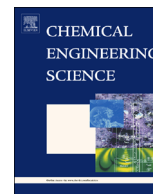




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In situ monitoring of acrylic acid polymerization in aqueous solution using rheo-Raman technique. Experimental investigation and theoretical modelling



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HIGHLIGHTS

- In situ monitoring of acrylic acid polymerization in aqueous solution was carried out.
- Coupled rheology and Raman spectroscopy data were correlated to reaction progress.
- A theoretical model was proposed combining kinetic scheme and rheological equations.
- Experimental values were depicted over a wide range of reaction and process conditions.
- Gel effect occurrence was mapped vs. reactant concentrations and applied shear rate.

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ABSTRACT

Acrylic acid free radical polymerization in aqueous solution was studied using a new experimental setup coupling Raman spectroscopy and flow rheology in a Couette-like geometry. In situ monitoring of polymer concentration and viscosity of reaction medium versus time was carried out, for different reactant concentrations (acrylic acid and initiator) and process conditions (temperature and shear rate). Experimental variations of polymer concentration and reaction medium viscosity before the occurrence of gel effect as a function of reactant concentration and process conditions were obtained. An overall model combining kinetic scheme and rheological equation was proposed. Kinetic and rheological parameters of the model were identified and found consistent with literature. Gel effect was detected as a sharp increase of polymer concentration much faster than the calculated trend. The occurrence of gel effect was mapped as a function of monomer feed concentration and shear rate. These lab-scale data provided experimental and theoretical bases for process scale up to pilot-scale plant.

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1. Introduction

Water-soluble monomers like acrylic acid or acrylamide are used for preparing specialty polymers for applications like personal care or home care products, waste water treatment additives (flocculants), rheology modifiers... (Marinic Pajc and Janovic, 2003; Spychaj, 1989). Free radical polymerization has been widely used for polymerizing previous monomers. For these applications

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high molar masses were often suitable. Over the last decade, there has been a strong interest for intensification of chemical processes, which involved, amongst others, using more concentrated reaction media, increasing heat transfer and reducing reaction times. This trend also applied to polymerization reactors (Coselli Vasco de Toledo et al., 2005; Gharaghani et al., 2012; Leveson et al., 2004; Liu et al., 2013). With homogeneous reaction media, the progress of polymerization reaction has direct consequences on the rheological behavior and on the level of viscosity of the reaction medium. This induces strong modifications in heat and mass transfer and thus has to be taken into account when designing the process. Obviously, this effect is much more pronounced when using concentrated reaction media. Apart from heat and mass

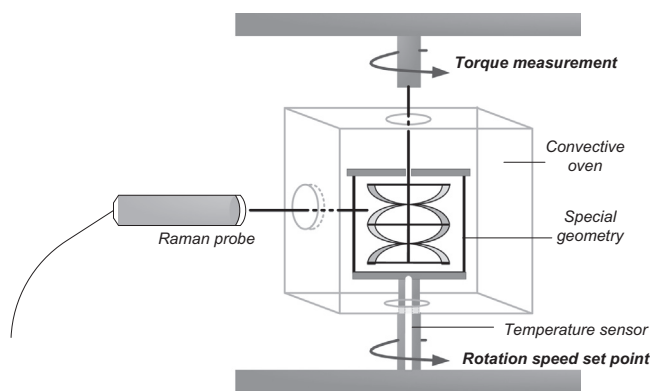


Fig. 1. Experimental device for coupled rheological and Raman spectroscopy measurements.

transfer, the rates of chemical reactions are also modified. Indeed, in bulk or concentrated homogeneous reaction media where free radical polymerization is carried out, gel effect is known to occur when monomer conversion becomes high enough, which corresponds to a high viscosity of the reaction medium (O'Neil et al., 1998). Gel effect results in a sharp increase of reaction rate which is accompanied by a strong heat release. This phenomenon represents a significant risk of reaction runaway (heat transfer being increasingly impeded because of rising viscosity). It is generally admitted that gel effect is caused by the decrease of the rate of diffusion of reacting species, and particularly growing macro-radicals. Consequently, the rate of termination elementary reactions is strongly reduced as compared to other elementary reactions like propagation or initiation (Achilias, 2007; Chiu et al., 1983; Garcia et al., 2002; O'Neil and Torkelson, 1999; Tulig and Tirrell, 1981). Initiation step involves only small molecules and radicals whose diffusion rate is not strongly affected by viscosity. Propagation reactions involve monomers and growing radicals and consequently are slowed down upon viscosity increase. Finally, termination reactions involve two growing radicals and are thus strongly affected by viscosity increase. The overall effect is a strong increase of the rate of monomer consumption because of the increased radical concentration.

Gel effect has been investigated particularly in the case of bulk polymerization of styrene and acrylate monomers like methyl methacrylate. Experimental studies and theoretical models have been reported (Srinivas et al., 1996). In the particular case of acrylic acid, only a few papers dealt about gel effect and none of them provided data relating process conditions to the occurrence of gel effect (Barth et al., 2012; Bortel et al., 1998; Buback et al., 2007; Catalgil-Giz et al., 2004; Cutié et al., 1997; Kuchta et al., 2000; Lacik et al., 2001; Lacik et al., 2003; Lacik et al., 2004; Lorber et al., 2010; Scott and Peppas, 1997).

When considering the available literature, it appeared that experimental studies of gel effect generally focused on one particular aspect, either the overall polymerization rate or the rheology of reaction medium. Very few papers reported experimental setups convenient for acquiring data about reaction progress and rheology of reaction medium (Botella et al., 2004; Kale and O'Driscoll, 1982). Recently, we introduced a new experimental device coupling Raman spectroscopy to rheological measurements in a Couette-like geometry (Chevrel et al., 2012). We showed that this setup allowed an easy non intrusive, in situ monitoring of monomer conversion and viscosity of reaction medium under defined shear rates. In addition, thanks to Couette analogy, it was possible to use mixer-type geometry while keeping the ability to determine reliable values of viscosity under defined shear rate conditions (Ait-Kadi et al., 2002). Since acrylic acid is an important

industrial monomer, it appeared that there was a need for developing models of polymerization reactors supported by experimental data that could be used for reliable design and optimization of industrial plants. The combination of rheo-Raman coupled technique with a reactor-like rheometer and mathematical modelling of reaction medium appeared as a relevant way to provide such knowledge.

In that study, we investigated free radical polymerization of nonionized acrylic acid in moderate and concentrated aqueous solutions (up to 60 wt%) initiated by potassium persulfate using coupled spectroscopic and rheological measurements in a reactor-like geometry. Operational parameters like reactant concentrations (monomer and initiator), temperature and shear rate were systematically varied. Experimental data about monomer conversion and rheology of reaction medium were compared to calculations based on a kinetic model and rheological equations taken from literature.

2. Material and methods

2.1. Coupled rheology and Raman spectroscopy setup

An original setup coupling rheological measurements and Raman spectroscopy has been developed during this study and was described in detail in a previous paper (Chevrel et al., 2012). It included a rheometer equipped with a laboratory-made geometry: a small-scale batch reactor of 15 ml mixed by a double helical ribbon (Fig. 1). Its glass wall permitted using of an external Raman probe for in-situ analysis of reactive mixture. The temperature was measured by a temperature sensor placed at the bottom of the geometry and it was controlled by the convective oven of the rheometer. It was possible to heat-up and to perform polymerization reactions in the device while monitoring both viscosity and monomer conversion.

2.2. Calibration of the rheometer and the Raman signal

Viscosity can be extracted from rheological measurements realised in a Ares G2 rheometer (TA instruments). The small-scale tank is moved at a given rotation speed which corresponds to a certain shear rate while torque is measured on the motionless mixer. An appropriate calibration, including a Couette geometry analogy and measurements of reference Newtonian fluids, was performed in order to deduce viscosity from torque measurements. This preliminary step was done following the procedure described by Ait-Kadi (Ait-Kadi et al., 2002). A measure per second was realised for every experiment.

Raman spectroscopy was chosen to monitor solution polymerization of acrylic acid because water signature is weak and monomers generally present a strong response (Fonseca et al., 2009). The measurements were proceeded with a RXN1 (Kaiser Optical Systems) with a non contact fiber optic probe offering a spectral resolution of 1.5 cm^{-1} . The laser excitation wavelength was 532 nm and the laser power was 100 mW. Specific signature of the three species, monomer, polymer and water were found in Raman spectra corresponding to one of the vibration mode of the double bond of monomer (C=C) at 1635 cm^{-1} , of one of the asymmetric C-H bond of the polymer at 2935 cm^{-1} and of the O-H bond of water at 3400 cm^{-1} (Fig. 2). Monitoring of conversion was achieved by using the area of the polymer peak at 2935 cm^{-1} . Similar results could be obtained with the peak of monomer (Fig. 2). However, the use of peak area at 2935 cm^{-1} seemed to be more sensible especially at low monomer conversions. Normalization of the signal was done on the water signature as its quantity remained constant along the reaction. Nevertheless,

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