Online Monitoring of Controlled Radical Polymerisation Reactions

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ABSTRACT

Monitoring the progress of polymerisation processes as they occur within a reactor has important implications for commercial polymer manufacture. Minimising reactor down time, optimising the product and increasing the efficiency of the process can have a high impact upon the profitability of polymer production. In this paper, the online monitoring of controlled free radical polymerisations shall be presented via high throughput experimentation. A variety of both chromatographic and continuous techniques for monitoring polymerisation processes to obtain 'snap shots' of the reactor contents shall be discussed. Parameters that may be monitored in this way include molecular weight and molecular weight distribution, viscosity and percentage conversion. Rapid liquid chromatographic methods that rely on sampling of the reactor, followed by a short column analysis and continuous techniques that give an instantaneous measurement of state, shall be compared and contrasted.

Introduction

- Monitoring the progress of polymerisation processes has important implications for commercial polymer manufacture

- Can lead to minimised down time, optimised product and increased process efficiency

- Continuous techniques can be used for monitoring polymerisation processes

- In this presentation the examples of online monitoring of radical polymerisations shall be discussed using PMC continuous methodologies

Typical Polymerisation System
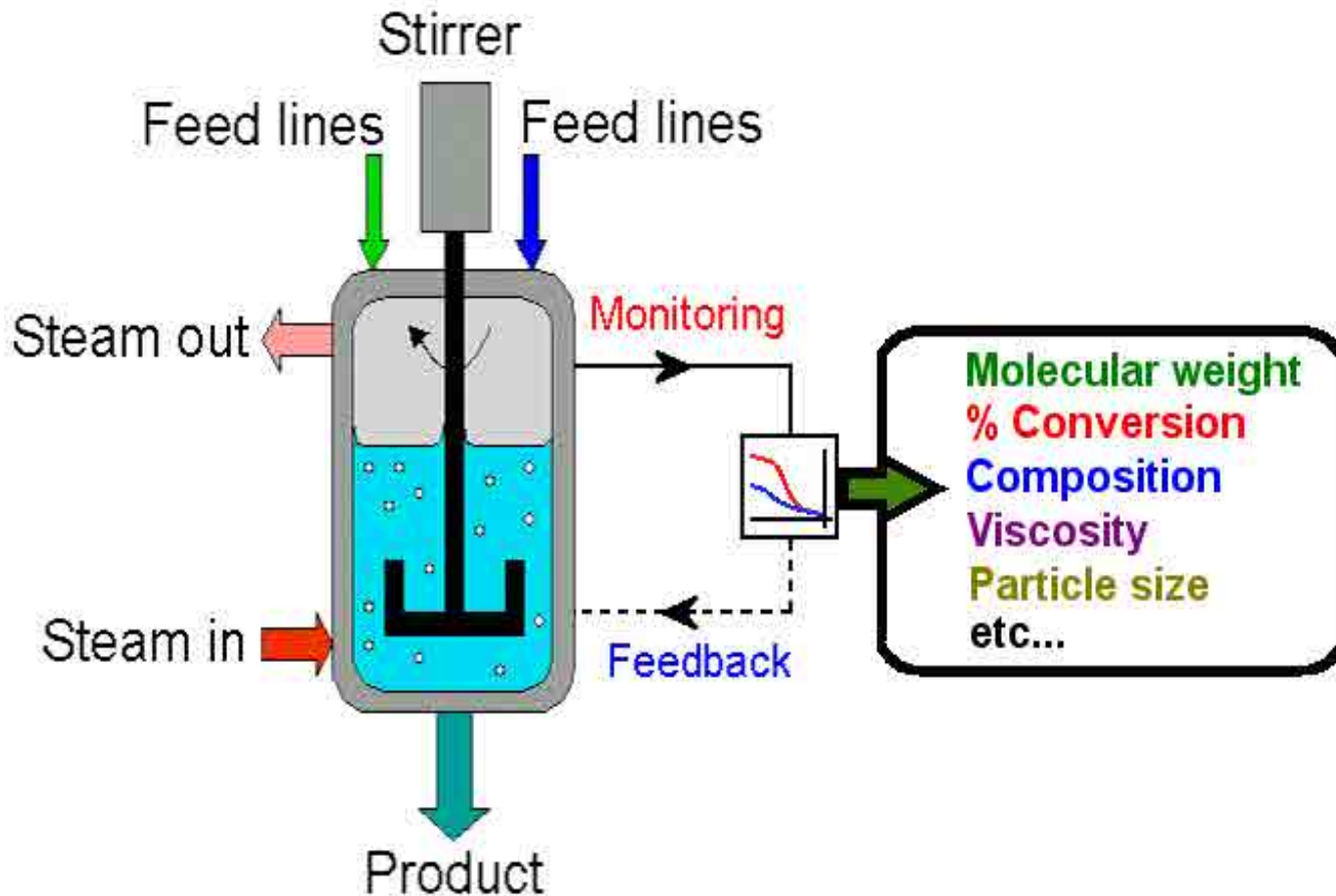
Goals of Online Monitoring

- Laboratory based analytical technique to aid in discovery and understanding of kinetics and mechanisms

- To optimize polymerisation reactions, both at the laboratory and pilot plant level

- Ultimately, to monitor and provide full feedback control for full scale industrial reactors
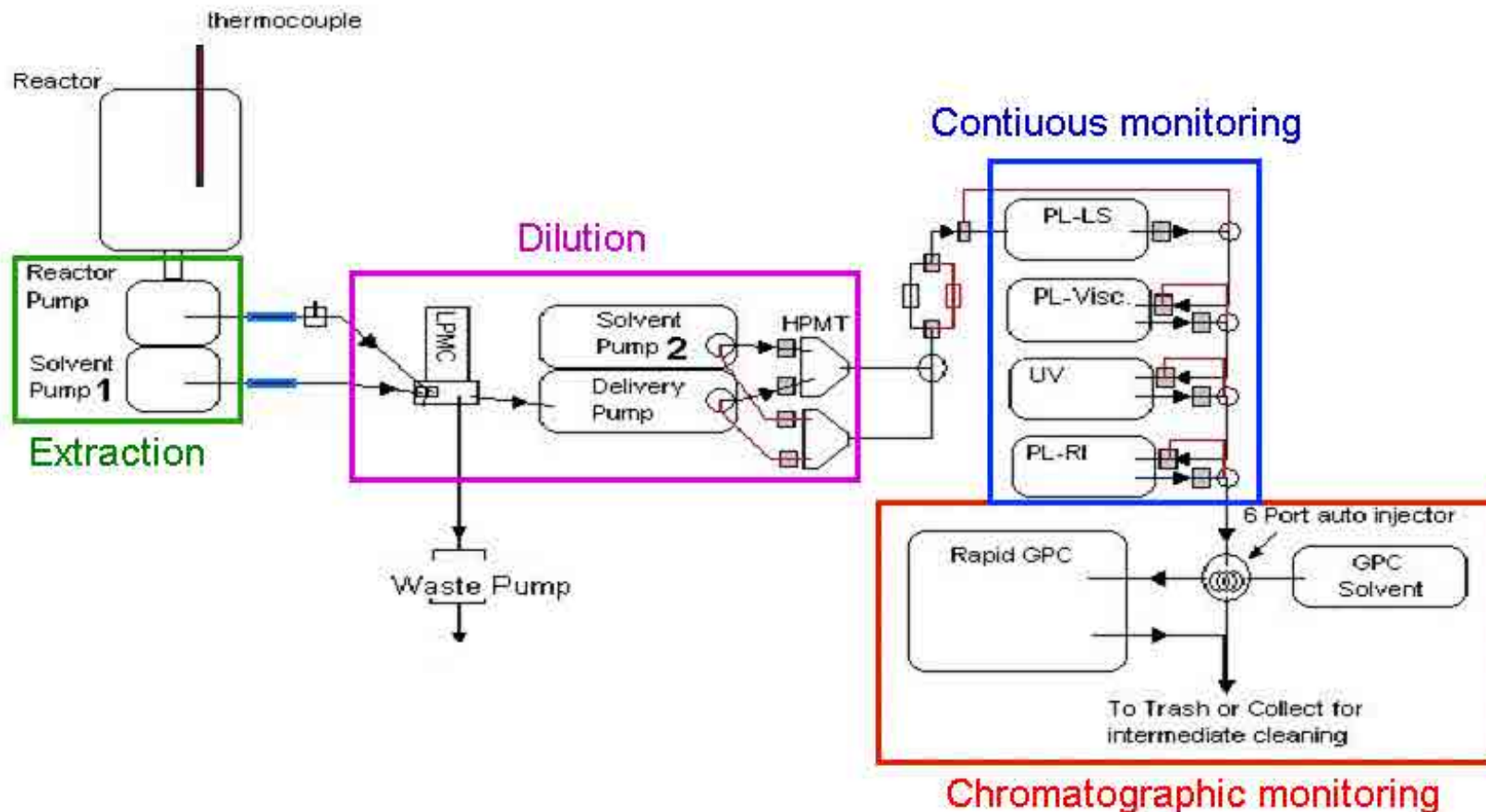
Principle of Online Monitoring

Continuously extract and dilute reactor liquid producing a stream through the chromatography system or detector train so dilute that detector signals are dominated by the properties of single polymers, not their interactions.

Continuous Monitoring Scheme

Extraction/Dilution

A small controlled stream, typically 100ul/min of polymer solution is extracted from the reactor using a

reactor pump

and delivered to a

low pressure mixing chamber (LPMC)

where a continuous stream of dilution solvent is introduced with a

solvent pump 1

a rate that effects a dilution ratio of typically, 10:1

Extraction/Dilution
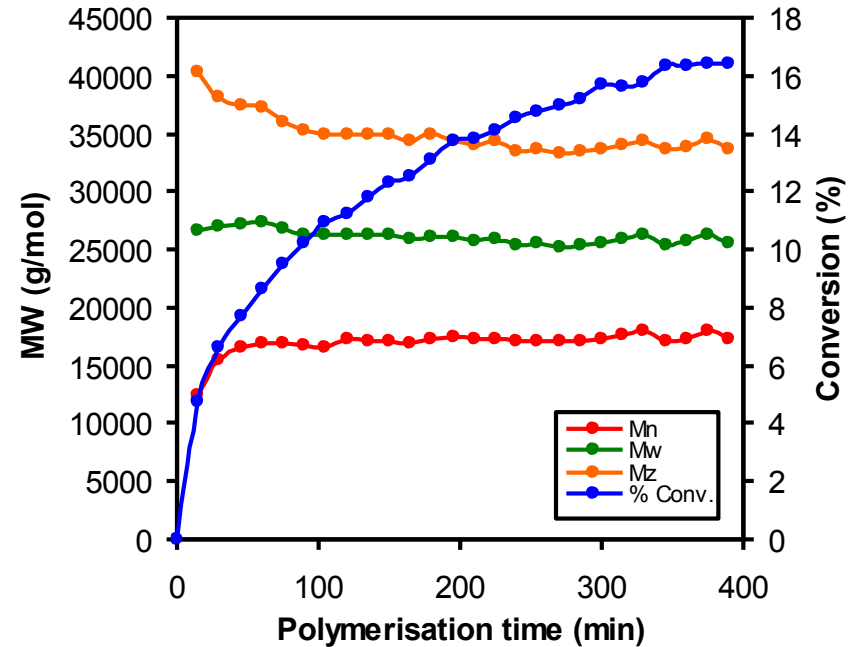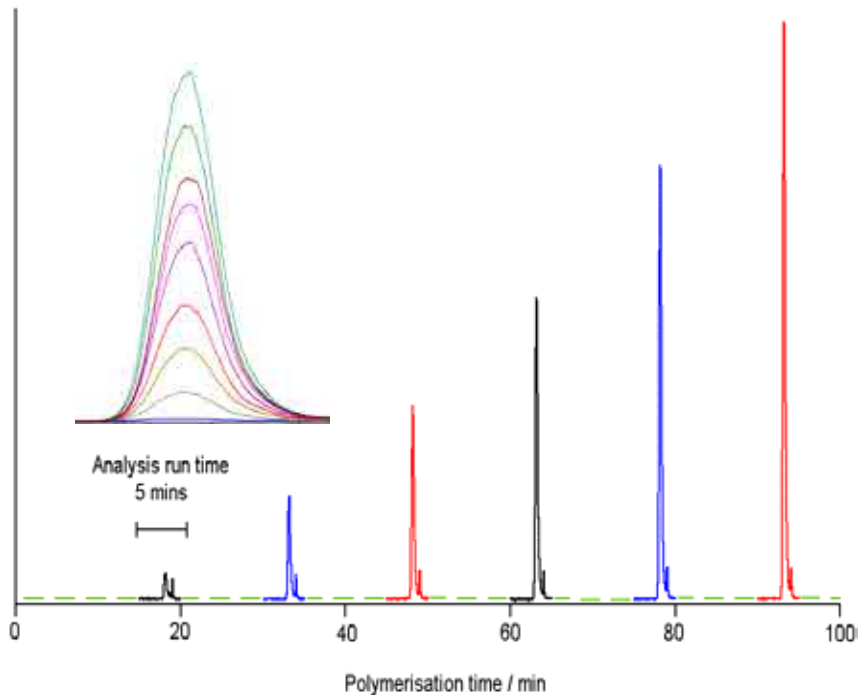
The diluted polymer solution is pumped using a

delivery pump

and is further diluted using

solvent pump 2

that effects a dilution ratio of typically 10:1 (giving an overall dilution ratio of 100:1) at an appropriate flow rate into the detector "train" consistent with the requirements of the detectors
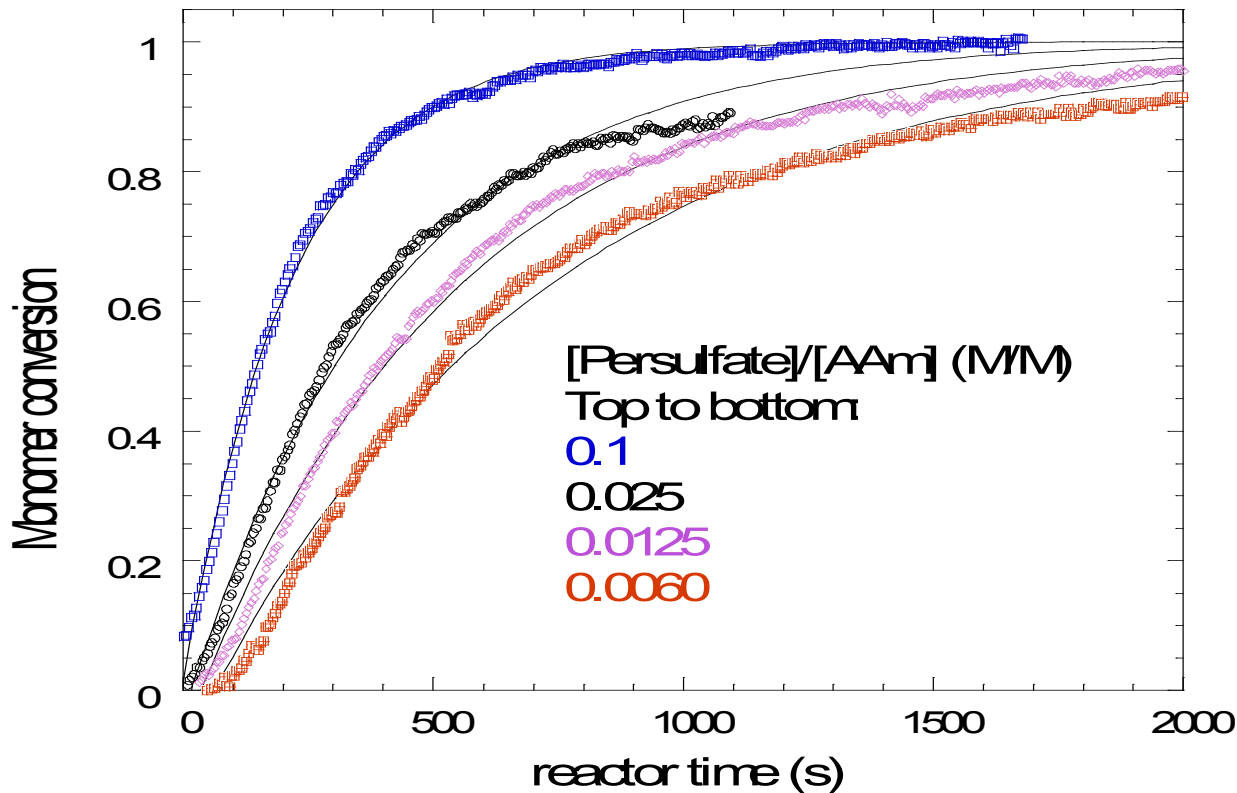
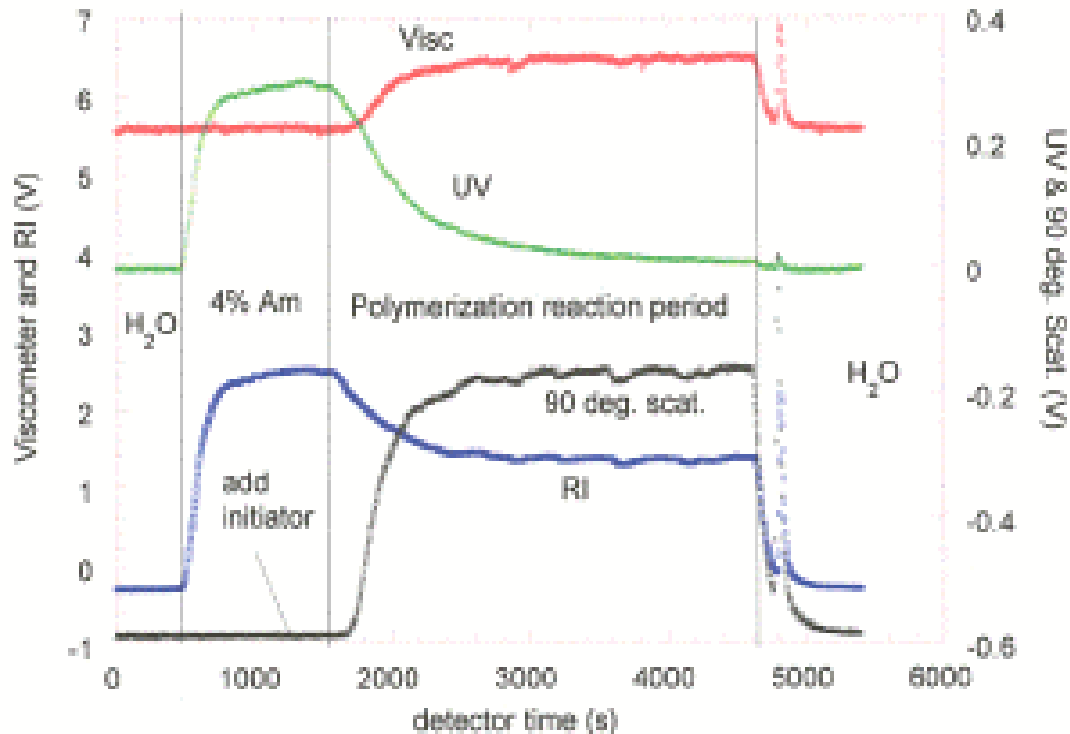# Case Study 1 - Polymerisation of Styrene

- Solution phase polymerisation of styrene in toluene using free radical initiation

- PL HTS-C (150x7.5mm) columns used with ELSD detection to monitor the reaction

- Monitor all the molecular weight averages as a function of polymerisation time

- During this initial stage of the reaction, molecular weights do not vary with time

Case Study 2 - Monomer Conversion Data: Free Radical Polymerisation of Acrylamide
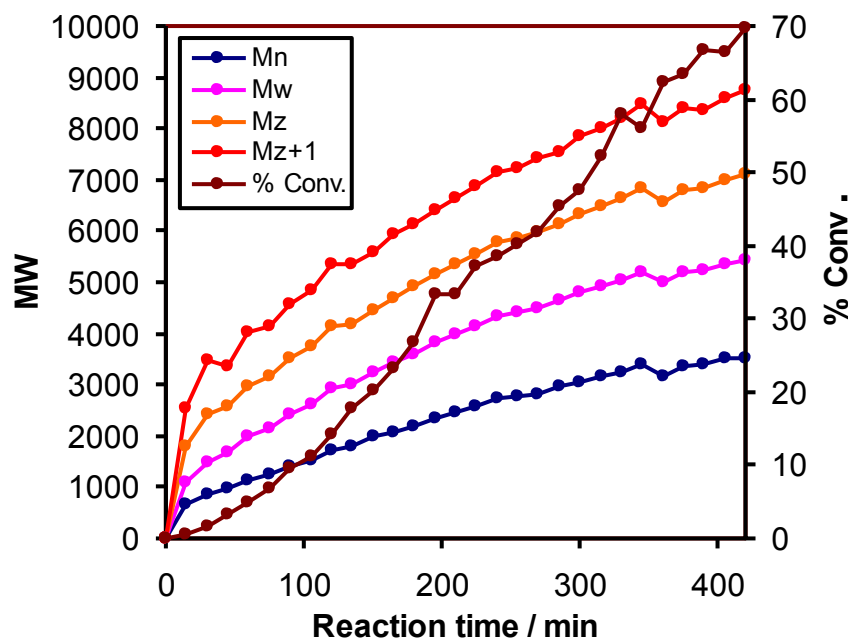
Case Study 3 – Continuous Monitoring of Acrylamide Polymerisation
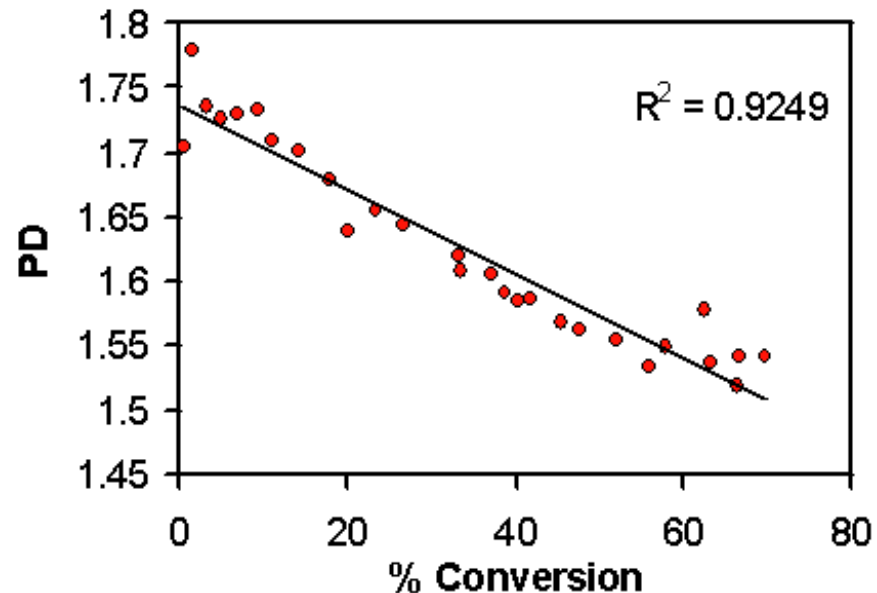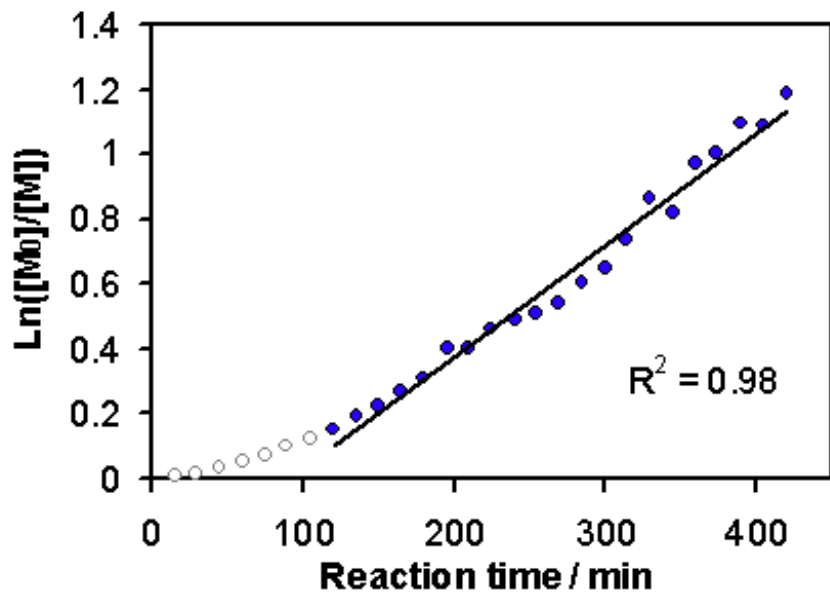

Raw data for acrylamide polymerisation with sodium persulfate at T=70C. 4% AAm

Case Study 4 – Random Atom Transfer Radical Polymerisation of Styrene and MMA


- Cu(I)Br/bipyridine mediated polymerisation in toluene initiated with Ethyl 2-bromoisobutyrate

- Steady growth in Mn (and other averages) typical of a pseudo 'living' polymerisation
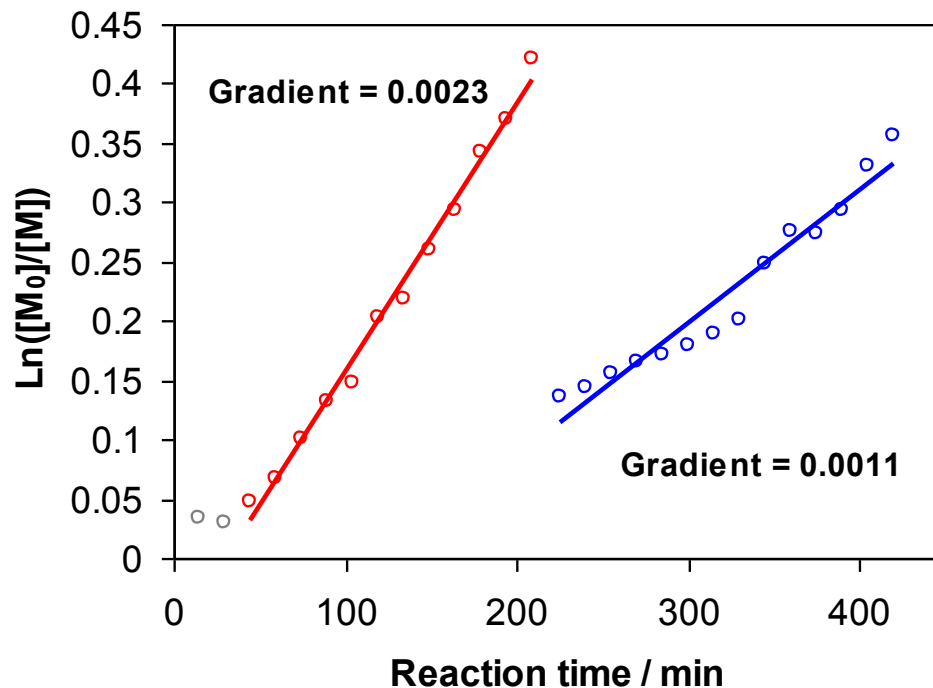
- Conversion data can be combined with molecular weight data to generate kinetic information

- Polymerisation showing pseudo 1st-order behaviour as expected for an ATRP reaction

- Relatively broad PD could be associated with the presence of inhibitors in the monomer

Case Study 5 – 'Blocky' Atom Transfer Radical Polymerisation of Styrene and MMA
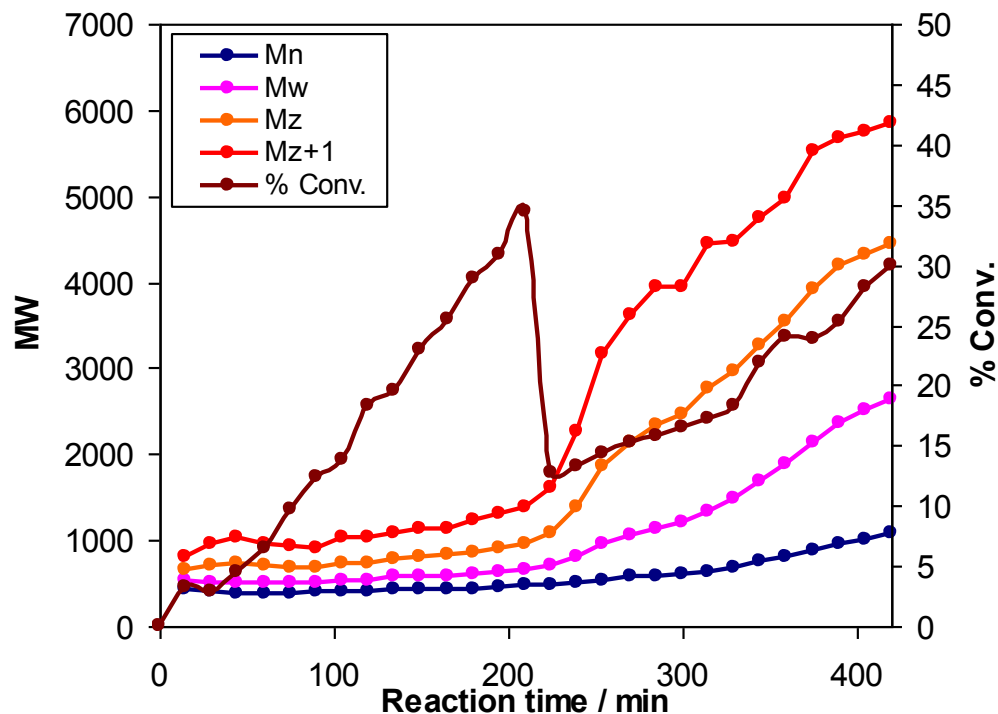

- Polystyrene block grown first, followed by a mixed styrene/MMA block
- Reaction is diluted by monomer and solvent during the second step
- With the addition of the MMA polymer chain lengths increase dramatically

- Conversion and molecular weight data can be combined to give kinetic information

- Pseudo 1st order kinetics observed as expected

- Reaction is diluted by monomer and solvent during the second step so the relative reaction rate halves
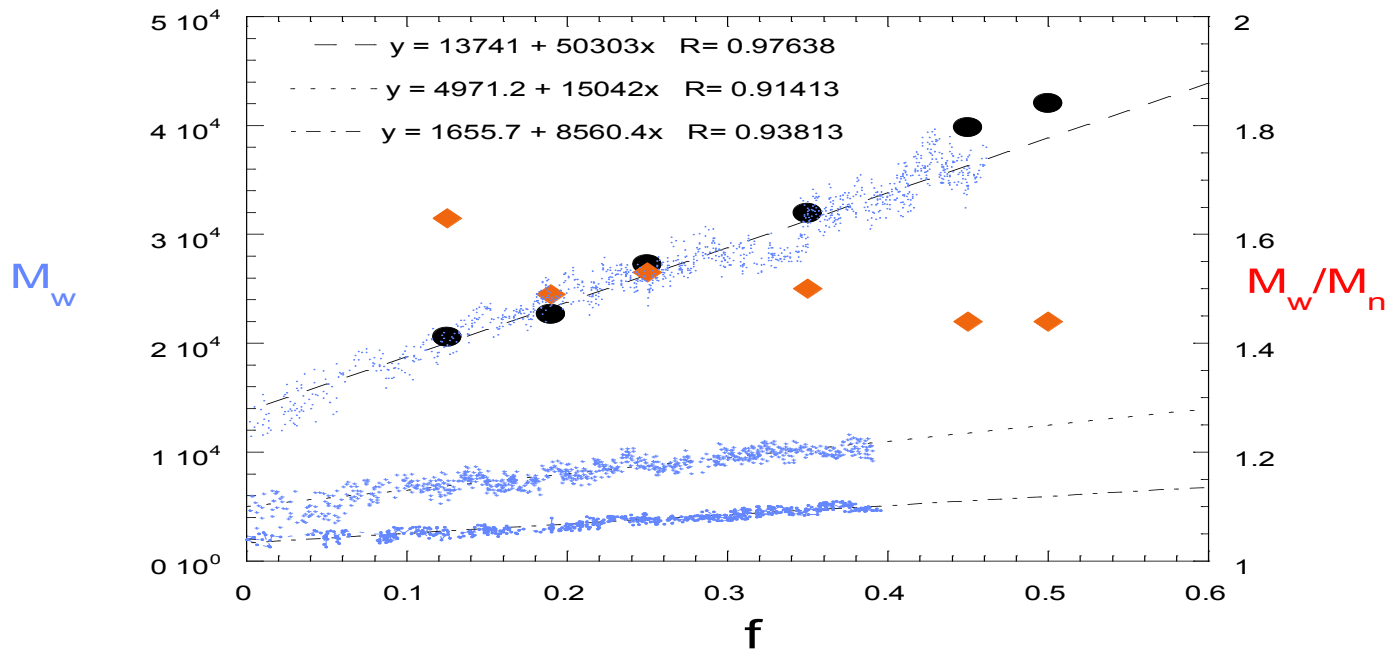
Case Study 6 - Example of Continuous Measurement
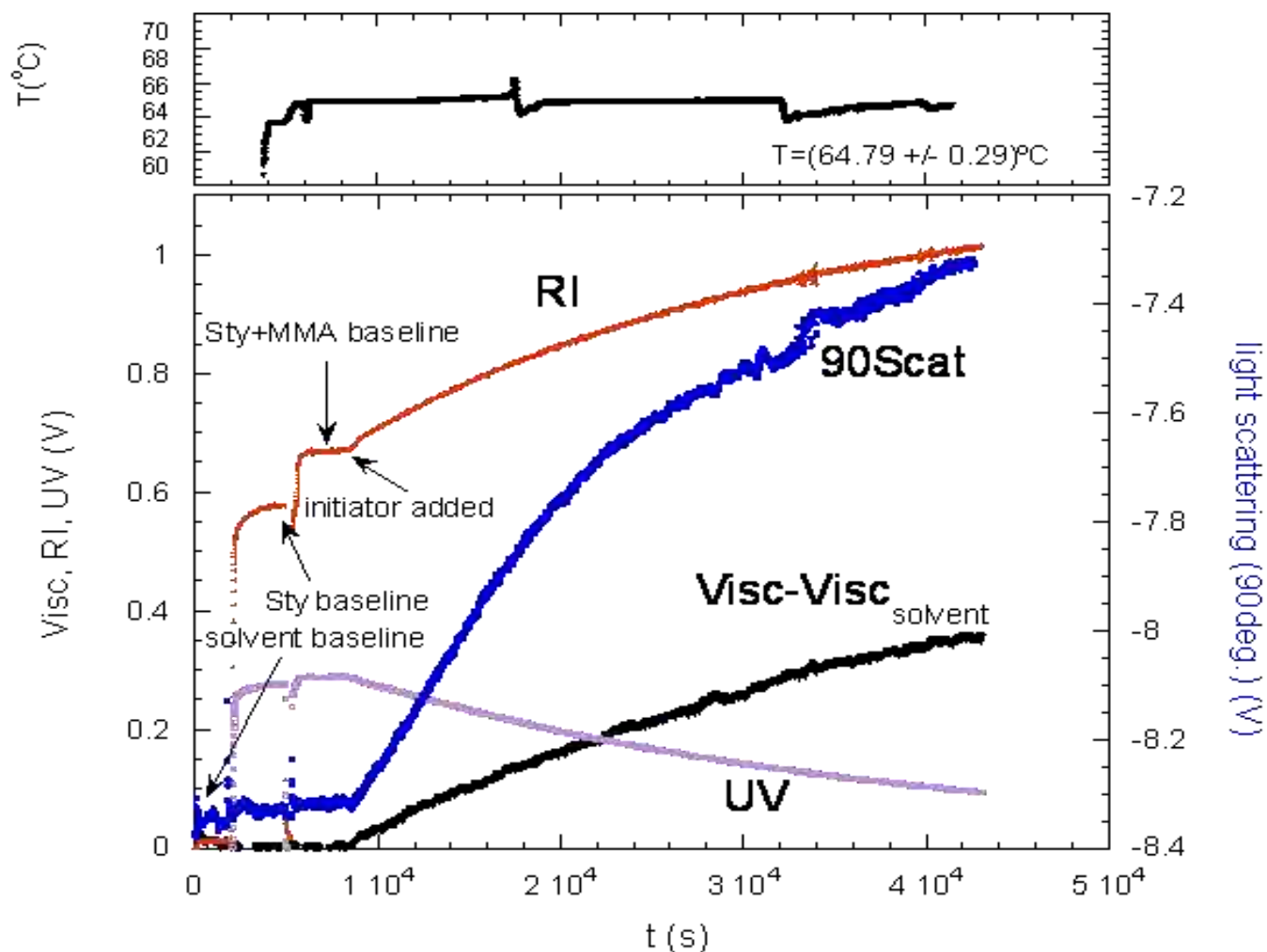
Case Study 7 - Example of Continuous Measurement – System Interruptions
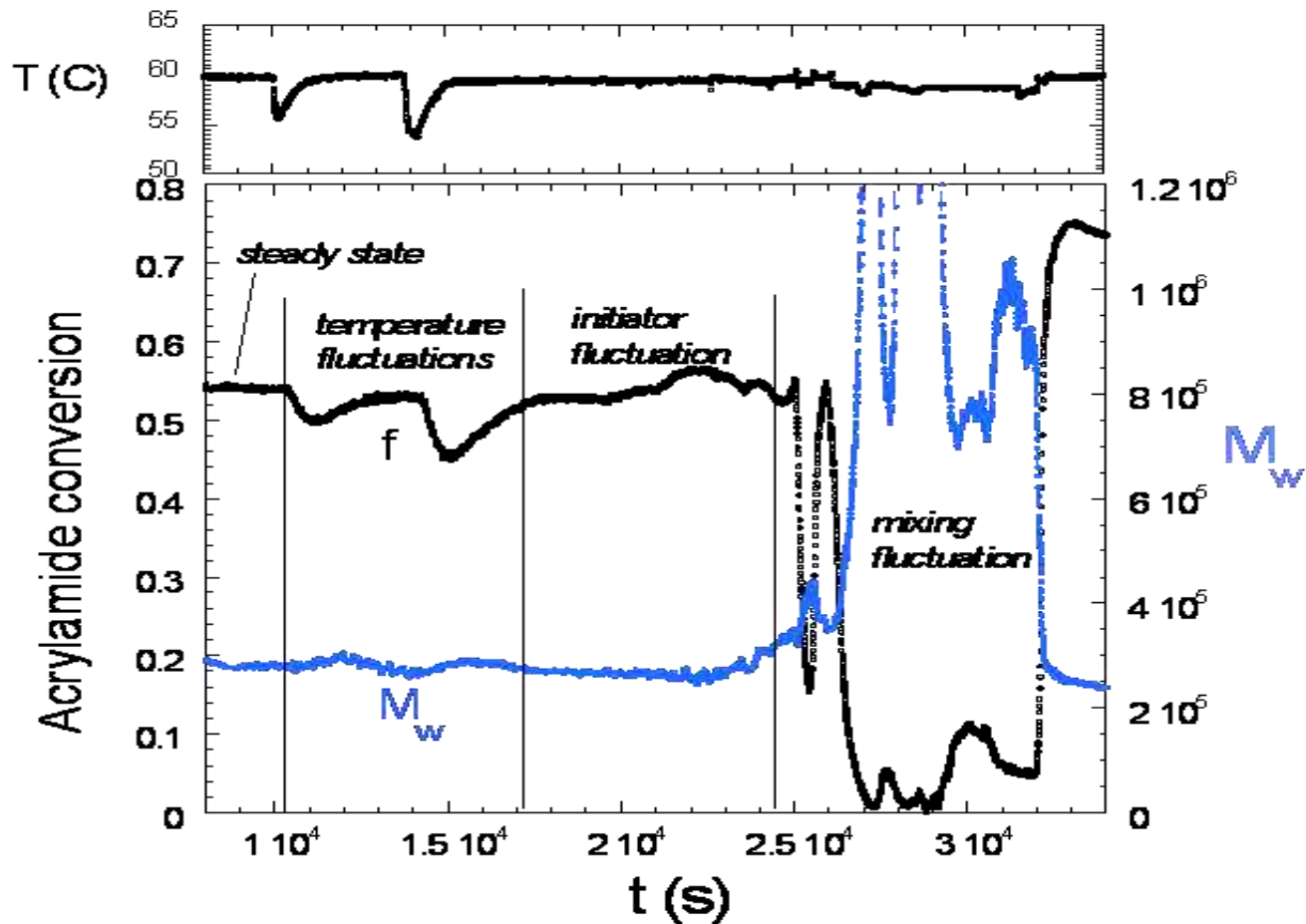
Case Study 8 - Controlled Radical Polymerisation (SG1/BuAcr)

(From Chauvin, Alb, Bertin, Tordo, Reed, Macromole. Chem., 203, 2029, 2002)

PMC measurements correlated with conventional GPC for three reactions

■ Mw by GPC   ■ Mw/Mn by GPC

Conclusions

- Online monitoring of polymerisation reactions by liquid chromatography and continuous monitoring techniques can provide key information

- Molecular weight averages and conversions as a function of reaction time can be determined by rapid GPC

- Molecular weight distribution can also be determined by continuous monitoring by applying modelling to the sample

- Online monitoring could provide potential for carefully controlling polymerisation reactions, greatly improving product quality and production efficiency