

TRACKING OFFLINE CONVERSION SOLUTION POLYMERIZATION OF METHYL METHACRYLATE / VINYL ACETATE IN TOLUENE IN A REACTOR CALORIMETER

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ABSTRACT

Analyses systems by chromatography in gaseous phase and by gravimetric have been used for the offline follow-up of the conversion of monomers during the copolymerization in solution of methyl methacrylate (MMA) and vinyl acetate (AVc) conducted in the calorimetric reactor (batch).

In the present work, an empirical model was generated using of the calibration curve connecting the spectral data CPG to the measured conversion by gravimetric. The obtained calibration was characterized by a correlation coefficient of 99.57 %.

The rate of conversion of MMA (91 %) is higher compared to AVc (28 %) according to the rate of reactivity ($r_{MMA} = 28$ and $r_{AVc} = 0.029$). The results obtained by gravimetric and CPG are well adapted for the follow-up of the polymerization reaction.

Key words: Copolymerization in solution, Monomers, Chromatography, Calorimetry, Conversion.

1 INTRODUCTION

The industry of polymers becomes more and more competitive. The manufacturers of the polymer facing increasing pressures to reduce production costs should provide more stringent requirements in polymer quality. The production of polymers with specific characteristics requires thus a continuous follow-up and a control of the process to ensure the desired qualities. Consequently, the reactor must be equipped with sensors on-line measurement accuracy of these characteristics in real time.

The elaboration of methods of controlling the polymer quality (in terms of reactor operation and monitoring of the trajectory of the characteristics of polymers) during a polymerization is the key of the efficiency of the production of tailor-made polymers high qualities and the improvement of the functioning process and also the improvement of the economic standpoint. Among the numerous variables involved in polymerization reactions, the conversion of the monomer is obviously one of the most important that can be

measured [1]. It is closely linked to security requirements and productivity in industrial scale processes. The quality of the obtained polymers is also determined through the kinetic complex and the relations structures characteristics and their evolution during the reaction of polymerization. Several sensors are described in the literature to measure the on-line conversion of the monomer [1, 2]. There are several techniques using the supervision by spectroscopy IR and this by applying the Fourier transform in the field of infrared [3, 4]. However, data analysis remains delicate and methods are developed to reduce the difficulties caused by the dilution system and the discretization process [5].

In this document, we show the results of copolymerization in solution of MMA / AVc with the initiator (AIBN) in the toluene in batch.

The calorimetric reactor has been used to put in effect this reaction, and the method gravimetric and the CPG for the offline monitoring of our

samples to calculate the conversion of monomers.

2 EXPERIMENTAL PROCEDURE

- Instrumentation

We realized all the syntheses in a glass insulated reactor of 2 liters which is equipped with a condenser, a jacket supplied by a thermostatically controlled water bath, a lid and a valve sample, figure 1. The jacket has two side entrances to introduce allowing introducing probes of temperature (Pt-100). We can measure the temperature on line input and output of water in the jacket. A probe (Pt-100) placed directly in the reactor can track in real time the reaction temperature. The stirrings ensured by a steel blade type anchor. A program developed in Visual Basic allows us to control a solenoid valve connected to the thermostatic bath and a pump that allows introducing various compounds (monomer, surfactant, initiator, ...) for reactions in semi-continuous.



Figure 1. Experimental System (Calorimeter Reactor)

- Procedures

We perform the copolymerization in batch process; all the reagents are introduced at first. We begin by heating up the thermostatic bath and the circulation of the water in the jacket of the reactor. We set the temperature of the bath to 60°C so that it is of 60°C in the reactor, the temperature at which the polymerization is carried out. All the products are weighed using a precision balance and then introduced into the reactor. We begin by introducing the toluene. We start then the circulation of nitrogen in the reactor hanging approximately 45 min to remove the oxygen, which may be an inhibitor

of the reaction. We set the stirring speed to 200 rpm. We put then both monomers (MMA / AVc) in the reactor. The reagent is degassed for 15 min. When the temperature reaches 60°C we can then begin the reaction by introducing the initiator the AIBN. More details on reaction conditions are presented in the table 1. During the reaction, approximately 10 samples were removed using the bottom-valve jacketed reactor for gravimetric measurements of the conversion and to follow the progress of the reaction thanks to the measure of the dry extract (use a thermo balance Mettler U16 Moisture Analyzer).

Table 1. Experimental Conditions for the Copolymerization of MMA / AVc

Quantity	Speed of Stirring 200 rpm	
	1st assay in 60°C	2nd assay in 70°C
Methacrylate of methyl (MMA)	190 g	190 g
Vinyl acetate (AVc)	190 g	190g
Toluene	1600 g	1600 g
AIBN	8 g	14 g

At regular time intervals, samples are taken at the reactor outlet. By gravimetric we determine the conversion of these samples: we measure by weighing the quantity of polymer contained in a known mass of solution made (taken) after evaporation of water and residual monomer. The mass of obtained polymer is related to the total mass of solution in this reactor.

For a batch process, the conversion is calculated from the ratio between the mass of the polymer and the mass of the monomer initially introduced, equation (1) and (2) were used to calculate the percentage of the dry extract and the mass percentage of the conversion of monomers.

$$E_s = \frac{M}{M_{\text{solution}}} \times 100 \quad (1)$$

$$X = \frac{E_s}{M_{\text{MMA}} + M_{\text{AVc}}} \times 100 = \frac{M}{M_{\text{MMA}} + M_{\text{AVc}}} \times 100 \quad (2)$$

To improve quality control of polymers characteristics such as the composition of copolymers, it is necessary to be able to follow the progress of polymerization reaction in the first place, this means follow main measures such as the individual conversions of monomers. The chromatography in gaseous phase (CPG) was used to measure offline conversions of individual monomers. The sample is injected through a septum (rubber pellet) using a microsyringe. The injector temperature is 250 °C which allows vaporizing the sample. The latter is then directed to the capillary column (from 15 to 100 meters). The used detector is a FID (detector with ionization of flame). The retention time of each compound is given in the table 2.

Table 2. Values of the Retention Time

Products	Retention time (min)
Methacrylate of methyl (MMA)	3
Vinyl acetate (AVc)	1.5
Toluene	2.8

In parallel, we drew the curve of calibration using 10 flasks in which the well-determined quantities of toluene and monomers are introduced. A reliable model calibration was obtained from a data set. The relationship between the masses of monomers and areas of spectra is given by this expression:

$$\frac{M_{MMA}}{M_{AVc}} = 0.173 \times \frac{S_{MMA}}{S_{AVc}} - 0.0022 \quad (3)$$

The calculation of the individual conversion of each monomer is determined by this expression:

$$X_{MMA} = \frac{(M_{initial} - M_{calculated})}{M_{initial\ MMA\ in\ the\ reactor}} \times 100 \quad (4)$$

$$X_{AVc} = \frac{(M_{initial} - M_{calculated})}{M_{initial\ AVc\ in\ the\ reactor}} \times 100 \quad (5)$$

3 RESULTS AND DISCUSSIONS

To perform the calorimetric reactions follow-up, we have exported under Excel the reactor temperatures, the entry and the exit of the jacket by taking a value every 10 min. The

evolution of the reactor temperatures, the entry and the exit of the jacket in time during the phase of the heating is given in figure 2 for the first assay and in figure 3 for the second assay. By comparing both experiences, we notice that after 10 min the temperature increases more slowly during the first assay. We also note that the temperature of the reactional mixture falls at the time of the addition of the initiator and then increases. During the copolymerization, the temperature variation is represented on figures 4 and 5 for both assays. Both figures show some fluctuations in the temperature profile, we also observe that there is no big difference between the inlet and outlet temperatures of the jacket, which remains practically constant.

Figures 6 and 7 represent the variation of the conversion according to time for both assays. After 5 hours, the conversion reaches 31 % for the first assay, whereas for the second, it is 48 %. This variation is due to the increase of the quantity of the initiator, which makes the reaction faster. The offline follow-up of the conversion of copolymerization of MMA / AVc has been also studied by Hong Hua and Al. [6] by using ATR-FTR spectroscopy. They found a final conversion of 60 % in weight, but it does not specify the obtaining time of the conversion value. We obtained 48 % for a reaction time of 6 hours, which allows to say that the gravimetric method is well adapted for monitoring the conversion.

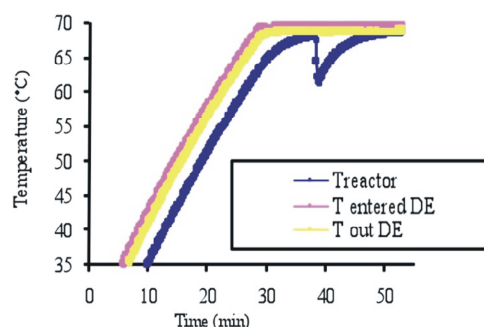


Figure 2. Profiles of Temperature during the Phase of heating (1st assay)

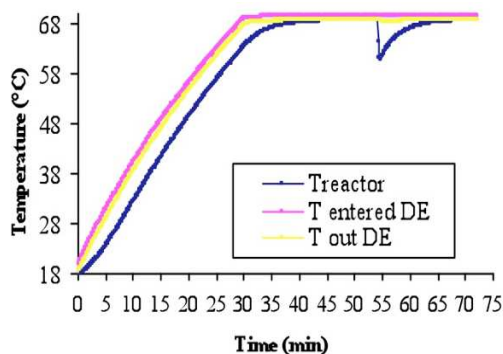


Figure 3. Profiles of Temperature during the Phase of heating (2nd assay)

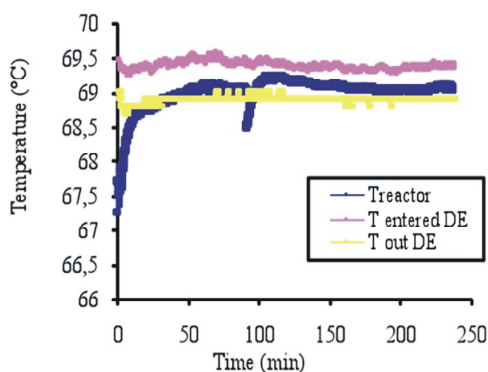


Figure 4. Profiles of Temperature during the Copolymerization (1st assay)

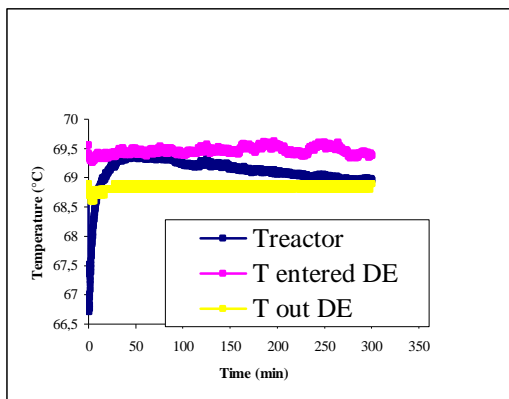


Figure 5. Profiles of Temperature during the Copolymerization (2nd assay)

Another calibration model has been established and this was from samples taken directly by the reactional environment when placed in the toluene by keeping the same operating conditions, (that is, initial temperatures and molar fractions of MMA and AVc have been maintained the same). The results gave a calibration this demonstrates the precision of the method. Each spectrum is then processed to provide an estimate of the conversion. The

relationship between the spectral data and the conversion of the monomer was obtained through the model of calibration.

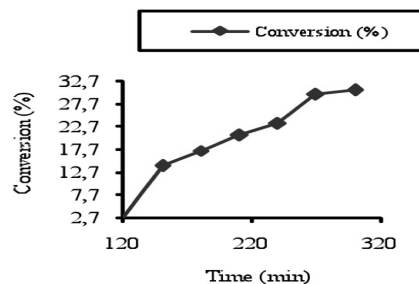


Figure 6. Variation of the Conversion (1st assay)

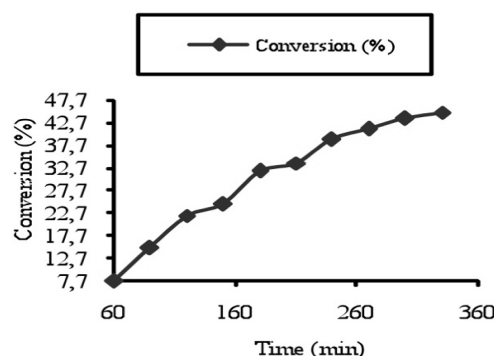


Figure 7. Variation of the Conversion (2nd assay)

The calibration curve is given in figure 8. The individual conversion for MMA and AVc is represented by figures 9 and 10 for the first assay and figures 11 and 12 for the second one. We observe that conversion rate for MMA is higher compared AVc that may be explained by the fact that the MMA is much more reagent than AVc according to the rates of reactivity which we found ($r_{MMA} = 26$ and $r_{AVc} = 0.0319$). Literature [7] provides for these rates ($r_{MMA} = 24.025$ and $r_{AVc} = 0.026$).

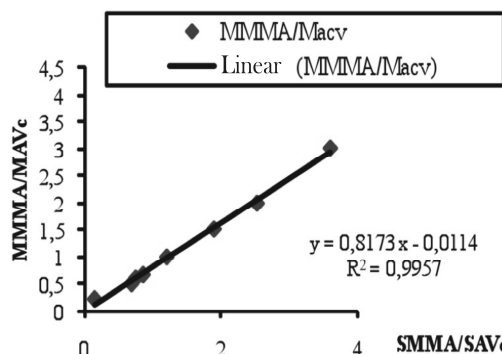


Figure 8. Calibration Curve in Chromatography

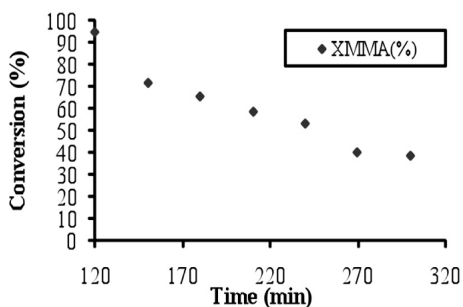


Figure 9. Variation of the Conversion for MMA (1st assay)

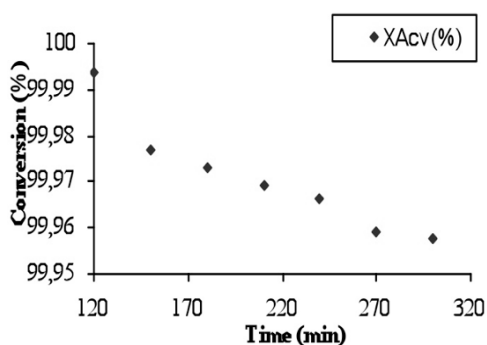


Figure 10. Variation of the Conversion for AVc (1st assay)

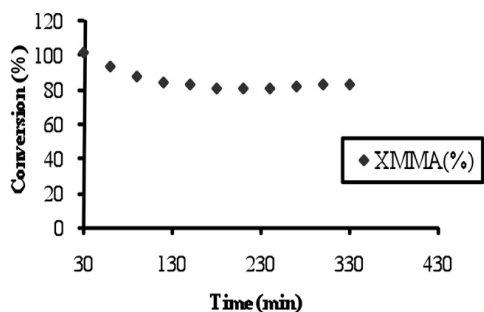


Figure 11. Variation of the Conversion for MMA (2nd assay)

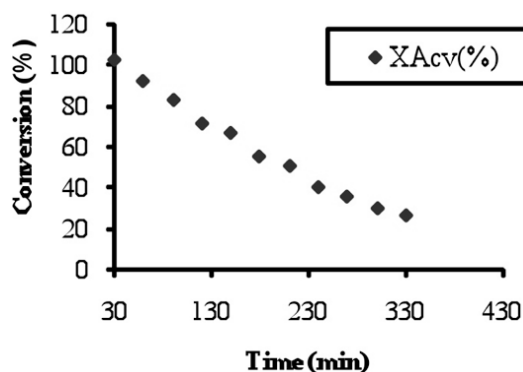


Figure 12. Variation of the Conversion for AVc (2nd assay)

The present study has demonstrated that gravimetric and chromatography (CPG) techniques can be applied to control the reactions of copolymerization in solution in a calorimetric reactor.

The results obtained from the offline control of copolymerization in solution MMA / AVc are well adapted for the follow-up of the reaction of polymerization and the control of the reactor temperature.

The data acquired by CPG show a good concordance with those resulting from the gravimetric. The obtained results show that this offline measurement technique allows improving the polymerization process by varying different operating parameters of the production process. This work can be pursued by involving other techniques such as the spectrometry for the on-line study and the monitoring of the copolymerization in solution.

REFERENCES

- [1] O.Kammona, E. G. hatzi, C. Kiparissides, *Journal of Materials Science, Rev. Macromol. Chem. Phys*, 57 C39, 1999.
- [2] A.Urretabizkaia, G. Arzamendi, M. Unzué, J. Asua, *Journal of Polymer Science (Part A: Polym.Chem.)*, 32, 1779.
- [3] H. Hua, M. A. Dubé, *Polymer Science*, 39 (11), 1860-1876, 2001.
- [4] R. Jovanovic, M. A. Dubé, *Journal Applied Polymer Science*, 82 (12), 2958-2977, 2001.
- [5] E. G. Chatzi, O. Kammona, C. Kiparissides, *Journal Applied Polymer Science*, 63 (6), 799 809, 1997.
- [6] H. Hong, A. Marc, M. A. Dubé, *Journal of Polymer Science*, 42, 6009-6018, 2001.
- [7] M. J. Scolah, H. Hua, M. A Dubé, Bulk and Solution copolymerization of methyl methacrylate and vinyl acetate, *Journal Applied Polymer Science*, 2001.

ABBREVIATIONS

- MMA: Methyl Methacrylate
 AVc: Vinyl acetate
 AIBN: Azobisisobutyronitrile
 X: Mass conversion
 CPG: Chromatography in gaseous phase
 E_s: Dry extract

4 CONCLUSION