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The On-Line Monitoring of Methyl Methacrylate – Vinyl Acetate Emulsion Copolymerisation

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SUMMARY: The emulsion copolymerization of methyl methacrylate and vinyl acetate has been studied using a pilot calorimeter in order to follow both the overall and individual conversion of monomer on-line.

Introduction

In order to follow the advancement of a polymerisation and to improve the control of polymer properties such as copolymer composition and glass transition temperatures that are often difficult to measure in real time, it is important to define control strategies that exploit the relationships between the polymer microstructure, polymer "quality" and process conditions. Before one can do this, it is necessary to possess a physical system that can be used to interpret on-line data and follow key physical quantities. These data can in turn be used in mechanistic models of the reaction to accurately predict the above-mentioned properties (and others should the need arise).

Efforts using calorimetry to follow the reaction have been widely discussed in the literature for several years[1,2,3)]. Some commercially available laboratory scale calorimeters require that the different terms in the energy balance be known a priori - in particular, the overall heat transfer coefficient UA. On the other hand, another tool has been developed[4,5,6)] that uses a combined hardware and software approach that allows us to estimate UA and the heat losses on-line with no a priori knowledge of them. This system is tested in the current work using the emulsion copolymerisation of methyl methacrylate (MMA) and vinyl acetate (VAc), a

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copolymerisation that is interesting for several reasons, the major one being that because of the complex phenomena that occur here (e.g. dynamic nucleation of particles, radical absorption/desorption, etc.) it is often difficult to model, especially in the face of perturbations to normal reactor operation.

The emulsion homopolymerisation of both VAc and of MMA, as well as their copolymerisation have been studied extensively in the literature[7,8,9,10,11,12,13,14,15,16,17)]. Models for such complex systems have been presented in the literature[1]. The only drawback is that it is necessary to know the termination rate constant for both polymers, as well as the cross-termination rate constant. Without an excellent model of the gel effect in copolymerisation, especially in systems such as VAc/MA, VAc/MMA or VAc/BuA, it is very difficult to have enough information to model $\bar{n}$ correctly. It is clearly useful to have tools that help us to follow/evaluate what is really happening in the reactor.

In what follows, we will use a calorimetric tool to follow both the overall and individual conversion of monomer on-line. These results, combined with off-line will allow us to obtain a better understanding of the evolution of the system.

Modelling

We can predict the individual monomer conversions in real time using on these measurements a non-linear state estimator based on a simple basic model of a batch polymerisation of the form[18)]:

$$\frac{dN_i}{dt} = -\mu(t)\left[M_i^P(t)\right]\left[k_{Pij}P_i(t) + k_{Pji}(1 - P_i(t))\right] \tag{1}$$

where:

$$\mu(\mathrm{t}) = \frac{\bar{n}(t).N_p(t)V_e}{N_a} \tag{2}$$

where N_i is the number of moles of monomer "i", $[M_i^P]$ the concentration of monomer "i" in the particles and P_i is the probability of finding a radical ending in a group "i". Note that the state estimator returns the value of N_1, N_2 and the parameter μ as a function of time.

Experimental

Batch emulsion copolymerizations of methyl methacrylate (MMA) and vinyl acetate (VAc) were carried out at 70^0C in a bench-scale calorimeter. The recipes used in these experiments are given in Table 1. Experimental conditions for synthesis and characterization are given in a previous paper[19)].

Table 1. Initial conditions for the emulsion copolymerisation of MMA and VAc.

	CP30-70	**CP50-50**	**CP70-30**
MMA	180	300	420
VAc	420	300	180
AOT-75*	4.0	4.0	4.0

All experiments: $NaHCO_3$: 1.84 g, KPS: 1.84 g, Water: 2400 g
* Sodium dioctyl sulfosuccinate - SDSS (75% SDSS in water 25%)

Results

The step-wise behaviour cited above is clearly evident on the graphs of Figure 1, where we can see that the vinyl acetate polymerises with a violent release of heat once the MMA has been entirely consumed. It is interesting to note that this increase in reaction rate is not due to secondary nucleation of particles as we pass from an MMA-dominated system to a VAc-dominated polymerisation. This can be seen from Figure 2 where it is clear that N_p, although a function of the initial composition of the mixture, is relatively constant during all three experiments when the reaction begins to accelerate. It can be concluded that although one might expect a certain amount of renucleation (sudden increase in the number of radicals in solution in the aqueous phase) when we are in what can essentially be treated as a homopolymerisation phase, the step-wise change in the rate of polymerisation is due to chemical effects only. This probably stems from the fact that the k_p for VAc at 60°C is on the order of 9460 l/mol/s and that of MMA is about 840 l/mol/s at the same temperature[20)]. Thus, even if $\bar{n}$ drops significantly, the reaction will still go very quickly once VAc begins to become the dominant radical in the reaction.

Although N_p is obviously a function of the relative amounts of the two different monomers, it does not seem to change significantly after the first 10 to 15 minutes of polymerisation, indicating that neither secondary nucleation, nor limited coalescence of the particles took place. The larger number of particles in the VAc-rich system is probably due to higher amounts of homogeneous nucleation. It is well-known that VAc is more soluble than MMA in water, and if all other things remain the same, one could logically expect more oligomers to be formed in systems where VAc is in high quantities.

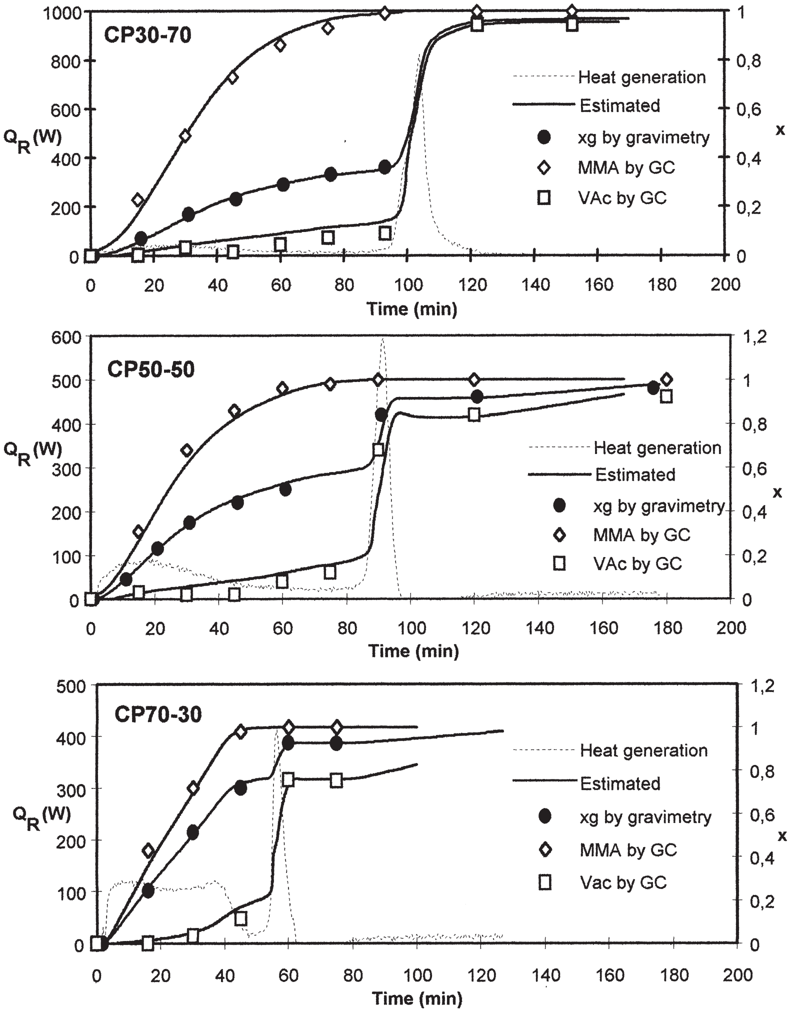

Figure 1 : Overall conversion and Q_R as a function of time for the emulsion copolymerisation of MMA and VAc.

Although the model is inexact (it doesn't include water phase polymerisation), the error in μ returned by the estimator will be quite small given that polymerisation in the aqueous phase will represent at most 1 or 2% of the total reaction rate. We can therefore use μ x *Np* to get a good estimate of how $\bar{n}$ varies in this system (Figure 3).

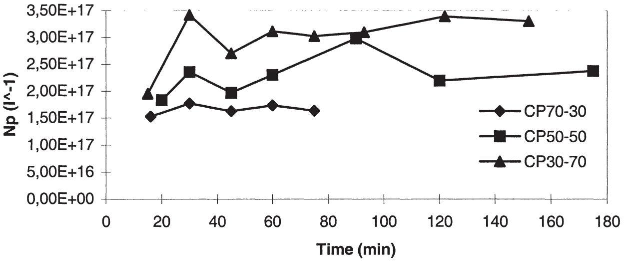

Figure 2: Evolution of *Np* as a function of time for the emulsion copolymerisation of MMA and VAc.

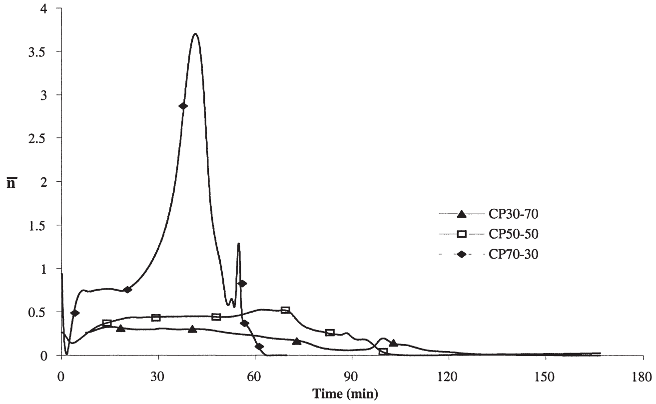

Figure 3. Evolution of $\bar{n}$ as a function of time for the emulsion copolymerisation of MMA and VAc.

Conclusion

In principle, this rapidly evolving, bi-functional behaviour should make it very difficult to follow the evolution of the reaction on-line - especially where the reaction changes from MMA to VAc polymerisation, but the robustness of the technique proposed here allows us to do so. The success of the system in estimating the real value of the conversion on-line is due to the adaptive nature of the approach, which allows us to obtain precise estimates of UA as it evolves in the reactor. Contrary to the case in a large number of the previously cited works, this technique allows one to follow UA regardless of what is happening in the reactor (short of total flocculation of course). So if there is temporary inhibition of the reaction for instance, we would be able to see it directly, and estimate its consequences on the advancement of the polymerisation.

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