

## Kinetic Study of the Solution Polymerization of Methacrylamide Initiated with Potassium Persulfate Using in-Situ Raman Spectroscopy and Novel Multivariate Data Analysis – Band-Target Entropy Minimization (BTEM)

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### Abstract

With the increasing demand for novel process analytical technologies in recent years, Raman spectroscopy has been one of the powerful choices for in-situ reaction monitoring. In this paper, we discuss the use of in-situ Raman spectroscopy and the novel multivariate data analysis method, Band-Target Entropy Minimization (BTEM), to monitor the polymerization of methacrylamide using potassium persulfate (KPS) as the initiator. Kinetic studies were carried out varying the following conditions: initial monomer concentration, initial KPS concentration and polymerization temperature. In-situ Raman spectroscopy is employed to continuously measure the contents of the reaction mixture for a few hours. The collected reaction spectra are then subjected to BTEM to elucidate the pure component spectra, the concentration profiles of the components and the conversion of the monomer. The conversion data is then used together with optimization tools to obtain kinetic parameters for the polymerization.

### Introduction

Raman spectroscopy has been applied as an *in situ* monitoring tool to a wide variety of polymerizing systems of vinyl monomers. Most notably, the kinetics of styrene polymerization has been extensively investigated<sup>1-4</sup>. Other systems investigated include derivatives of acrylic acid and other vinyl ester monomers<sup>3, 5, 6</sup>. While the absence of sampling procedures renders spectroscopic techniques more favourable for real-time analysis, the advantages of Raman spectroscopy over infrared (IR) spectroscopy are well known in kinetic studies<sup>1</sup>. While IR spectroscopy measures transmission and requires preparation of thin sample layers, Raman spectroscopy, which works by a scattering process, is able to examine samples in bulk. The aqueous medium of the polymerization process gives rise to little problem in Raman compared to IR spectroscopy since water gives rise to very weak Raman scattering. The addition of initiator, which is usually low in amounts, also doesn't interfere with the system's Raman spectra. This is because Raman spectroscopy, which produces spectroscopic data based on the weak Stokes scattering, is insensitive to low concentrations. In all, Raman spectroscopy as a non-invasive and non-destructive tool is ideal for examining the kinetics of a polymerizing system in aqueous solution.

This paper extends the application of *in situ* Raman spectroscopy to the monomer methacrylamide. It also develops the method of investigating a liquid system with the InVia Reflex Renishaw Raman microscope, thereby proving that it's possible to obtain reproducible data while eliminating any contact between the analytical tool and the polymerizing system.

## Results and Discussion

Three series of polymerization reactions were carried out, each varying 1) initial monomer concentration, 2) initial KPS concentration and 3) polymerization temperature respectively. All Raman spectra collected from these three series of reactions were combined into one data matrix and preprocessed with adjacent 5-point smoothing to reduce noises, and then with background fluorescence subtraction using a third-order modified polynomial fitting. Next, BTEM<sup>7-11</sup>, a novel self-modeling curve resolution technique, is used to extract Raman spectra for the pure components in the system –namely aqueous methacrylamide, aqueous poly-methacrylamide and the quartz flow cell background – from the multi-component mixture spectra acquired from *in situ* monitoring.

Using multivariate data analysis such as BTEM increases the accuracy of data analysis, which accounts for the whole spectral information. Firstly, the pure component spectra of observable components in the reaction mixture spectra are resolved, and secondly, signal contributions of these observed components are obtained by solving the associated inverse problem using the pure component spectral information. In the current study, the contributions of each individual component to the total measured spectra were back-calculated using resolved BTEM pure component spectra of monomer, polymer, and background. This generated concentration profiles of each pure component, which were then normalized against the background concentration profile. The fractional conversion profiles of the monomer could be calculated from the background-normalized monomer concentration profile.

In radical polymerization reactions, the empirical expression for monomer consumption rate is:

$$R = -\frac{d[M]}{dt} = k_{eff} [I]^a [M]^b$$

While the conversion of the monomer,  $X_M = \frac{[M]_0 - [M]}{[M]_0}$ , and taking initiator concentration to be constant, the rate could be expressed in terms of conversion as the following:

$$R = -\frac{d[X_M]}{dt} = k_{eff} [I_0]^a [M]_0^{b-1} (1 - [M])^b$$

The value of a, b and  $k_{eff}$  were assumed to be invariant at the same temperature over various initial monomer and initiator concentrations. Fitting the rate expression into the data in the first two series of experiments, the optimal values of a and b were found to be 0.554 and 1.408 with an average fitting error of 7.6% for monomer conversions up to circa 65%. Next, fitting the rate expression to the data in the third series of experiments yielded the values of  $k_{eff}$  at their corresponding temperatures of polymerization. The resultant Arrhenius plot gives good linearity and shows that the activation energy of the polymerization of methacrylamide initiated with KPS in aqueous solution is about 121 kJ/mol.

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