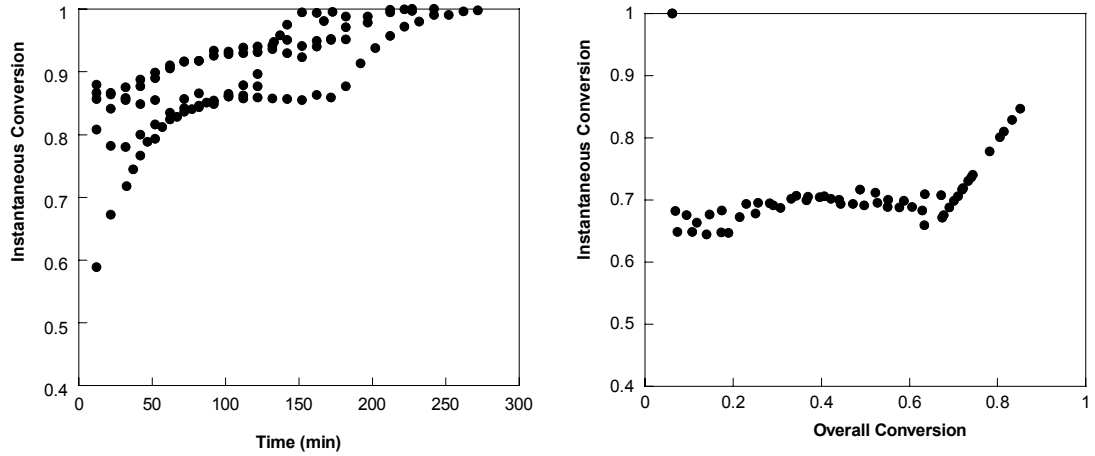

Figure 1. Instantaneous conversions for the semibatch emulsion copolymerizations used to compare Raman spectroscopy and calorimetry: (left) BA/MMA; (right) VAc/BA.

VAc/BA system (Non-starved conditions)

Figure 2 presents the comparison of the overall conversion predicted by the two monitoring techniques and by gravimetry (reference technique). It can be seen that the predictions of both Raman and calorimetry were close to the gravimetric values.

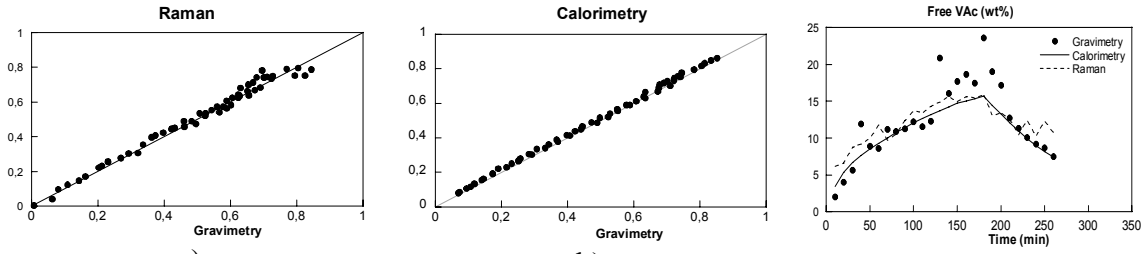

Figure 2. Overall conversion(a and b) and free VAc monomer concentration(c). Comparison of calorimetry and Raman spectroscopy with the reference techniques (gravimetry and gas chromatography).

Figure 2 also shows the unreacted VAc (weight fraction based upon the total reactor mass) as measured by the reference technique (gas chromatography), and by calorimetry and Raman spectroscopy. Both techniques provided a good prediction of the free concentration of VAc in the reactor and they were comparable to the chromatographic values. Furthermore, both techniques captured well the change in the profile when the feeding period was over and monomer concentration decreased.

BA/MMA system (Starved conditions)

As shown in Figure 1, the instantaneous conversion for this comonomer system was higher during the whole process. This means that monomer concentrations were also significantly lower than in the previous case, specially the concentration of MMA, which is the more reactive monomer in this system. Consequently, the heat released by polymerization was much lower too.

Figure 3 presents the comparison of the overall conversion measured by gravimetry and the two online techniques for the copolymerizations experiments carried out with the MMA/BA comonomer system. As it can be seen, in general there is no much difference for both techniques, and they compared well with gravimetry.

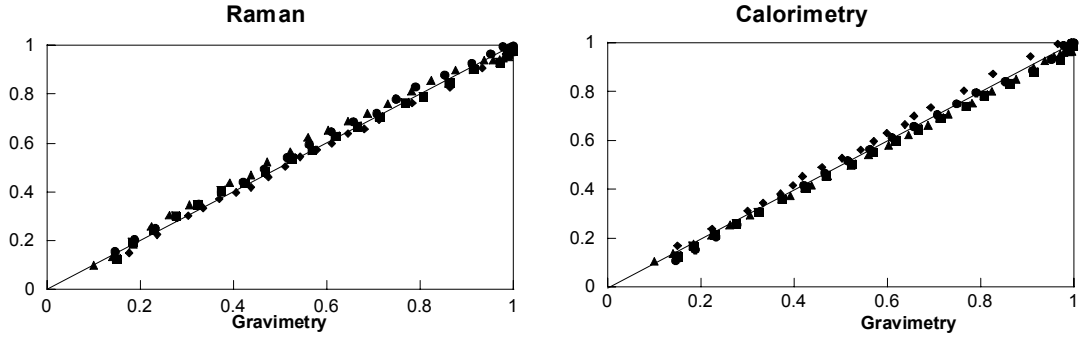

Figure 3. Comparison of the overall conversions measured by gravimetry for the BA/MMA system: Raman spectroscopy (left) and Calorimetry (right).

Figures 4 show the comparison of the instantaneous conversion and the MMA and BA monomer concentrations calculated by means of the gravimetry and by Raman spectroscopy and calorimetry for one of the experiments carried out with this comonomer system.

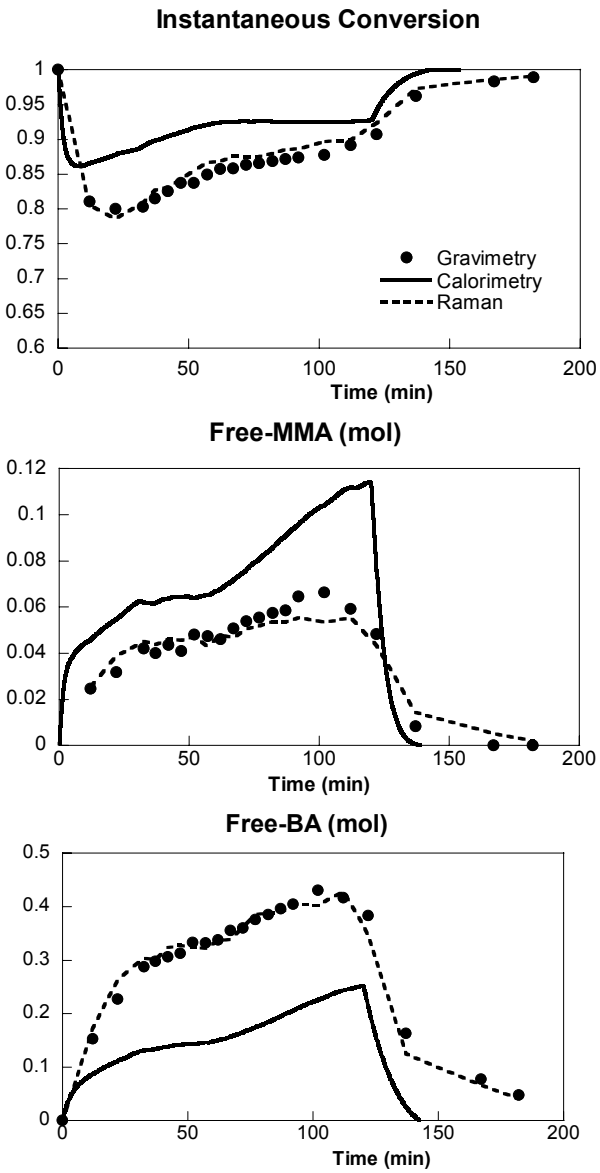

Figure 4. Comparison of the instantaneous conversion and free amounts of MMA and BA in the semibatch experiments as measured by the three techniques.

This graph shows that the prediction of the instantaneous conversion and free monomer concentrations were better for the FT-Raman spectroscopy than for reaction calorimetry. Similar results were obtained for other experiments carried out at different monomer ratios and with different feeding times for the monomer.

In conclusion the study revealed that under non-starved conditions both calorimetry and Raman spectroscopy provided comparable results. However, significant differences were found for the BA/MMA semibatch emulsion copolymerization carried out under starved conditions. The overall conversion predicted by both techniques was good, but for the instantaneous conversion and free concentrations of monomer. Raman spectroscopy was far more accurate than calorimetry.

Acknowledgements

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(6) Kammona; O. E.G. Chatzi; C. Kiparissides. *Rev. Macromol. Chem. Phys.*, **1999**, C39:57.

Monitoring of Emulsion Polymerization Reactors: Calorimetry vs Raman Spectroscopy

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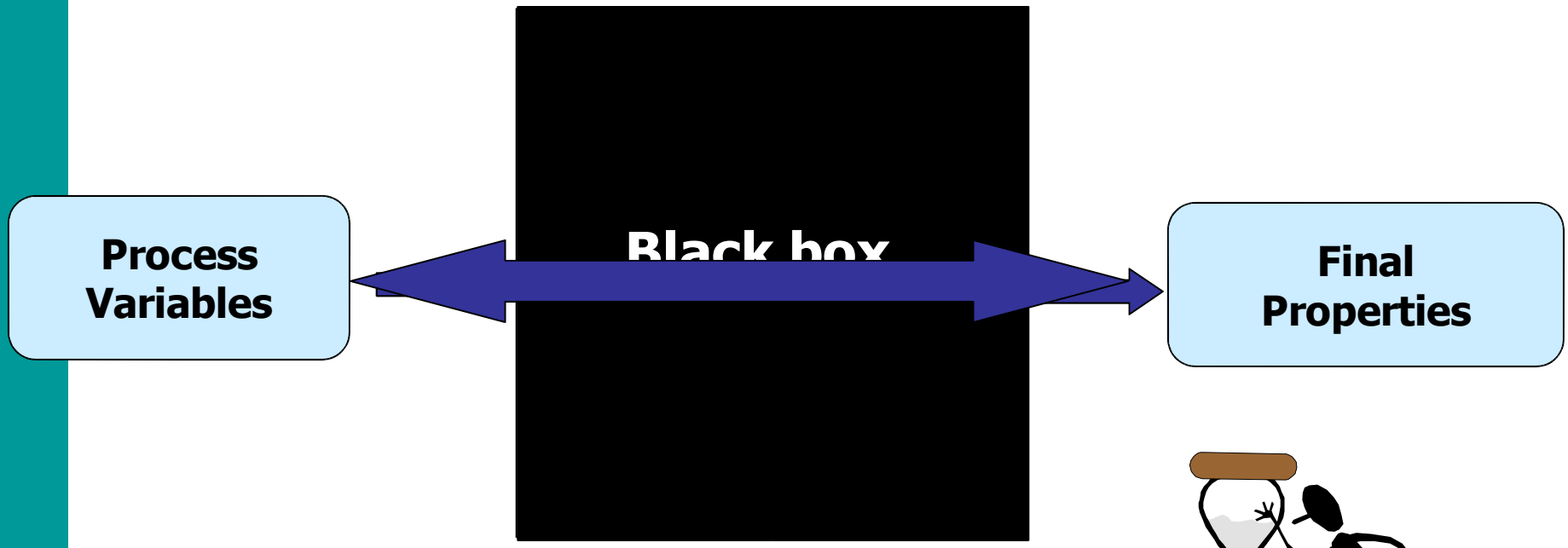
Outline

- Introduction
- On-line Monitoring by means of Reaction calorimetry
  - Estimation of Qr and UA
  - Estimation of free-monomer
- On-line monitoring by means of Raman spectroscopy
  - VAc/BA and all acrylic systems
  - Calibration Models (PLS)
  - Calibration validation
- Raman spectroscopy vs. Reaction calorimetry
  - VAc/BA (non starved)
  - BA/MMA (starved)
- Conclusions

Introduction

Produce materials in a consistent way with desired final properties meeting market needs

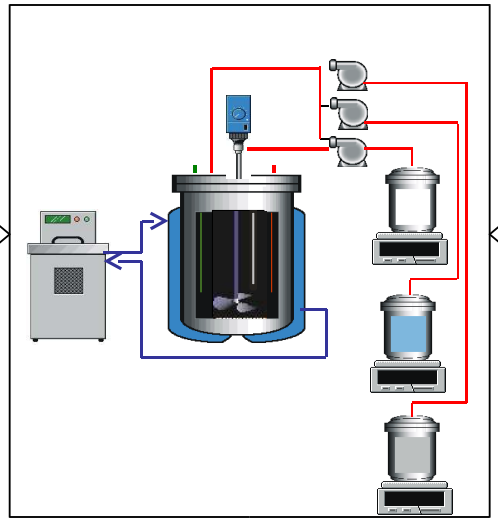


Common approach:

Trial and Error procedures

Introduction

Process Variables



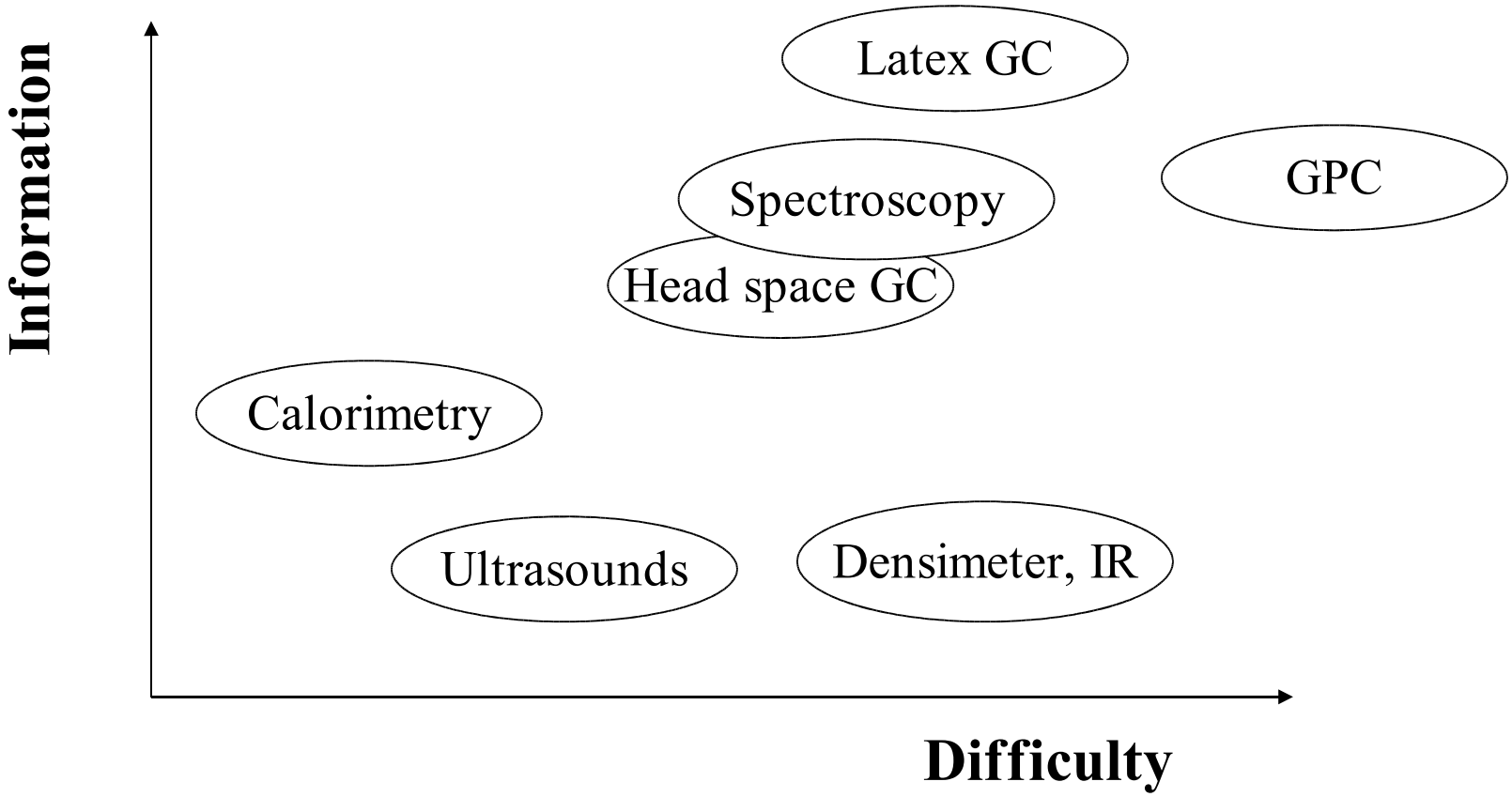
Polymer Microstructure

Final Properties

- Knowledge of the process Mathematical modeling
- Accurate on-line monitoring, optimization and control

Microstructure-Properties Model Equation

Introduction



Monitoring emulsion polymerizations

Reaction Calorimetry

+

Raman Spectroscopy

Advantages of Calorimetry

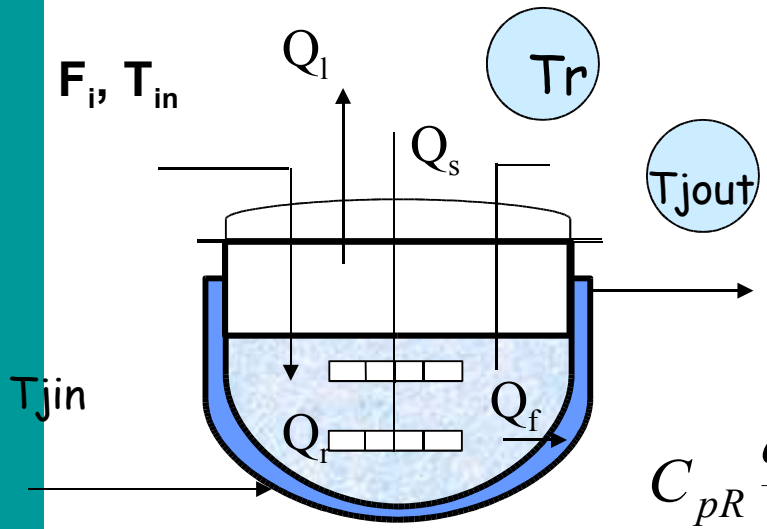
- Non-invasive technique
- Easy to implement in industrial environment and cheap
- Adequate for online control
- Provides continuous information of the heat of reaction

Advantages of Raman

- Non invasive technique
- Direct measurement of unreacted monomers, solids content
- Possible in industrial reactors

Reaction Calorimetry

Heat Flow Calorimetry



Q_r= Heat of Reaction

Q_f= Heat Flow

Q_l= Heat Losses

Q_s= Heat due to Stirring

$\sum F_i c_{pi}(T_i - T_r)$ = Feed sensible Heat

$$C_{pR}\frac{dT_r}{dt} = \sum_i F_i c_{pi}(T_{in} - T_r) + Q_r + Q_f + Q_s + Q_l$$

$$Q_f = UA(T_j - T_r)$$

Heat of Reaction

Parameter

Tjin≈Tjout=Tj

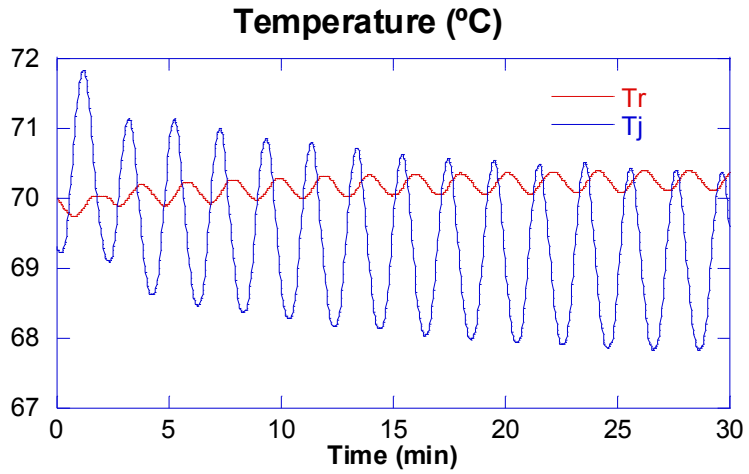
High flow rates of the cooling fluid ⇒ **SMALL SIZE REACTORS**

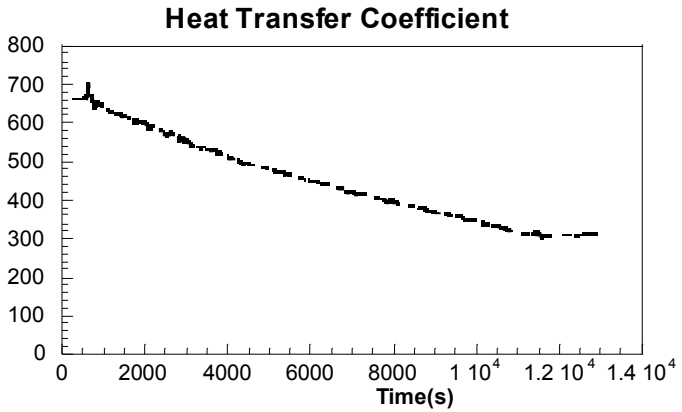
Reaction Calorimetry: Estimation of UA and Qr

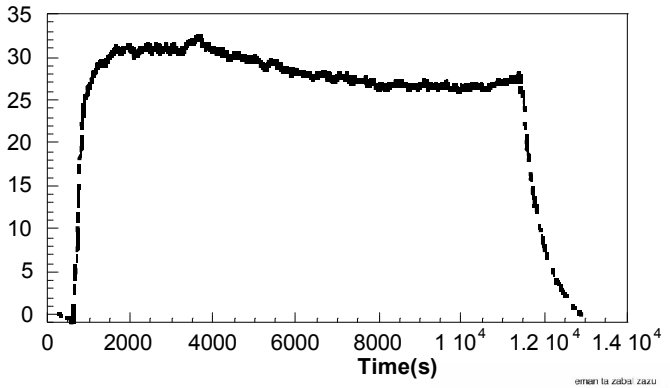
Oscillation Calorimetry: Smart Calc Mettler-Toledo

Evolution of the heat transfer monitored ⟶ Accurate Heat of Reaction

$$UA = \frac{C_{pr}\omega}{\tan\left(\arccos\left(\frac{\delta T_r}{\delta T_j}\right)\right)}$$







$$Q_r = Q_a + Q_f + Q_{feed}$$

Reaction Calorimetry: Estimation of conversion

$$\text{Overall Conversion} = \frac{Polymer(t)}{Total_Monomer(t_f)} = \frac{\int_0^t Q_r dt}{\sum M_{i,T}(t_f)(-\Delta H_i)}$$

$$\text{Instantaneous Conversion} = \frac{Polymer(t)}{Monomer_Fed(t)} = \frac{\int_0^t Q_r dt}{\sum M_{i,T}(t)(-\Delta H_i)}$$

$$Polymer(t) = \sum_i (i_0 + F_i t - i)$$

$$Monomer_Fed(t) \leq TotalMonomer(t_f)$$

Reaction Calorimetry: Estimation of free monomers

Inference of unreacted amount of monomer

$$\frac{di}{dt} = -Rp_i + F_i = -\frac{Q_r}{(-\Delta H_A)\frac{1}{D_{iA}} + (-\Delta H_B)\frac{1}{D_{iB}} + (-\Delta H_C)\frac{1}{D_{iC}}} + F_i \qquad \text{i=A, B, C}$$

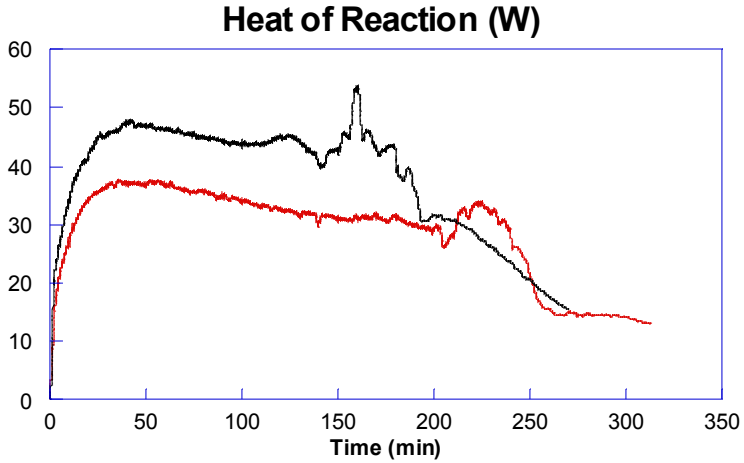
$$D_{ij} = \frac{Rp_i}{Rp_j} = \frac{r_i + [j]_p/[i]_p}{r_j([j]_p/[i]_p)^2 + [j]_p/[i]_p}$$

Accuracy of the estimation:

- *Reactivity ratios*
- *Enthalpy of polymerization* $(-\Delta\bar{H})$
- *Partition Coefficients*

Reaction Calorimetry: An example (2)

VAc/BA=50/50 Semibatch Batch 55 wt% solids content



Feeding Time:

180 min

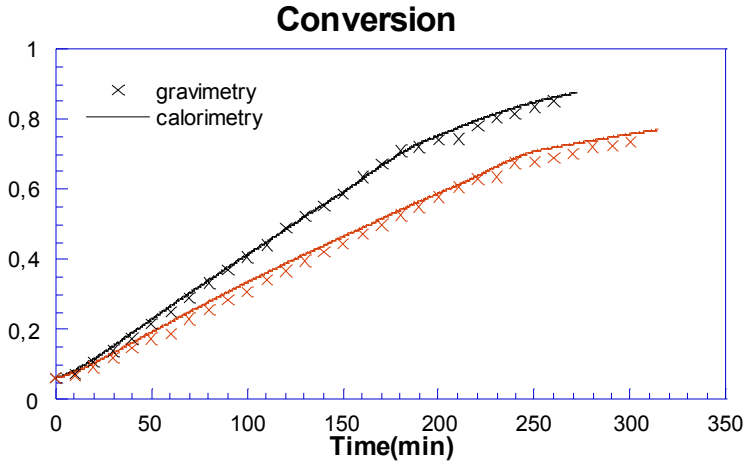
240 min

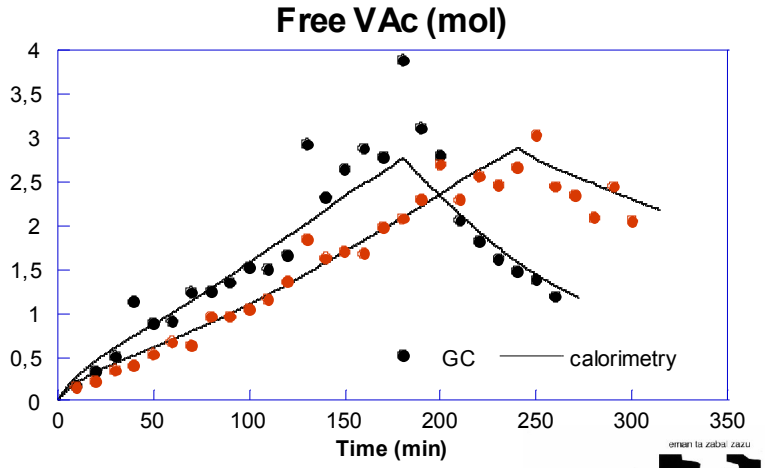
r_{VAc}=0.037

r_{BA}=6.36

ΔH_{VAc}= 89.5kJ/mol

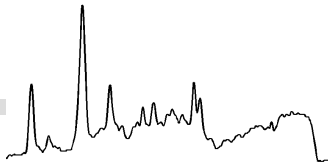
ΔH_{BA}=78.2kJ/mol



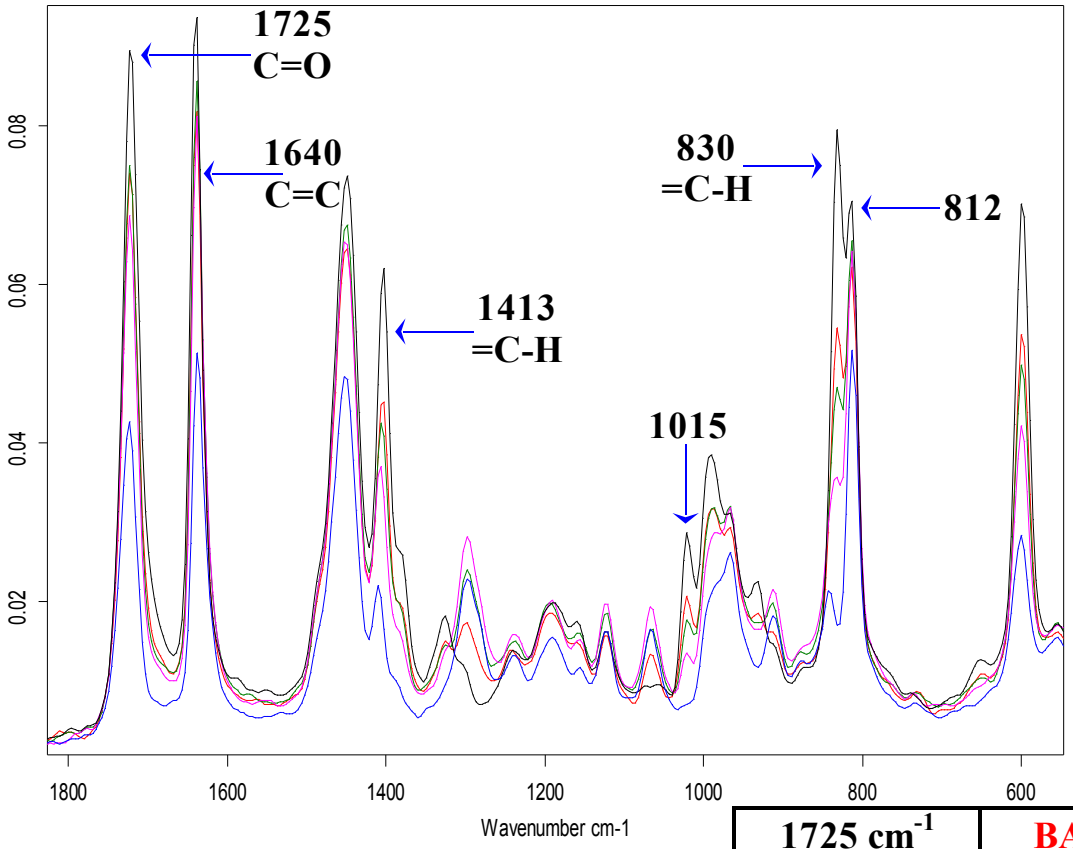


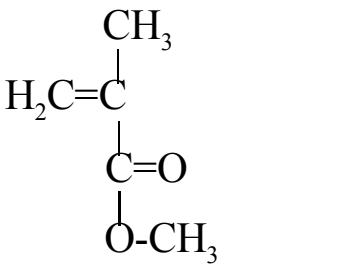
Raman spectroscopy

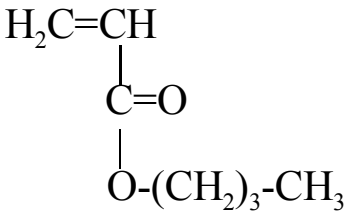
All-acrylic emulsion polymerizations



MMA/BA

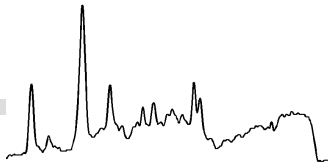


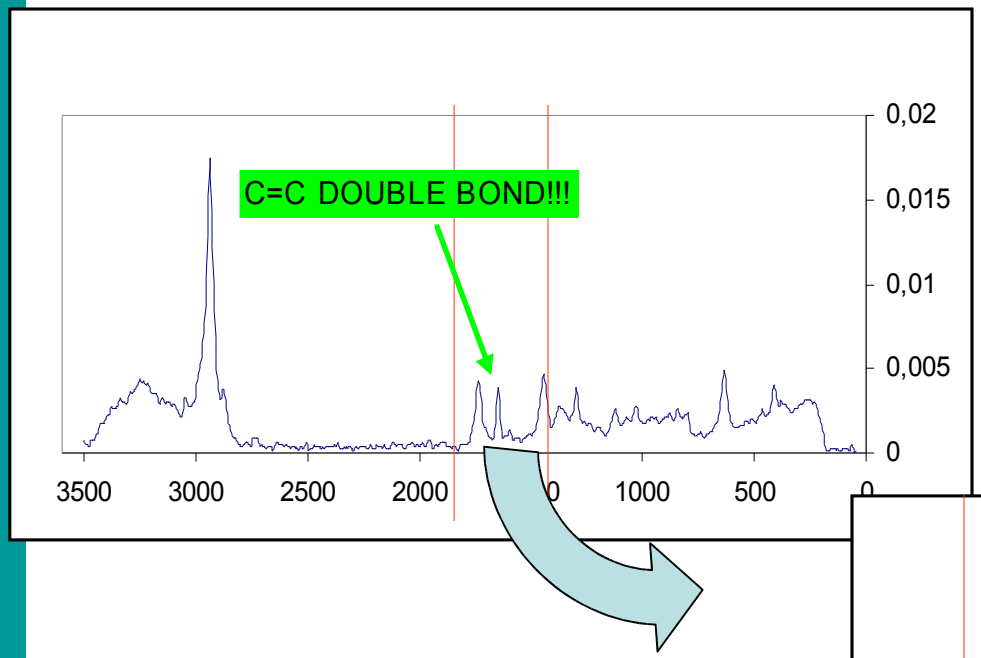




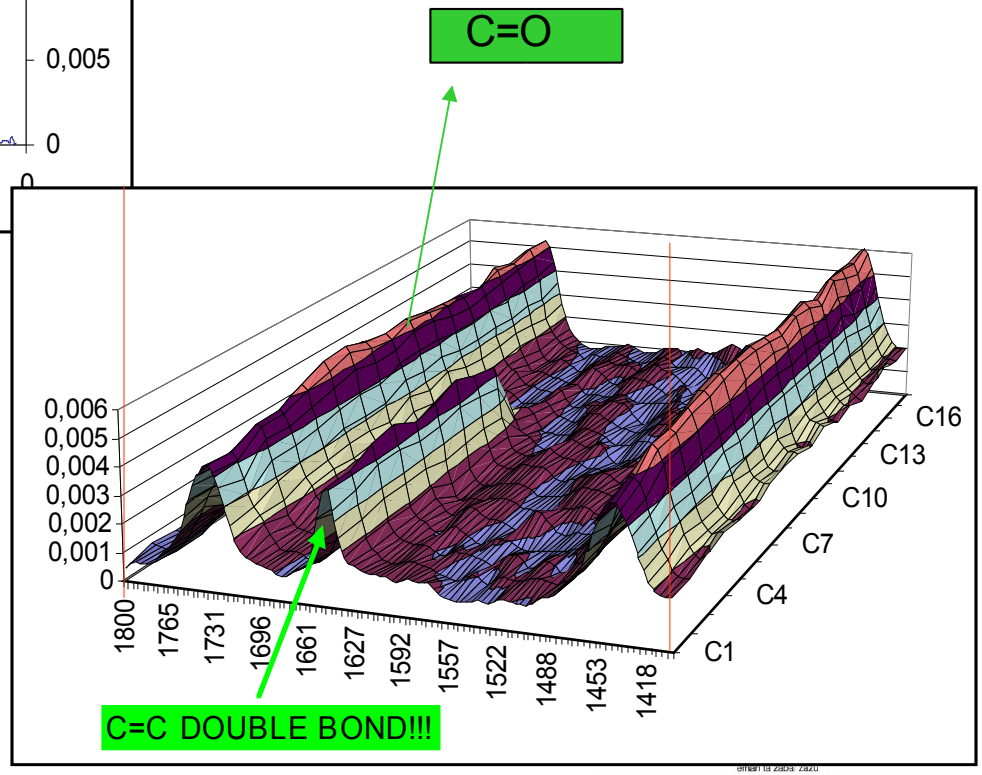
1725 cm^{-1}	BA_{total} + MMA_{total}
1640 cm^{-1}	MMA + BA
1450/1413 cm^{-1}	MMA
1015 cm^{-1}	MMA
830/812 cm^{-1}	MMA
812 cm^{-1}	PMMA

Raman Spectroscopy : Reaction monitoring

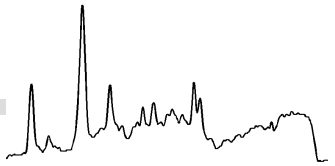


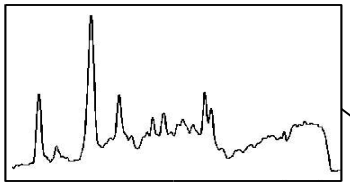


VAc/BA copolymerization



Raman Spectroscopy: Calibration





GC
Gravimetry

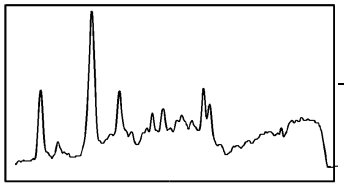
Known properties

Calibration

Model

1. CALIBRATION

Unknown Concentration

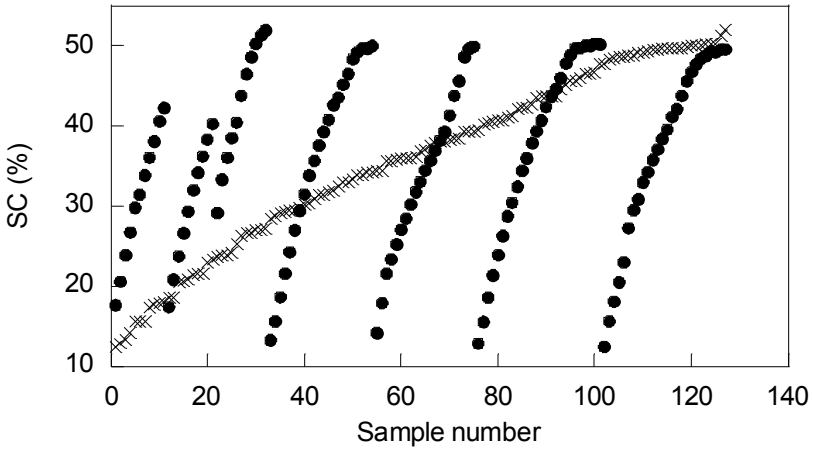


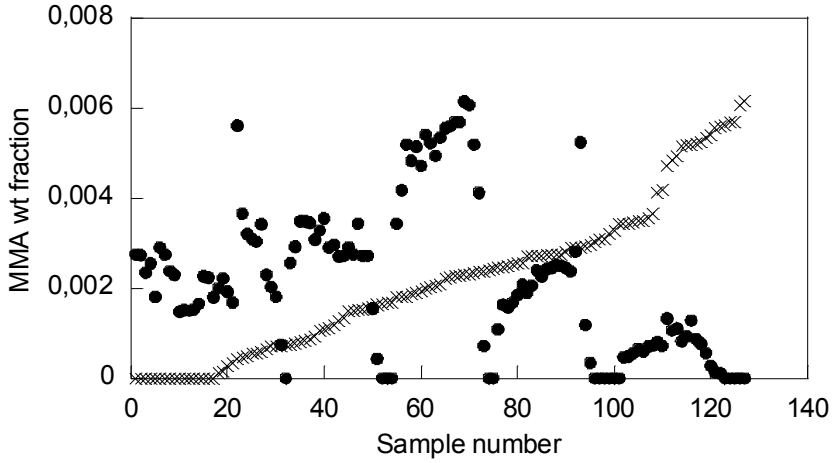
Model

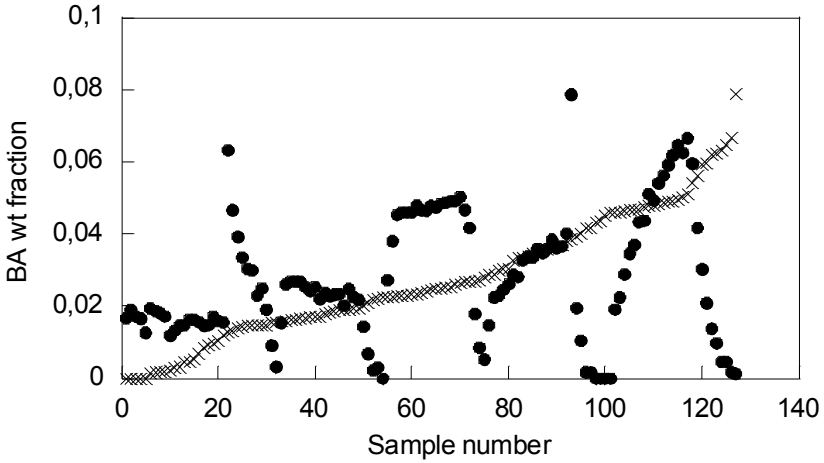
Estimated properties

2. PREDICTION

Calibration data: MMA/BA system

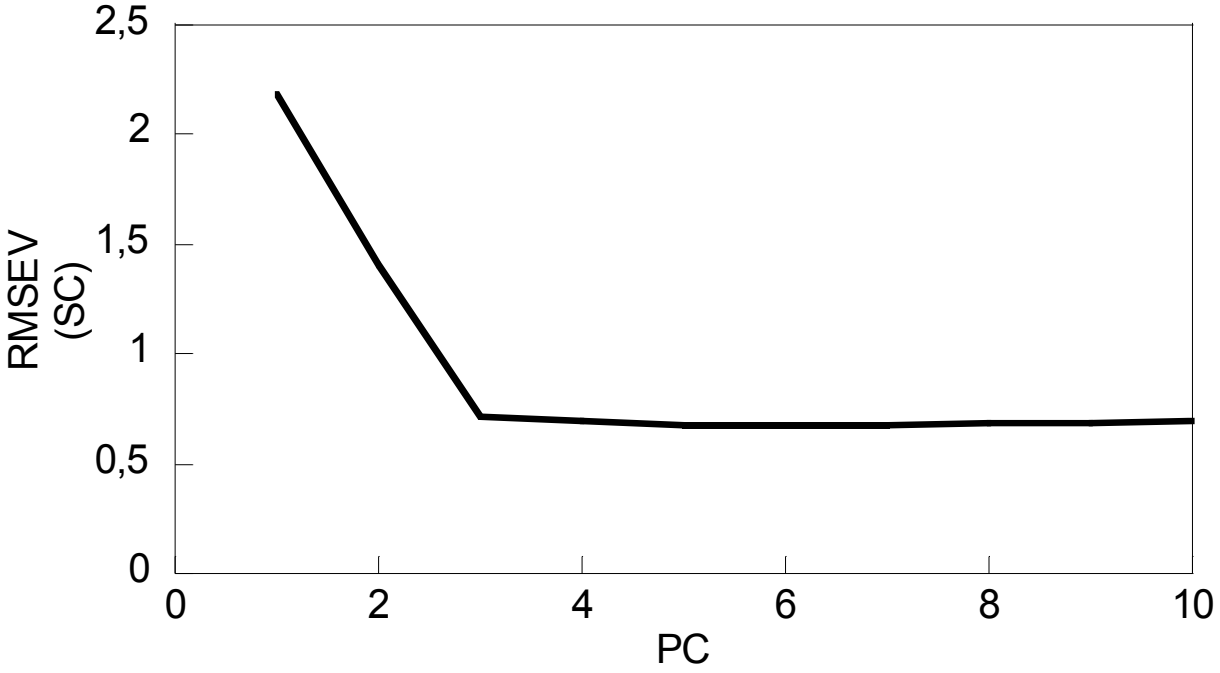






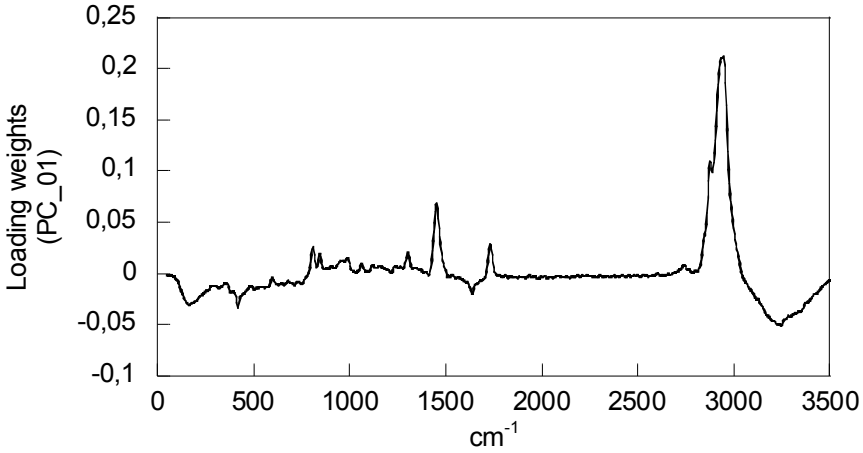
Example: Model for the SC (%)

- **A model using the whole normalized spectra, containing 3 PCs was considered the optimum.**

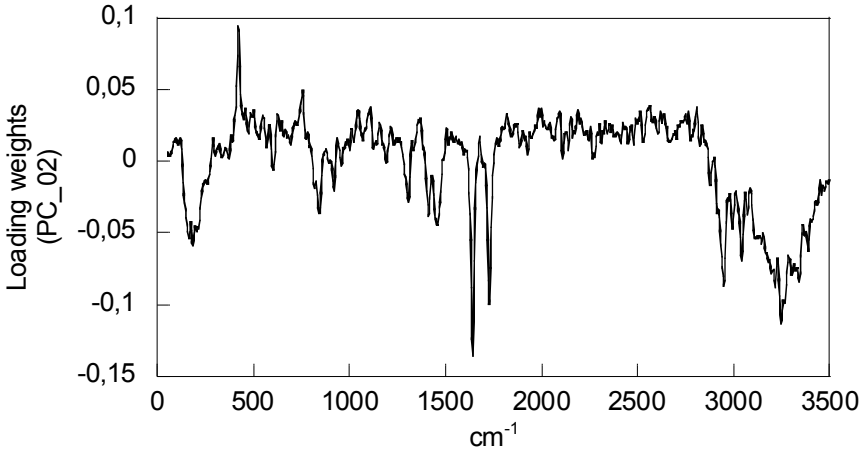


Example: Model for the SC (%)

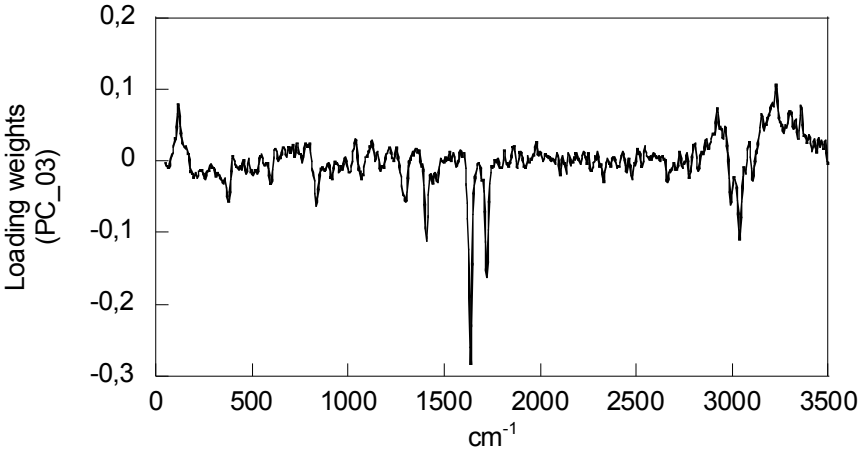
1st PC (X-expl,Y-expl):
90%, 96%



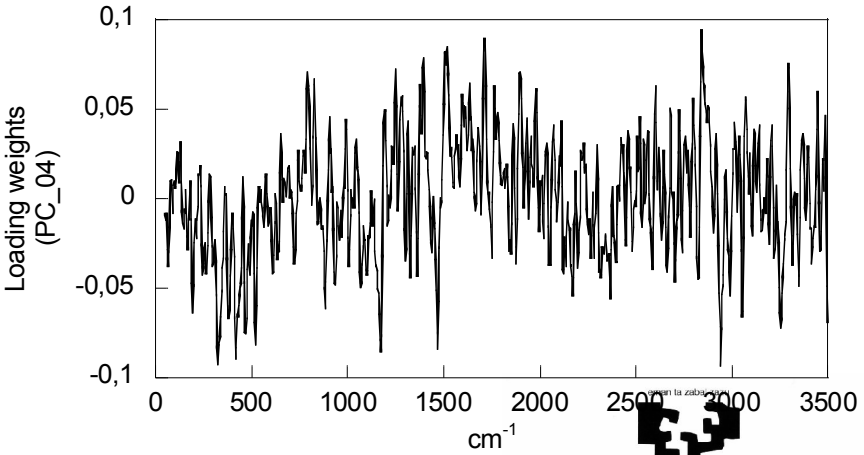
2nd PC (X-expl,Y-expl):
4%, 2%



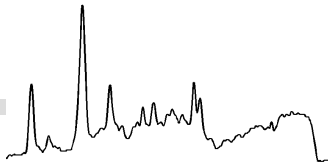
3rd PC (X-expl,Y-expl):
1%, 1%

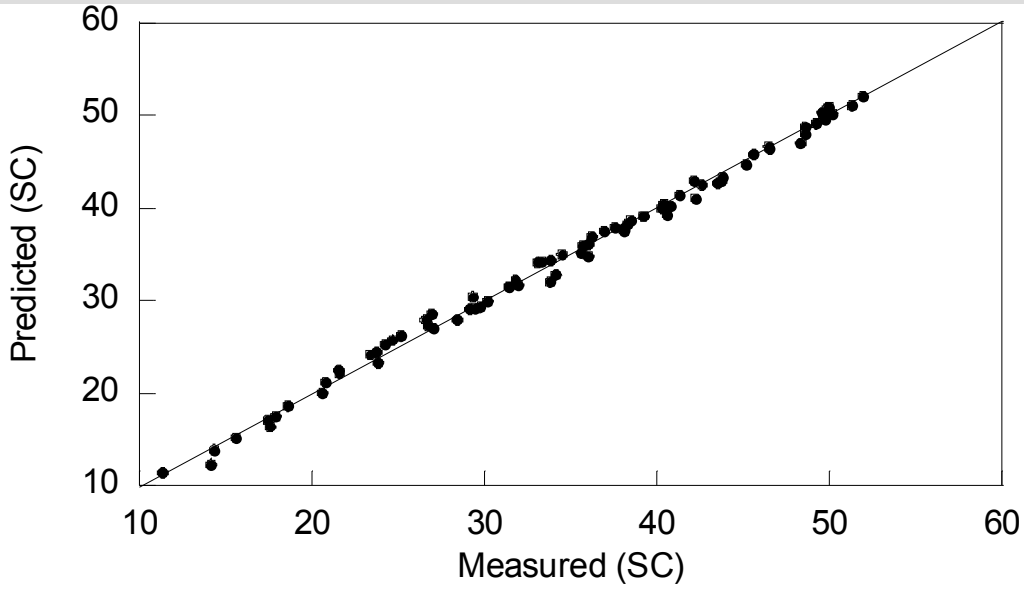


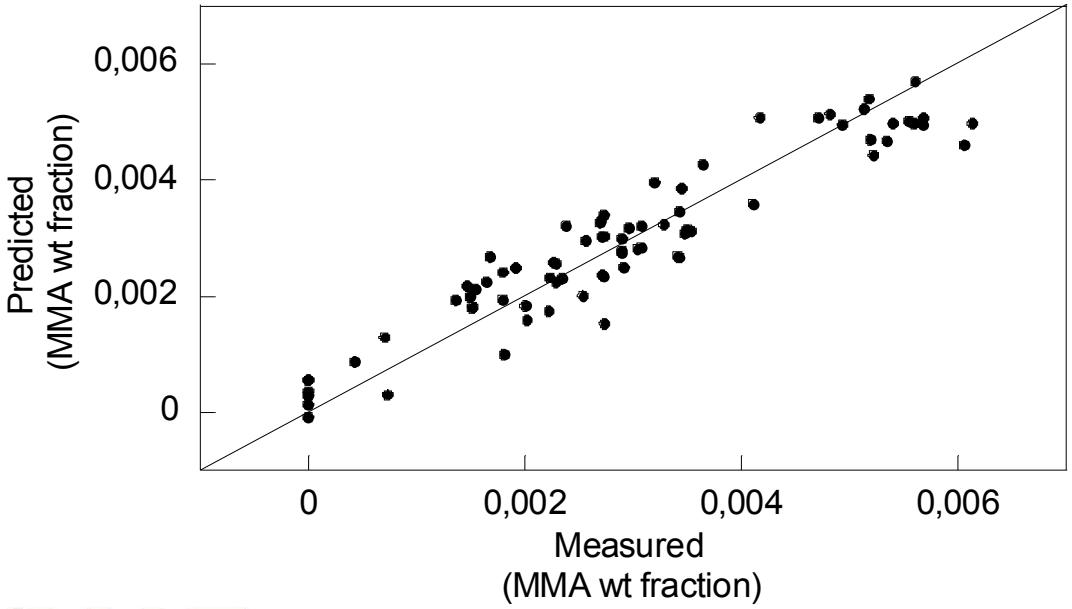
4th PC (X-expl,Y-expl):
0%, 0%



PLS Calibration models







POLYMAT
Instituto Universitario de Materiales Poliméricos - Material Polimerikoen Unibertsitate-Institutoa - Institute for Polymer Materials

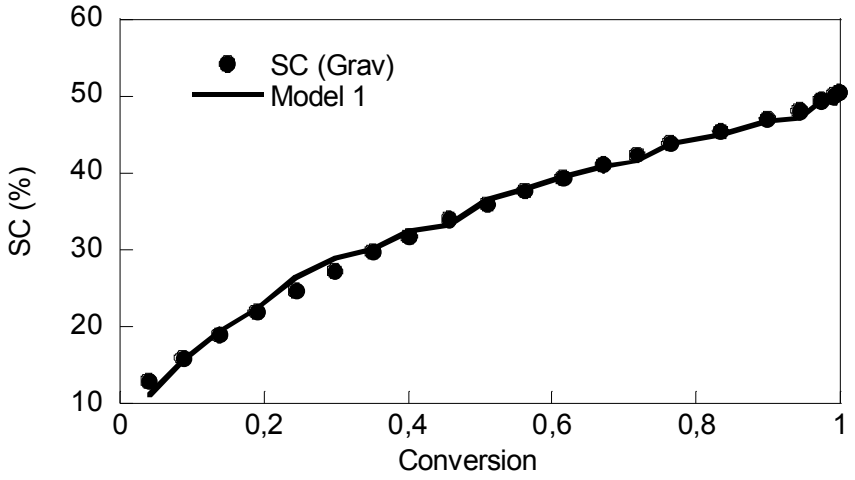
May 17, 2005

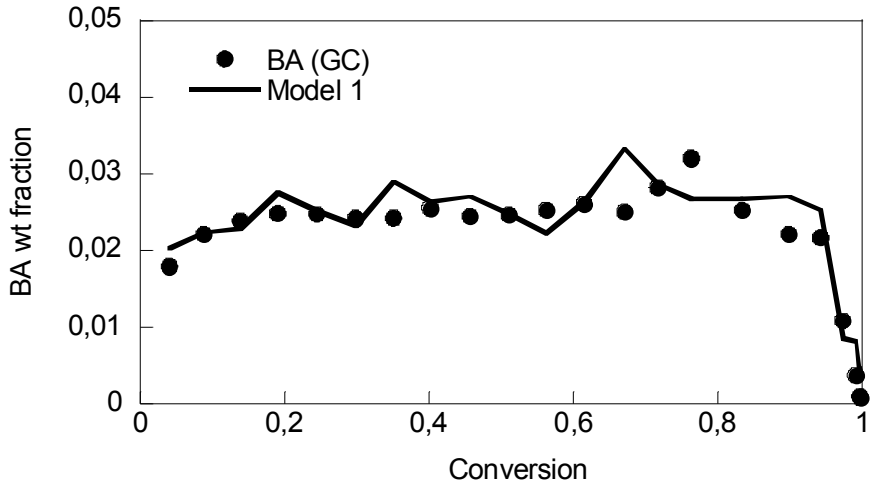
Universidad del País Vasco
Euskal Herriko Unibertsitatea
The University of the Basque Country

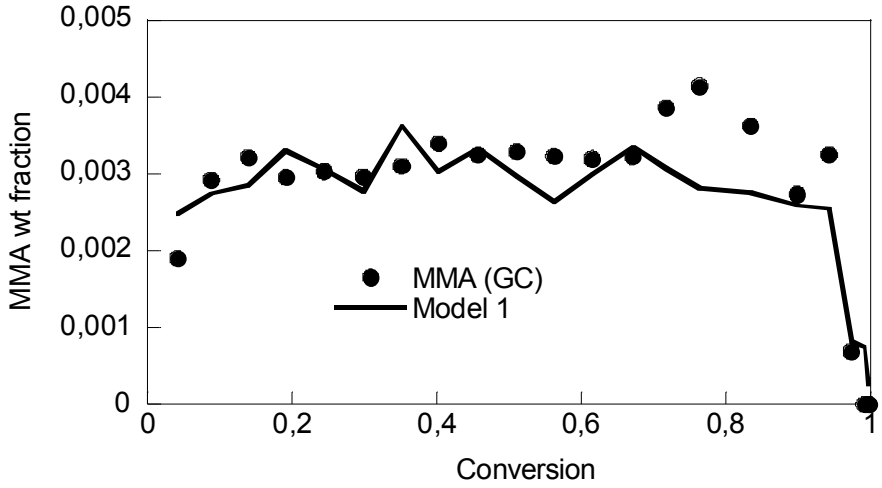
Validation of Calibration

Oihana Elizalde Ph.D 2005

BA/MMA=50/50 composition







Calorimetry vs Raman

- Two comonomer systems considered:
  BA/MMA and VAc/BA

- Overall and instantaneous conversions
  and Free Monomer:

  Gravimetry and Gas Chromatography (as reference)
  Reaction Calorimetry (RC1 Mettler-Toledo)
  Raman Spectroscopy (RFS-100 Bruker)

- Semibatch reactions of high solids content

  Starved(MMA/BA) and Non-starved (VAc/BA)

Calorimetry vs Raman : Experimental Details

VAc/BA/AA

Ingredient	Initial Charge	Stream 1	Stream 2
Water	99,5	-	99,5
Alipal	6,13	-	6,13
Arkopal	6,13	-	6,13
VAc	-	600	-
n-BA	-	141,1	-
AA	-	22,9	-
$K_2S_20_8$	2,29	-	-
$NaHCO_3$	2,52	-	-
Seed	527	-	-

Feeding time= 3 and 4 hours

BA/MMA

Ingredient	Initial Charge	Stream 1	Stream 2
Water	617	-	32,5
Dowfax	-	-	9,45
$K_2S_20_8$	Variable	-	-
$NaHCO_3$	Variable	-	-
n-BA+MMA	-	540	-
n-BA/MMA	-	Variable	-
Seed	63	-	-

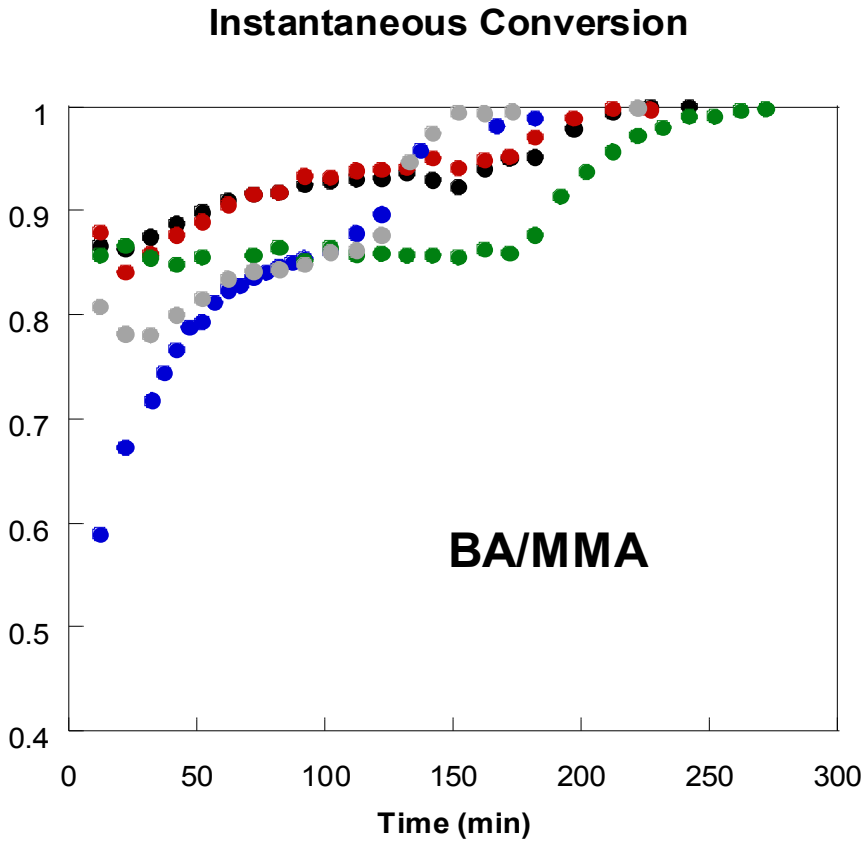
Feeding time= 2 and 3 hour

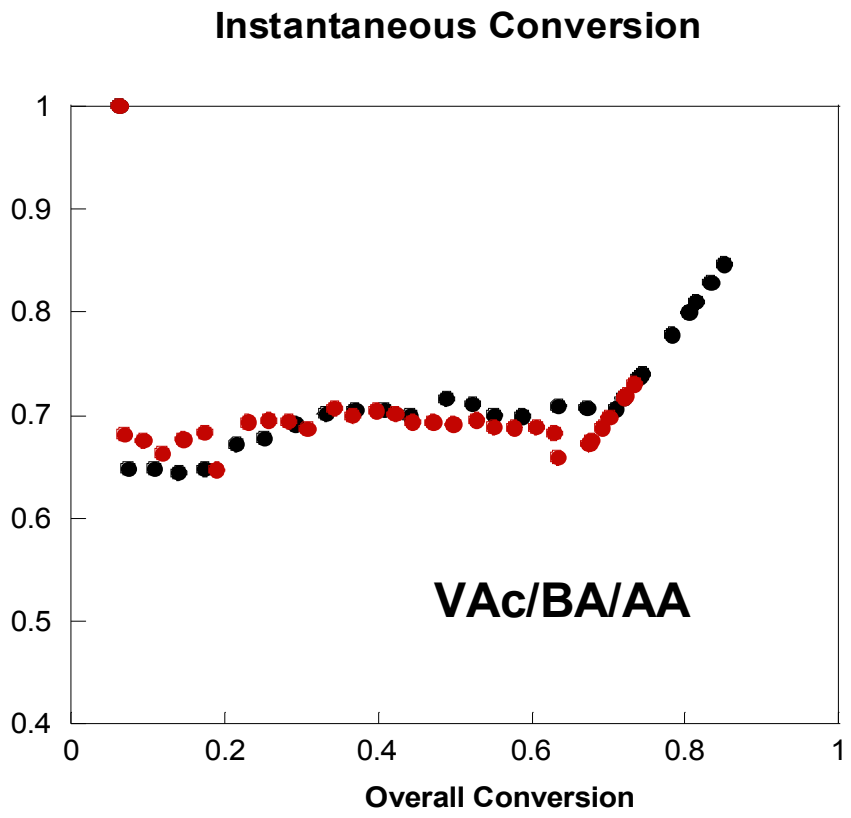
50/50(3), 70/30 and 90/10

Calorimetry vs Raman: Semibatch Operation

BA/MMA → **Starved Conditions 50/50 to 90/10**

VAc/BA → **Non Starved Conditions**

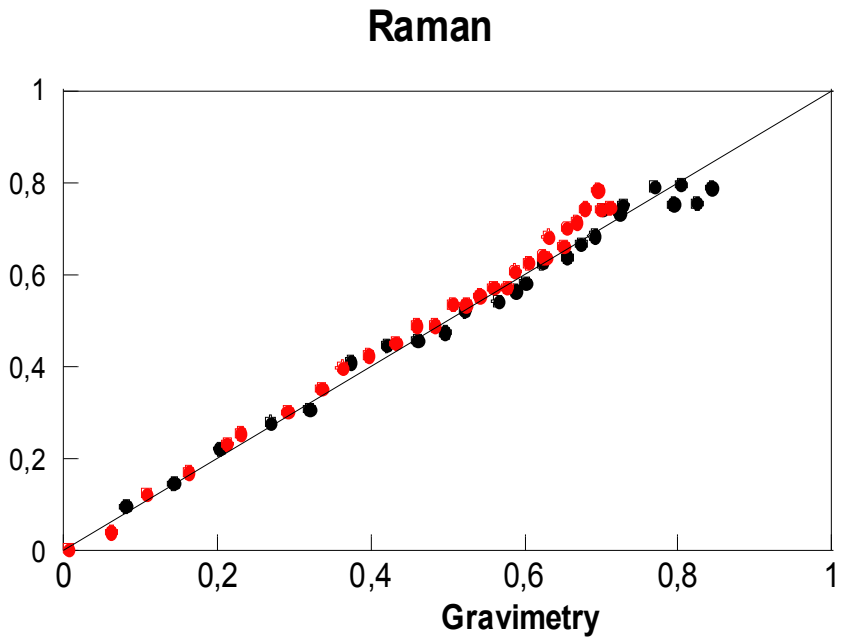


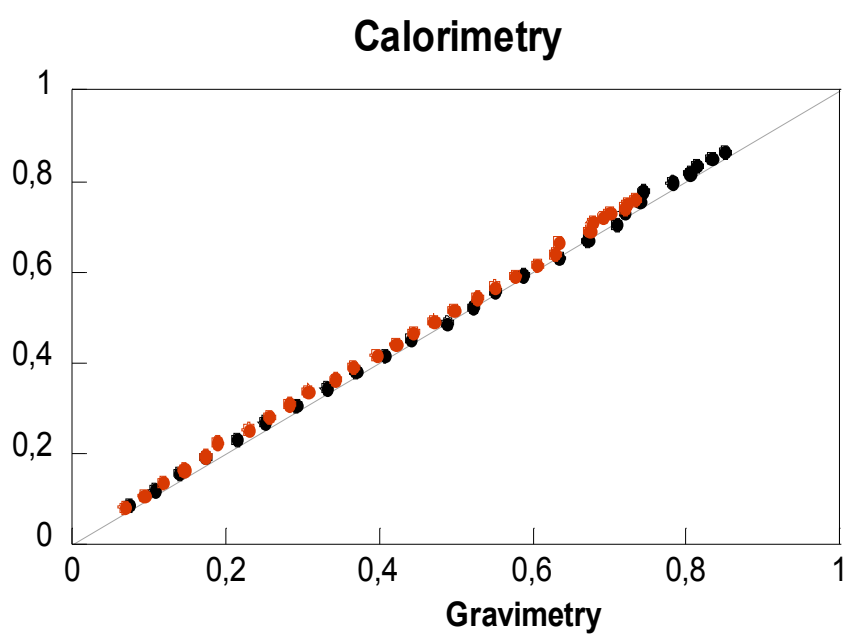


Gravimetric data

Calorimetry vs Raman: Overall Conversion

VAc/BA copolymerization. Non-starved

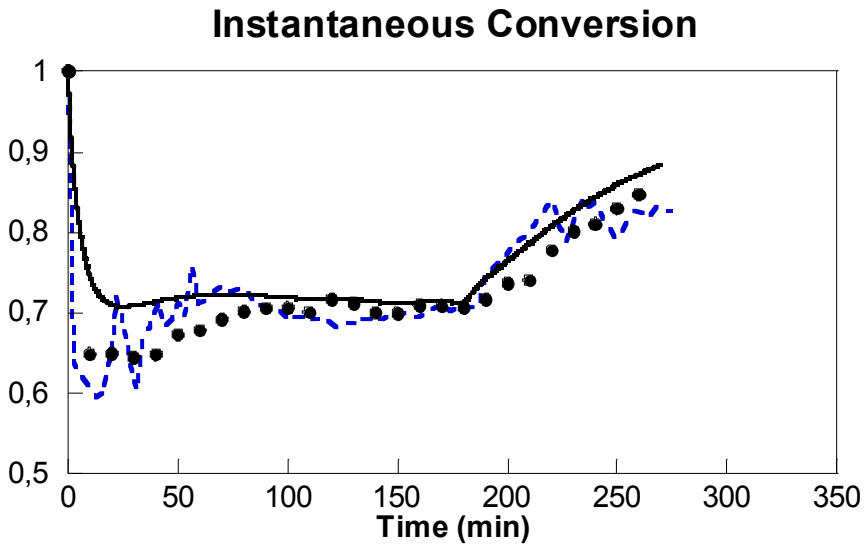


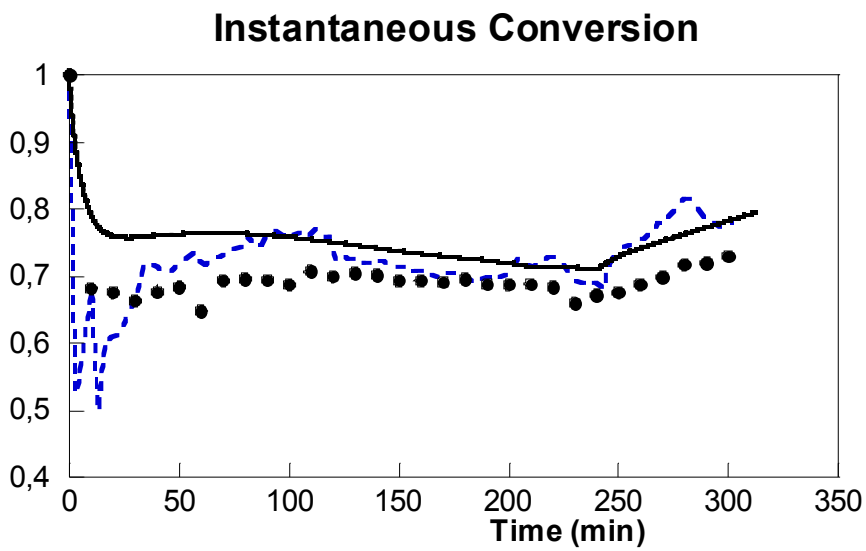


Raman and Calorimetry performed well

Calorimetry vs Raman: Instantaneous conversion

VAc/BA copolymerization. Non-starved



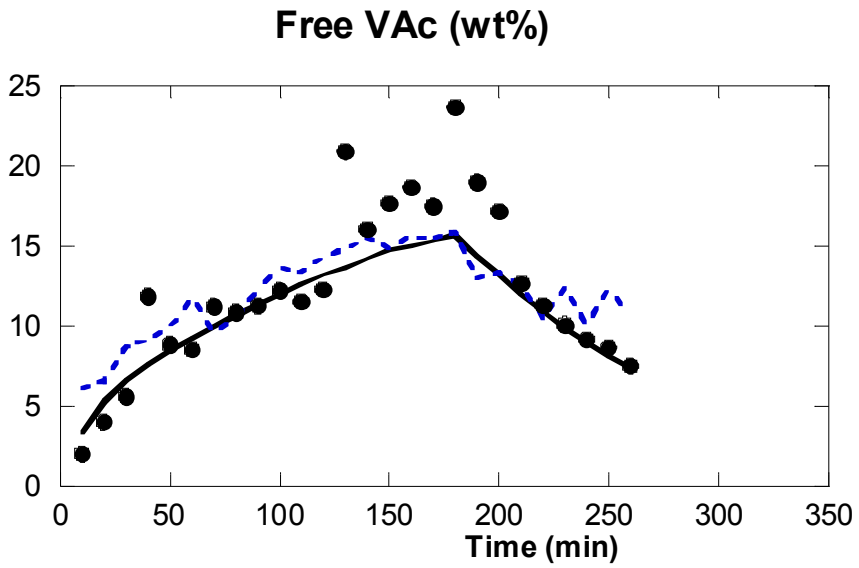


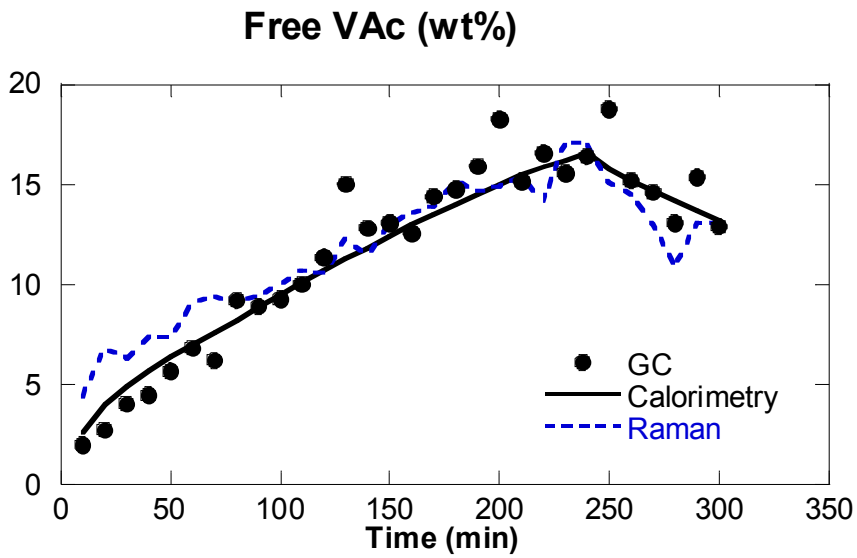
Calorimetry slightly overestimates
Raman is closer to gravimetry

In general reasonable good prediction for both

Calorimetry vs Raman: Free Monomer

VAc/BA copolymerization. Non-starved



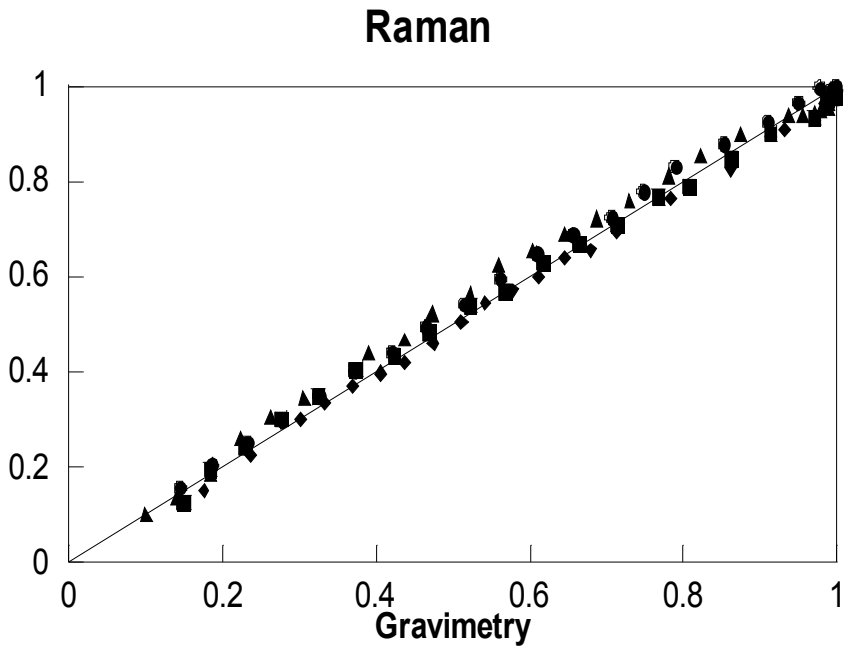


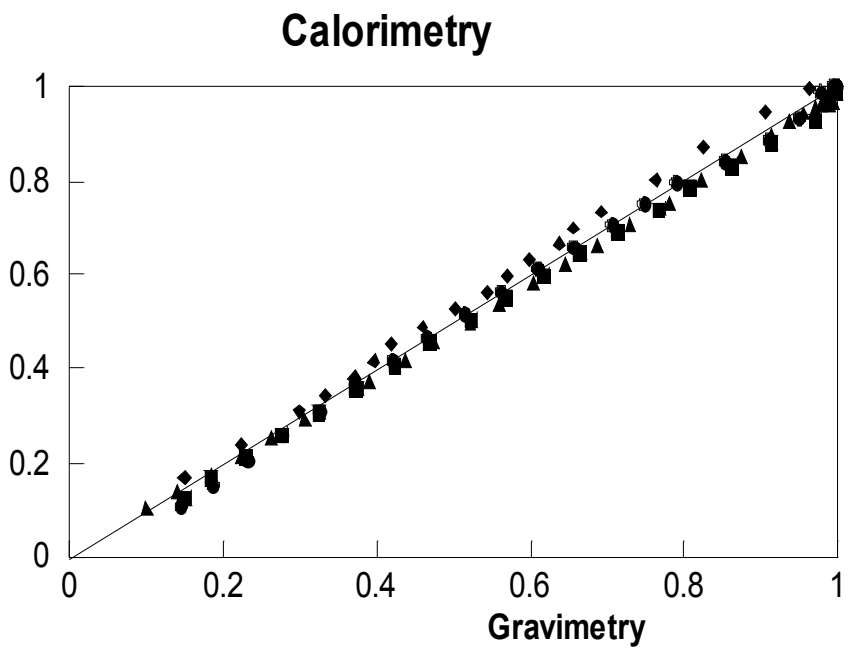
Calorimetry and Raman performed well

Chromatography (reference technique) scatters probably due to presence of droplets

Calorimetry vs Raman: Overall Conversion

BA/MMA Copolymerization: Starved Conditions

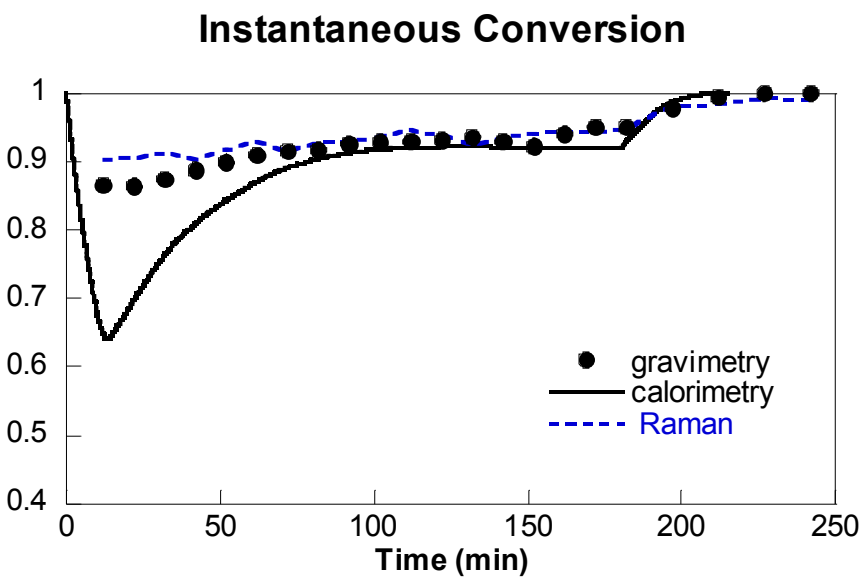


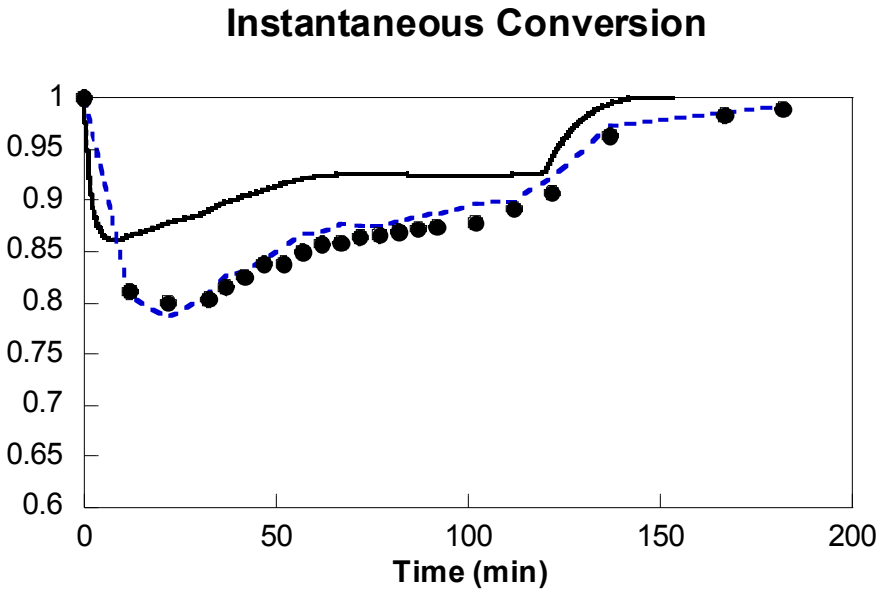


Good agreement for all techniques

Calorimetry vs Raman: Instantaneous conversion

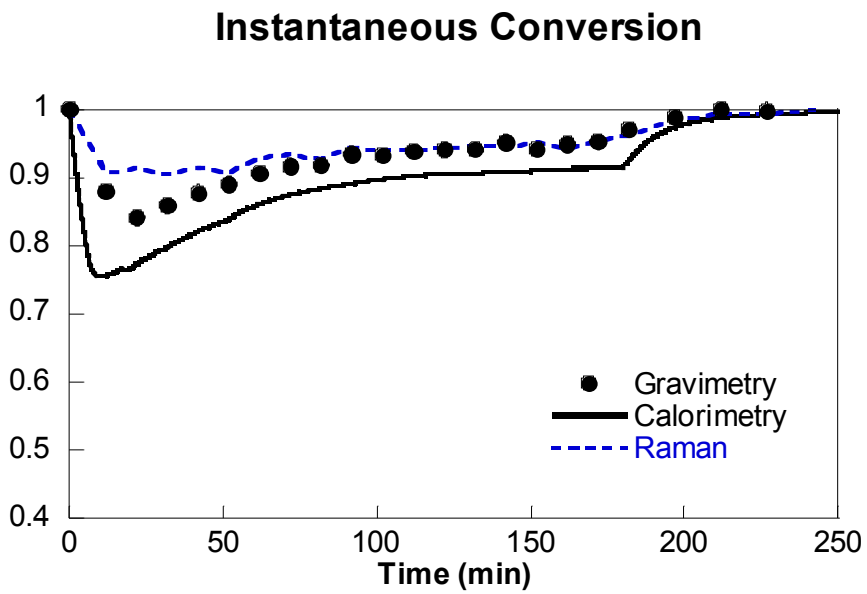
BA/MMA Copolymerization: Starved Conditions

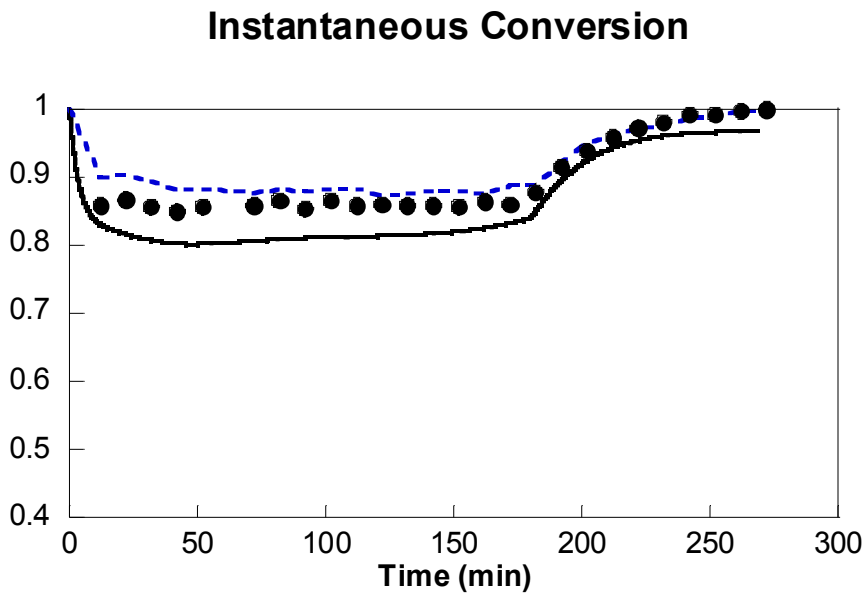




Calorimetry vs Raman: Instantaneous conversion

BA/MMA Copolymerization: Starved Conditions

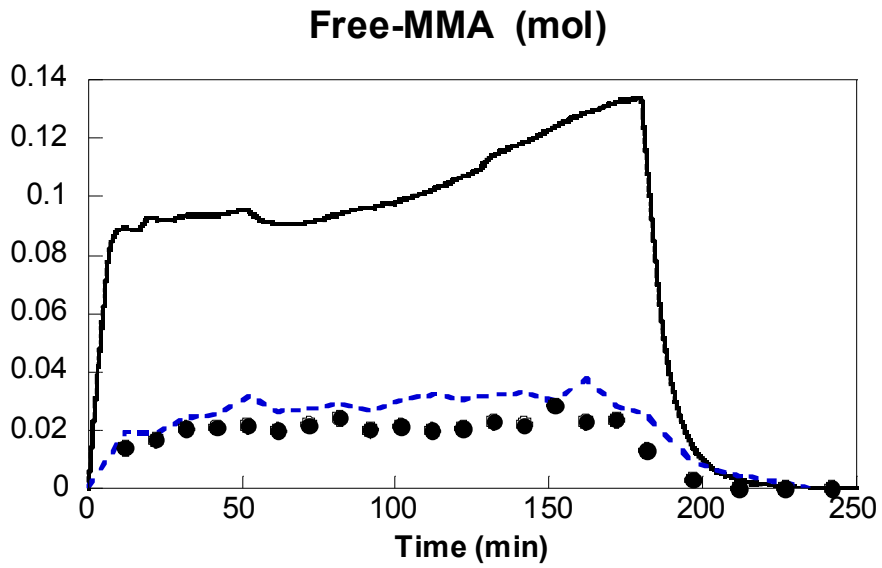


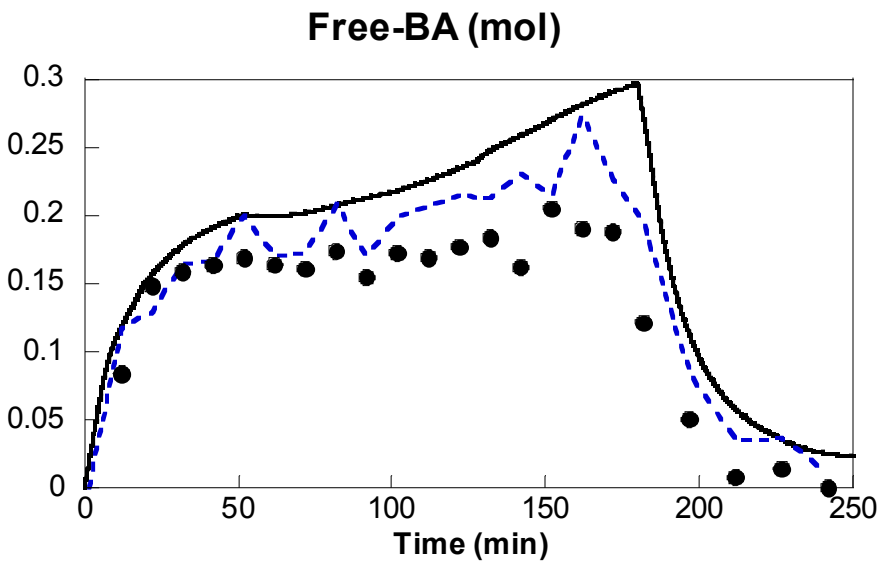


Both, Raman and Calorimetry predictions are worse
Raman is better than Calorimetry !!!

Calorimetry vs Raman: Free Monomer

BA/MMA Copolymerization: Starved Conditions

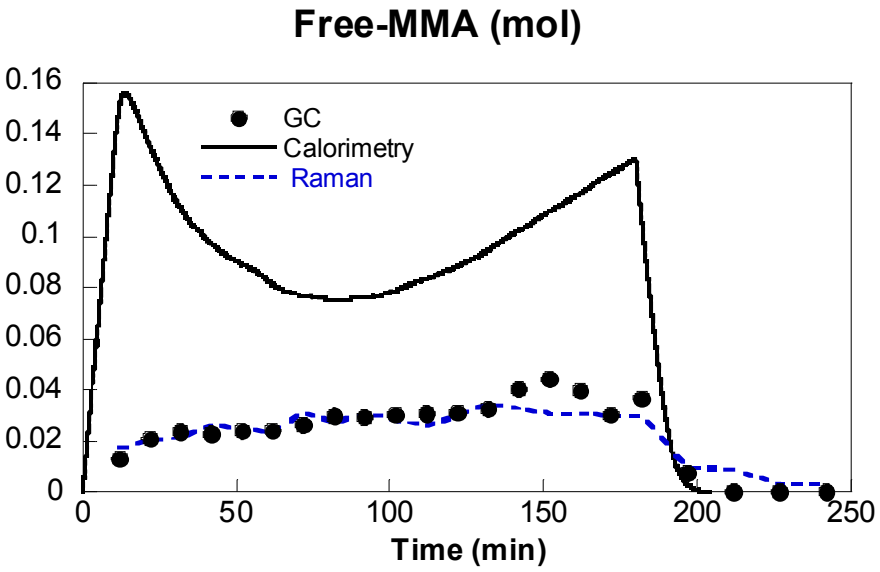


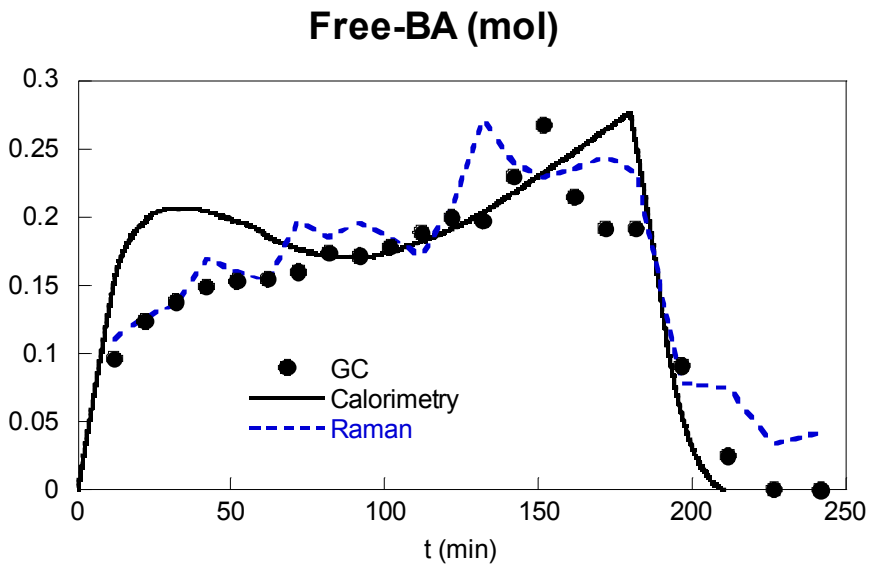


BA/MMA=50/50

Calorimetry vs Raman: Free Monomer

BA/MMA Copolymerization: Starved Conditions



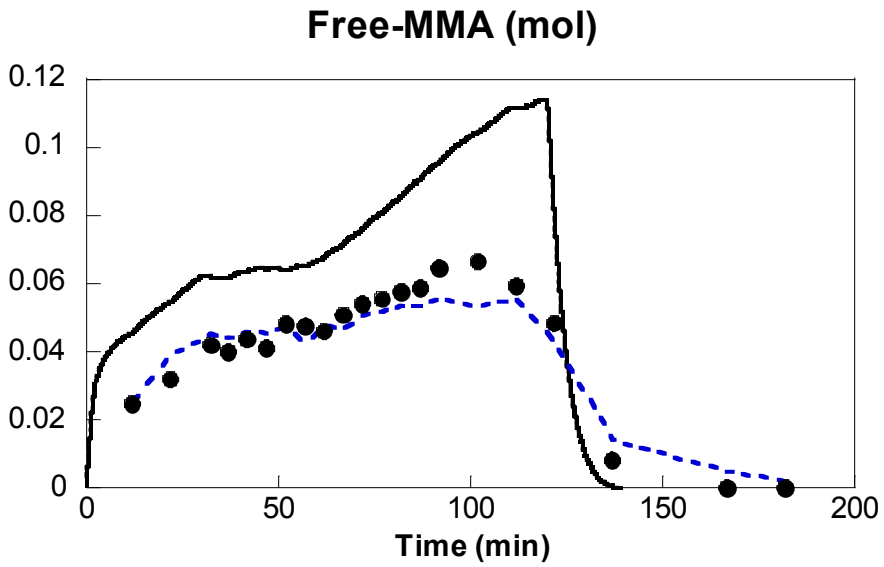


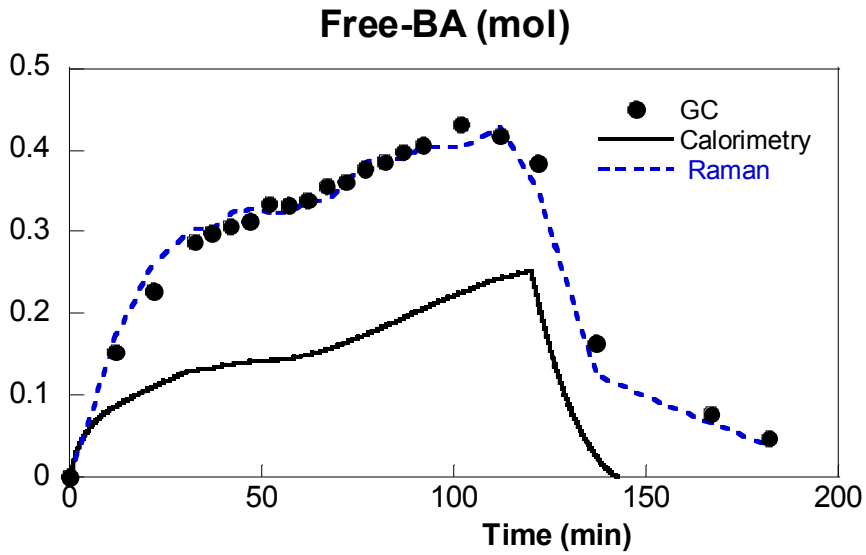
BA/MMA=50/50

Calorimetry vs Raman: Free Monomer

BA/MMA Copolymerization: Starved Conditions

BA/MMA=70/30

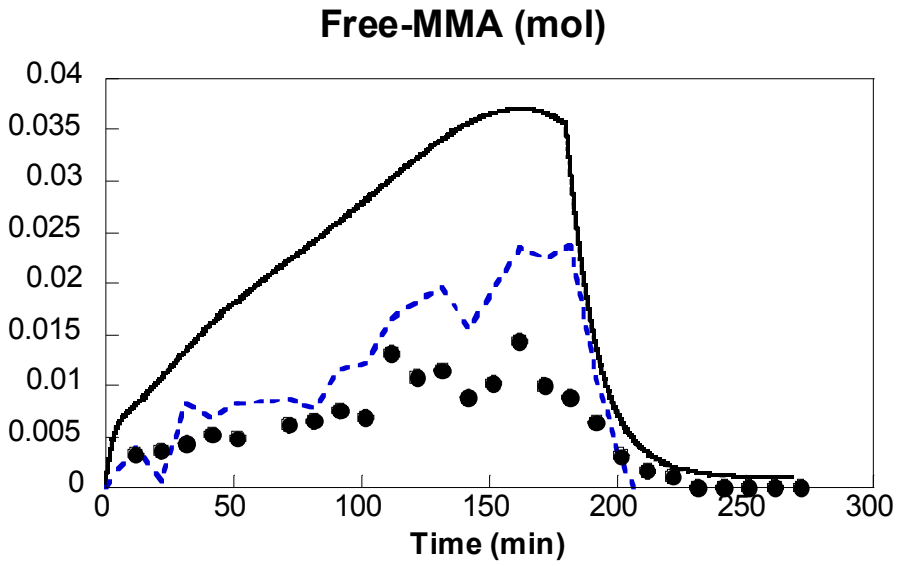


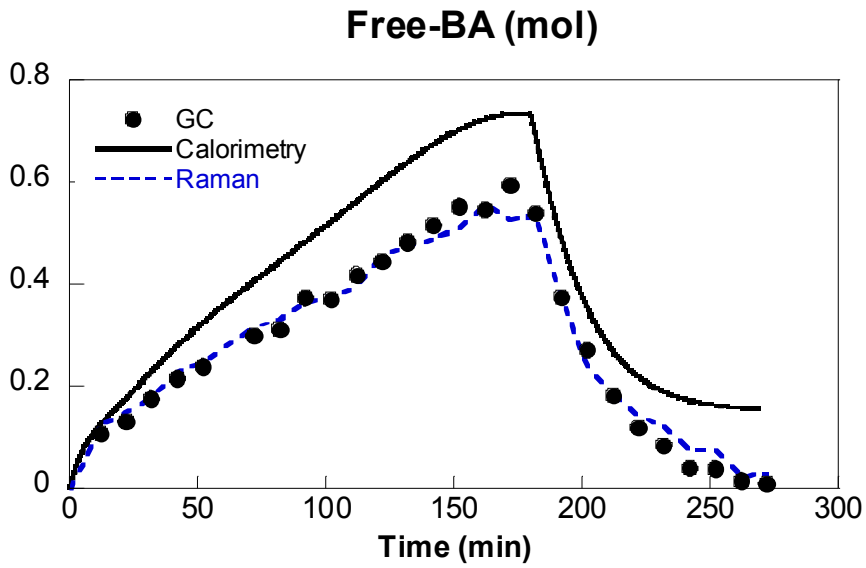


Calorimetry vs Raman: Free Monomer

BA/MMA Copolymerization: Starved Conditions

BA/MMA=90/10



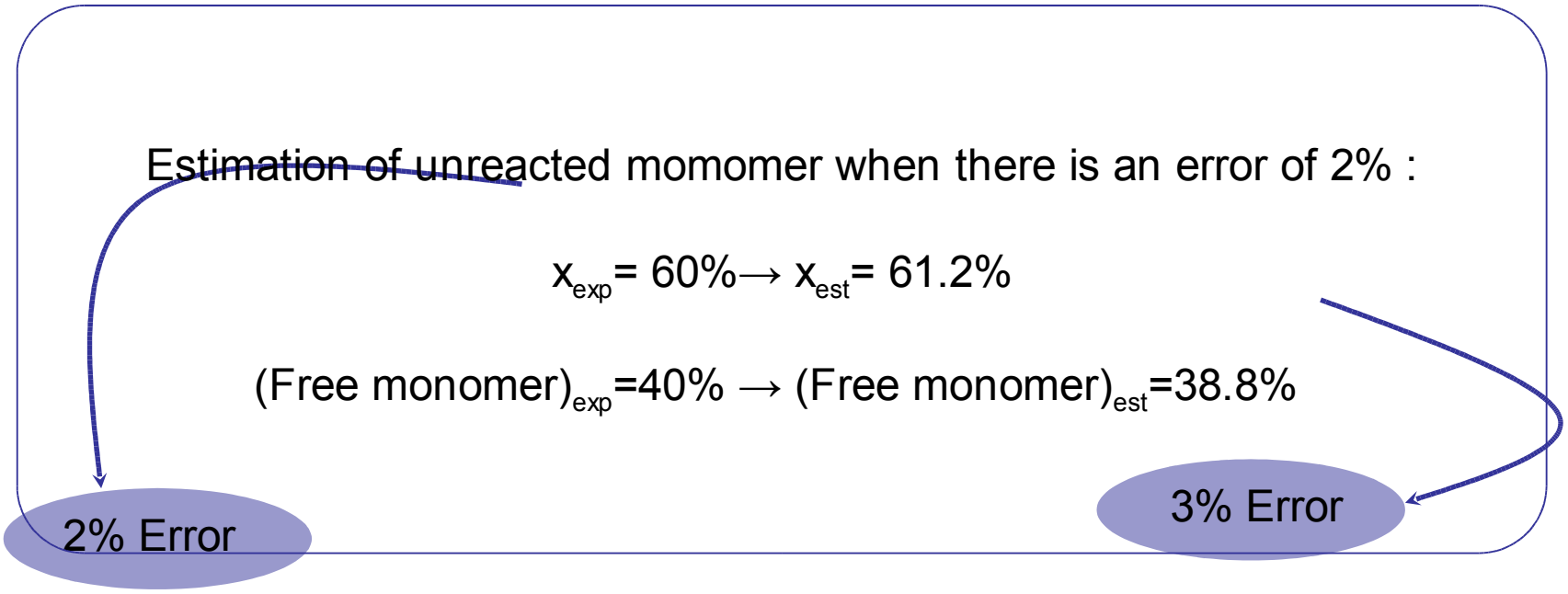


Calorimetry predicts incorrectly free monomer, specially MMA
Raman is superior to Calorimetry
Raman suffers predicting very low concentrations!!

Calorimetry

Error is inherent to the measurement

Example:



Calorimetry

Error is inherent to the measurement

Example:

Estimation of unreacted momomer when there is an error of 2%:

x_{exp}= 90%→ x_{est}= 91.8%

$(\text{Free monomer})_{exp}$=10% → $(\text{Free monomer})_{est}$=8.2%

2% Error

18% Error

Concluding Remarks

- Raman spectroscopy in combination with chemometrics can be used to monitor high solids content reactions, even when the bands of the monomers are overlapped (all acrylic or vinyl/acrylic mixtures) and the reactions are carried out under starved conditions.

- Calorimetry and Raman predict in a similar manner overall conversion. No significant differences for starved and non starved conditions. Calorimetry is easier!

- For instantantaneous conversion and free monomer:
  - Raman and Calorimetry provide similar predictions under non-starved conditions, namely, high monomer concentrations.
  - Raman spectroscopy gave much better predictions than reaction calorimetry under starved reactions.

Acknowledgments

- Ministerio de Educación y Ciencia (Project PPQ2000-1185 and scholarships for Oihana Elizalde and Maider Azpeitia)
- The University of the Basque Country (Project 00221.215-13594/2001)
- M.M. Reis acknowledges FAPESP (grant number : 03/06837-8 and 01/13017-1)