



Synthesis of poly(vinyl acetate–methyl methacrylate) copolymer microspheres using suspension polymerization

Md. Shahidul Islam^a, Jeong Hyun Yeum^b, Ajoy Kumar Das^{a,*}

^a Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Dhaka 1000, Bangladesh

^b Department of Advanced Organic Materials Science and Engineering, Kyungpook National University, Daegu 702-701, South Korea

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ABSTRACT

Poly(vinyl acetate–methyl methacrylate) (VAc–MMA) copolymer microspheres were prepared using suspension polymerization at low temperature initiated with 2,2'-azobis(2,4-dimethyl valeronitrile) (ADMVN). The poly(VAc–MMA) copolymer microspheres can be used over a large area where homopolymers, polyvinyl acetate (PVAc) and methyl methacrylate (PMMA) microspheres are capable of being put to use. The prepared microspheres were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Obtained copolymer microspheres have 200 μm average diameter and higher thermal stability than those of homopolymer.

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1. Introduction

As the polymer industry becomes more competitive, polymer manufacturers face increasing pressures for the production cost reductions and more stringent polymer quality requirements [1]. Therefore, the development of comprehensive methods to control polymer quality during a polymerization is the key to the efficient production of tailored, high-quality polymers and the improvement of plant operability and economics.

Polymeric microspheres have been arisen great interest in the fields of biology and medicine [2–6]. These microspheres can be prepared via monomer polymerization including conventional emulsion polymerization [7,8], dispersion polymerization [9], suspension polymerization [10,11] and seed polymerization [12], and activated swelling method [13]. Among these methods, suspension polymerization is simple and more suitable for massive production of microspheres [14].

In suspension polymerization, the monomer is dispersed in a liquid (usually water) by vigorous stirring and by the addition of stabilizers [15]. A monomer-soluble initiator is added in order to initiate chain-growth polymerization. The polymer is obtained in the form of microspheres at a high degree of conversion. The main advantage of this process is that the heat of polymerization can easily be removed via aqueous phase. Polymerization proceeds in the droplet phase and in most cases, occurs by a free radical mechanism. In order to prevent settling or creaming, agitation is

normally continued throughout the course of the reaction. Suspension polymerization usually requires the addition of small amounts of a stabilizer to hinder coalescence and break-up of droplets during polymerization [16]. The size distribution of the initial emulsion droplets and, hence, also of the polymer particles that are formed is dependent upon the balance between droplet break-up and droplet coalescence. This is in turn controlled by the type and speed of agitator used, the volume fraction of the monomer phase, and the type and concentration of stabilizer used.

Suspension polymerization can provide a suitable method for the production of copolymers at high conversions. If the copolymer is insoluble in its monomer or is cross-linked, then solution polymerization may be unsuitable due to low conversions and poor control of the reaction. The use of suspension polymerization can overcome such problems. The nature of the copolymer formed will depend upon the solubilities and reactivity ratios of the composite monomers. However, the reactivity ratios in suspension copolymerization often vary from those in solution (or emulsion) polymerization. This may be due to various factors including different mixing of monomers in the two methods [17] and a slight solubility of one (or more than one) of the monomers in the continuous phase [18]. A simulation procedure has been developed for the copolymerization of styrene and acrylonitrile by Hagberg [19], which predicts the molecular weight of the polymer formed, while allowing for the effect the water solubility of acrylonitrile will have on the reactivity ratios. Moreover, various types of copolymers such as vinyl chloride/methyl methacrylate [20], styrene/methyl methacrylate [21], vinyl pyrrolidone/ethylene dimethylacrylate [22] and vinyl chloride/divinyls [23] were produced using suspension polymerization.

* Corresponding author. Fax: +880 2 8615583.

E-mail address: ajoykddu@gmail.com (A.K. Das).

Table 1
Suspension copolymerization conditions of VAc/MMA system.

Conditions	Name/value
Type of initiator	ADMVN
Type of suspending agent	PVA
Initiator concentration	0.0001, 0.0005, 0.001 mol/mol of monomer
Suspending agent concentration	1.5 g/dl of water
Monomer/water	0.5 l/l
Rpm	500
Temperature	30, 40, 50 °C

Homopolymer of vinyl acetate (VAc) has been widely studied in the literature because of its excellent optical properties, biocompatibility and few foreign-body reactions in vivo [24]. Polymethyl methacrylate (PMMA) that is obtained from polymerization of methyl methacrylate is an important polymeric material with high light transmittance, colorlessness, chemical resistance and weathering corrosion resistance. Due to these superior characteristics, PMMA is used over a large area in coating, optical fiber, outdoor electrical applications, etc. [25–27]. Therefore, the copolymer of vinyl acetate and methyl methacrylate can be used in the aforementioned fields, which are agreeable for polyvinyl acetate and polymethyl methacrylate. Besides, vinyl acetate/methyl methacrylate copolymer and their corresponding homopolymers are commercially important components in many paints, adhesives and binders [28].

In the previous reports, PVAc, PVAc/Silver, and PVAc/montmorillonite [29,30] and PMMA and PMMA/silver [31] microspheres were prepared using the technique of suspension polymerization. In this paper, we report the results of suspension copolymerizations of VAc/MMA initiated with 2,2'-azobis(2,4-dimethyl valeronitrile) (ADMVN) at low temperature.

2. Experimental

2.1. Materials

Methyl methacrylate and vinyl acetate purchased from Aldrich were sequentially washed with NaHSO_3 aqueous solution and water and then dried with anhydrous CaCl_2 , followed by distillation in a nitrogen atmosphere under reduced pressure [32]. The monomer-soluble initiator, ADMVN (Wako), was recrystallized twice in methanol before use. Poly(vinyl alcohol) (PVA) with

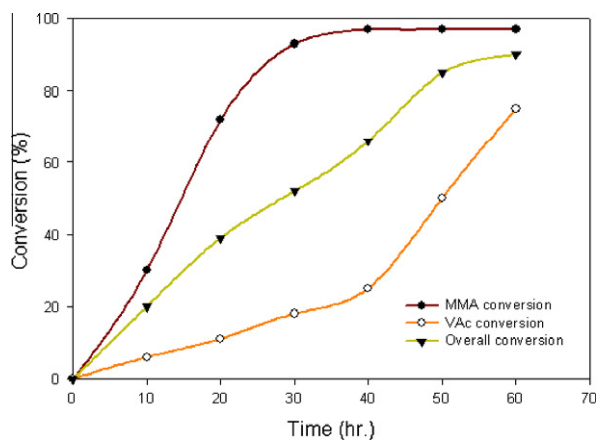


Fig. 1. VAc/MMA suspension copolymerization using ADMVN concentration of 0.0001 mol/mol of monomer at 30 °C with monomer ratio, VAc/MMA = 3/2 (by mole).

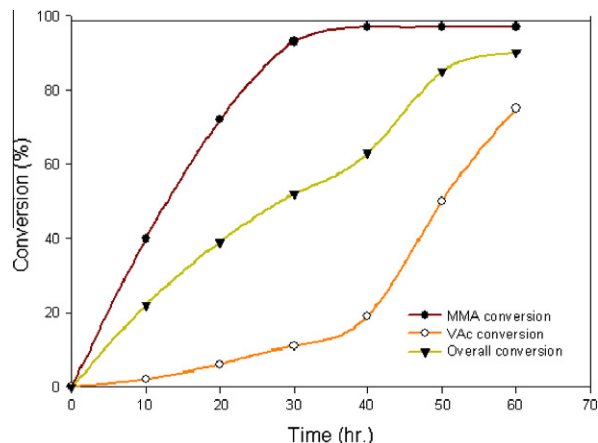


Fig. 2. VAc/MMA suspension copolymerization using ADMVN concentration of 0.0001 mol/mol of monomer at 30 °C with monomer ratio, VAc/MMA = 1/1 (by mole).

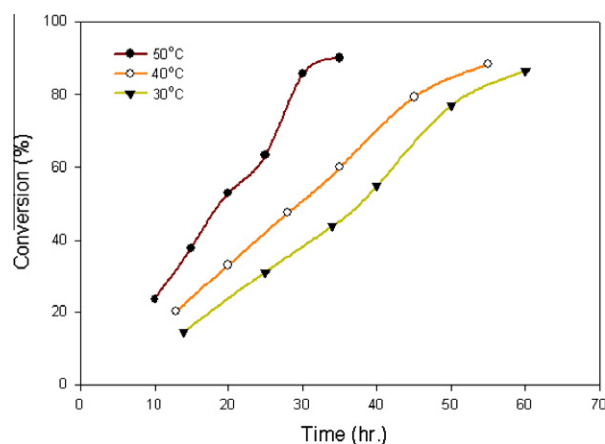


Fig. 3. VAc/MMA suspension copolymerization using ADMVN concentration of 0.0001 mol/mol of monomer in various temperature with monomer ratio, VAc/MMA = 1/1 (by mole).

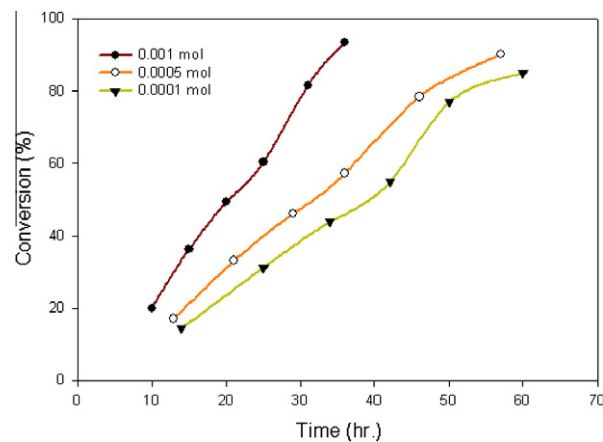


Fig. 4. VAc/MMA suspension copolymerization at 30 °C temperature using different ADMVN concentration with monomer ratio, VAc/MMA = 1/1 (by mole).

number-average molecular weight of 127,000 and degree of saponification of 88% (Aldrich Co.) was used as a suspending agent. Deionized water was put to profitable use for all the experiments.

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