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Modelling and optimization of process variables for the solution polymerization of styrene using response surface methodology

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Abstract   A satisfactory model for predicting monomer conversion in free radical polymerization has been a challenge due to the complexity and rigors associated with classical kinetic models. This renders the usage of such model an exciting endeavour in the academia but not exactly so in industrial practice. In this study, the individual and interactive effects of three processing conditions (reaction temperature, reaction time and initiator concentration) on monomer conversion in the solution polymerization of styrene using acetone as solvent was investigated in a batch reactor through the central composite design (CCD) model of response surface methodology (RSM) for experimental design, modelling and process optimization. The modelled optimization conditions are: reaction time of 30 min, reaction temperature of 120 °C, and initiator concentration of 0.1135 mol/l, with the corresponding monomer conversion of 76.82% as compared to the observed conversion of 70.86%. A robust model for predicting monomer conversion that is very suitable for routine industrial usage is thus obtained.

1. Introduction

Free radical polymerization (FRP) is a chain growth polymerization technique that is widely used in the industries due to its versatility in monomer selection and relative insensitivity to impurity (Mastan et al., 2015), especially in the synthesis of

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high molecular weight polymers (Krzysztof, 1998). Its essential feature is that polymer chains are initiated, propagated, and terminated almost instantaneously. Modelling of polymerization reaction is crucially vital in designing and optimizing reaction conditions for tailoring product properties in addition to enabling the prediction of conversion profile. Yong et al. (2015) opined that "it is of technological importance to develop an effective computational model for FRP, and thereby, aid in optimizing experimental conditions to achieve the desired polymerization products". Kinetic modelling of free radical polymerization is characterized by intricacies, inaccuracies and mathematical rigors which render its routine usage, especially in practice, a serious challenge. The model enables the prediction of such crucial parameters as monomer

conversion, number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI). The classical quasi-steady state approximation fails to provide accurate results especially at high conversion owing to an increased viscosity of the reaction mixtures in the face of continuous occurrence of initiation throughout the polymerization. This is further compounded by an increased temperature for this inherently exothermic reaction, especially in the absence of adequate heat removal. This dynamics of the host solution engenders phenomena such as gel, glass and cage effect which complicate kinetic modelling. Several workers have attempted incorporating each of these occurrences in their models to varying degree of success (Achilias and Kiparissides, 1988, 1992; Venkateshwaran and Kumar, 1992; Frounchi et al., 2002; Keramopoulos and Kiparissides, 2002, 2003; Achilias, 2007; Verros and Achilias, 2009). However, these efforts largely result in models with a limited range of application.

Recently, Garg et al. (2014a–d) derived an analytical solution for free radical polymerization and validated same for various possible scenarios to establish its general applicability. The effectiveness of the Garg model was further corroborated by its good prediction of monomer conversion in the solution polymerization of styrene using acetone as solvent (Owolabi et al., 2014). However, the model is still fraught with the inherent complexity and mathematical rigors of other kinetic models. Another recent effort by Yong et al. (2015) to model free radical polymerization using dissipative particle dynamics hardly address the enumerated shortcomings. There is therefore the need for a robust model that is valid for all range of conversion and yet simple enough for routine industrial application. Such model should be based on process parameters rather than live and dead chains as obtained in the kinetic models. To this end, the response surface methodology proves invaluable.

Response surface methodology (RSM) is a statistical experimental design that enables simultaneous varying of process variables, unlike what obtains in the conventional experimentation, thereby eliciting the interaction between such variables. It is a faster and more economical method for gathering research results than the classic one-variable at a time or full-factor experimentation (Krishnaiah et al., 2015). It also provides a model equation relating the response parameter to the process variables and optimization of the same. It is a veritable tool that has been deployed in a wide range of fields namely; transesterification (Betiku et al., 2015; Muppaneni et al., 2013), solvent extraction (Rai et al., 2016; Mohammadi et al., 2016), adsorption (Ahmed and Theydan, 2014; Ezechi et al., 2015), Fenton process (Kumar and Pal, 2012), drying operations (Krishnaiah et al., 2015), carrageenan production (Bono et al., 2014) etc.

In polymer and related fields, RSM has found application in some reported studies (Ghasemi et al. 2010; Lee et al., 2011; Nasef et al., 2011; Banerjee et al., 2012; Chieng et al., 2012; Zheng et al., 2015; Rojo et al., 2015; Razak et al., 2015; Fattahpour et al., 2015; Hirzin et al., 2015; Davoudpour et al., 2015). Razali et al. (2015) used RSM to study the grafting of polydiallydimethylammonium chloride (PolyDADMAC) to cassava starch using potassium persulphate (KPS) as a free radical initiator. Four variables were investigated via central composite design (CCD) namely; mole ratio of diallydimethylammonium chloride (DADMAC) to starch, reaction time, reaction temperature and initiator concentration to determine their individual and interactive effects on the grafting percentage. They obtained satisfactory results as the actual experimental yield at optimized conditions was very close to the value predicted by their derived model. Aroonsingkarat and Hansupalak (2013) studied the effect of processing conditions on monomer conversion in the graft copolymerization of polystyrene and rubber using response surface methodology via CCD. The reaction temperature, time, percentage of deproteinized rubber, and amount of chain transfer agent were the four variables investigated. In a related study, Sresungsuwan and Hansupalak (2013) investigated the influence of processing conditions on the mechanical properties of compatibilized styrene/natural rubber blend using CCD. To the best of our knowledge, no such study has been reported in the literature for solution polymerization of styrene.

In our previous contributions, we established the various factors influencing monomer conversion in the solution polymerization of styrene (solvent polarity, nature and concentration of initiator, monomer concentration, reaction temperature and time) and their limiting values (Kehinde et al., 2013; Owolabi et al., 2014, 2015). In the present study, we explore the effect of initiator concentration, reaction time and reaction temperature on monomer conversion in the solution polymerization of styrene with acetone as solvent. Response surface methodology via CCD was used to design the experiment, generate a model and optimize the process variables. The overall objective is to obtain a model equation for routine determination of monomer conversion as a function of these processing conditions.

2. Materials and methods

2.1. Materials

The chemicals used are styrene (99%) inhibited by 10–15 ppm 4-tertbutylcatechol, benzoyl peroxide (75%), methanol (CH_3OH) (99.8%), sodium sulphate (Na_2SO_4) (99%), sodium hydroxide (NaOH) (98%), and acetone (99.9%). All the reagents were of analytical grade, purchased from Sigma Aldrich in Germany and used as received except for styrene monomer which was de-stabilized as previously described (Kehinde et al., 2013; Owolabi et al., 2014, 2015).

2.2. Polymerization

The polymerization was conducted in a 62 mm diameter round bottom pressure double neck reaction flask equipped with a reflux system. The vapourized acetone was collected by a reflux condenser. In each run, specific amount of BPO and styrene monomer concentration (8.612 M) were dissolved in a desired volume of acetone to maintain a monomer to solvent ratio of 1:1. The reactor was maintained at the specified temperature and time as shown in Table 2. Thereafter, the reactor was opened up, and cooled to collect the resulting polymer solution. The clear polymer solution was added to about 3 ml of methanol in a beaker with continuous stirring to precipitate the polymer. The top clear solvent was decanted while the bottom polymer samples were air-dried to remove excess solvent and dried for 2 weeks at room conditions until a constant