Chemical Engineering Science 173 (2017) 493–506

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

# Real time monitoring of the quiescent suspension copolymerization of vinyl chloride with methyl methacrylate in microreactors – Part 3. A kinetic study by raman spectroscopy and evolution of droplet size

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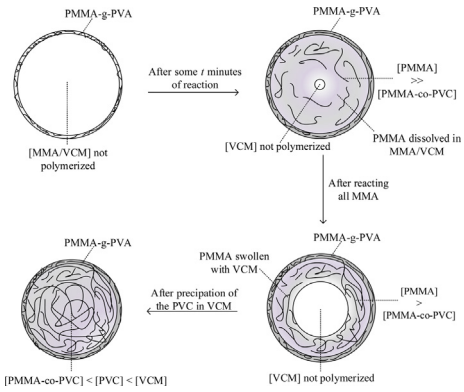
## HIGHLIGHTS

- Experimental work on the suspension copolymerization of VCM with MMA by using microreactors.
- The reaction kinetics was monitored by Raman spectroscopy.
- Evolution of the particle volumes was monitored and correlated to monomer conversion.
- Performances between bifunctional and monofunctional initiators were compared.
- A new mechanism based on the results from both video camera and Raman spectroscopy is proposed.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 2 May 2017
Received in revised form 1 August 2017
Accepted 12 August 2017
Available online 14 August 2017

*Keywords:*
Microreactors
Suspension copolymerization
Raman spectroscopy
Kinetics
Vinyl chloride
Methyl methacrylate

## ABSTRACT

The present work presents results on the copolymerization kinetics of methyl methacrylate (MMA) and vinyl chloride (VCM) monitored by Raman spectroscopy and on the evolution of droplets as captured by charge-coupled device (CCD) camera in a microcapillary reactor. Different experimental recipes were proposed using commercial initiators in order to compare the system performance when initiated with monofunctional and bifunctional peroxides. The experimental setup was able to capture the distinct stages of the copolymerization within a microreactor up to high conversions (>90%) in quiescent state. It is shown that the copolymerization of MMA with VCM leads to distinct morphological structures, when compared to VCM homopolymerization, forming a core and a shell after a certain critical conversion. A new mechanism is proposed for the copolymerization based on the results from both video camera and Raman spectroscopy.



## 1. Introduction

The usage of microreactors has increased steadily in the chemical engineering field (Jensen, 2001; Pattekar and Kothare, 2004; Sun et al., 2008; Chang et al., 2004; Iwasaki and Yoshida, 2005; Richard et al., 2013) and in other areas of study (Zhang et al., 2004; Salic et al., 2012; Massignani et al., 2010). The application of this technology has been proposed originally to allow for small-scale production and became a reality in the late 1980s and early 1990s (Benson and Ponton, 1993). In order to provide higher flexibility and allow for assessment of the capacity, safety

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http://dx.doi.org/10.1016/j.ces.2017.08.018
0009-2509/

and variability of the real process in a realistic way, microreactors should be regarded as complementary apparatuses for other existing large-scale facilities (Lerou et al., 1996; Wegeng et al., 1996). It is important to emphasize that microreactors may exhibit characteristic dimensions of the order of millimeters and sub-millimeter (Pattekar and Kothare, 2004; Richard et al., 2013).

Microreactors find potential use in many applications, including biocatalysis (Fernandes, 2010), biodiesel production (Sun et al., 2008; Richard et al., 2013), heterogeneous catalysis (Kiwi-Minsker and Renken, 2005), drug synthesis (Kang et al., 2008; Leroyer et al., 2013), hydrogen production (Pattekar and Kothare, 2004), photocatalysis (Gorges et al., 2004) and polymerization processes (Bodoc et al., 2012; Bally et al., 2010; Castor et al., 2015, 2016; Mahadevan et al., 2016). Following the general principles of the Green Chemistry, microreactors can be used to synthesize and purify organometallic compounds by atomic layer deposition (ALD) and chemical vapor deposition (CVD), allowing for safe operations and production of chemicals with higher degree of purity (Lipiecki et al., 2008, 2009).

Few studies have examined the free radical copolymerization of VCM in the literature. Tables 1 and 2 show the main patents and papers, respectively, regarding both mass and suspension copolymerization of vinyl chloride. It is worth mentioning that almost 81% of the PVC world production is based on suspension polymerization processes (Anon, 2011). Table 1 also highlights processes copolymerizations with some comonomers such as methyl methacrylate, acrylic acid esters and maleic anhydride. From Table 2 it becomes clear that the elasticity properties of the PVC have been improved when some particular comonomers are used, as reported by Kitamura et al. (1973) and Yong-Zhong et al. (2000), who also used a multifunctional monomer ethylene glycol dimethacrylate.

**Table 1**
Comonomers used in some patents to both mass and suspension polymerization based on vinyl chloride.

| Comonomers | Polymerization Processes | Authors |
|---|---|---|
| VCM/propylene-ethylene | Suspension | Müllner and Albert (1967) |
| VCM/ethylene | Suspension | Kamio et al. (1970) |
| MMA-g-PVC | Suspension | Williams (1970) |
| VCM/epichloridryn | Mass and Suspension | SOLVAY (1971) |
| VCM/vinyl actetate | Suspension | Yonkers et al. (1971) |
| poly(ethylene) in VCM | Suspension | Reiter and Reventas (1973) |
| VCM/ester monomers | Mass and Suspension | Kitamura et al. (1973) |
| VCM/esters of acid acrylic | Suspension | SOLVAY (1975) |
| VCM/poly(vinyl isobutyl ether) | Suspension | Sielfeld (1984) |
| VCM/maleic anhydride | Suspension | Martyak (2010) |

**Table 2**
Comonomers used in some papers of both mass and suspension VCM-based polymerizations.

| Comonomers | Polymerization processes | Authors |
|---|---|---|
| VCM/vinyl acetate | Mass | Marvel et al. (1942) |
| VCM/vinyl acetate | Suspension | Emmer and Bankoff (1954) |
| VCM/vinyl esters | Suspension | Port et al. (1955) |
| VCM/MMA | Mass | McNeill and Straiton (1977) |
| poli(butyl acrylate) in VCM | Mass | Walsh and Cheng (1982) |
| VCM/butyl acrylate | Suspension | Macho et al. (1998) |
| VCM/ethylene glycol dimethacrylate | Suspension | Yong-Zhong et al. (2000) |
| VCM/MMA | Suspension | Bichuch et al. (2003) |
| poly(butyl acrylate) in VCM | Suspension | Yuan et al. (2007) |

The applications of VCM-based copolymers and their characteristics are determined by the chemical nature of the comonomer (Flory, 1953) and their relative the comonomer concentration in the polymer chains. Attempts to cover a wider range of properties of PVC based products certainly involve molar mass changes, which can lead either to a material with difficult processing characteristics (high molar masses/**k** values) or to a fragile material (low molar masses/**k** values) (Burgess, 2005).

Copolymerization of VCM also provide a method for suppressing the formation of anomalous units of the vinyl chloride homopolymer chains. Anomalous entities are formed through rearrangements of the living radical during the reaction. If the cross-propagation step is faster than the isomerization of the living radical, the formation of anomalous structures can be suppressed in the copolymerization systems (Nass and Leonard, 1998).

Müllner and Albert (1967) studied the VCM-propylene copolymerization, and pointed out the difficulty to produce these copolymers with high molar masses due to the high transfer rate to the propylene. In addition, chains with high concentration of propylene are also hard to produce because of the low reactivity between propylene and VCM, producing low reaction rates. Burgess (2005) showed that in order to achieve a propylene concentration of 7.5% in the final copolymer, it would be necessary to use 34% of propylene in the initial mixture with VCM.

By far the most important commercially VCM-based copolymer is based on copolymerization with vinyl acetate (VAc), especially in bulk and solution polymerization processes (Marvel et al., 1942). One of the main functions of VAc is reducing the viscosity of the final polymer at the expense of smaller "softening point" and, to a lesser extent, worse thermal stability and worse strength of the material. **k** values usually produced in various compositions are between 40 and 55 (Burgess, 2005; Emmer and Bankoff, 1954), which makes the processing of the copolymer easier.

Bichuch et al. (2003) reported some specific characteristics of the PMMA-PVC copolymer obtained by free radical suspension polymerization, by using a mixture of organic peroxide initiators (lauroyl peroxide with Di-(2-ethylhexyl) peroxydicarbonate). The experimental strategy used by such authors was focused on the feed of small quantities of MMA throughout the reaction course because of the decelerating effect of MMA in the reaction, with low rates of copolymerization (composition of monomer mixture equal to 95% of VCM and 5% of MMA), when compared to the production of homopolymers in the same experimental conditions. According to the these authors, the **k**-values of the copolymers decrease as the MMA concentration increases (1–20 wt%).

The usage of microreactor to perform copolymerization reactions is relatively recent. Bayer et al. (2000) were described advantages of the microreactor technology in the engineer of polymerization reactions. These authors (Bayer et al., 2000) showed that molar mass distributions are narrower in the experiments carried out in microreactors in comparison to those in macroreactors, possibly because of the more homogeneous reaction conditions and better heat transfer rates. Nielsen et al. (2002) carried out the copolymerization of ethylene with 1-octene, among others reactions, in a microcapillary reactor of 200 μl equipped with an electric heating system.

It is also important to report that the use of commercial peroxide multifunctional initiators in free radical polymerizations are restricted to reaction temperatures above 90 °C (Benbachir and Benjelloun, 2001; Cerna et al., 2002; Fityani-Trimm et al., 2003; Sheng et al., 2004; Scorah et al., 2004; Galhardo et al., 2013; Soljic et al., 2009). Besides, no previous published material reported the use of peroxide multifunctional initiators to produce