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Kinetics of styrene free radical polymerisation in the spinning disc reactor

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Abstract

In order to understand the phenomenon taking place on the surface of the spinning disc reactor (SDR), a kinetic/mechanistic study of styrene free radical polymerisation was conducted in a SDR. The experiments were designed to enable assessing all kinetic parameters. Obtained experimental data were used in a modelling study. Once parameters (i.e. initiator efficiency f, rate constants k_d, k_P and k_t) were estimated for experimental runs carried out at different temperatures, the Arrhenius law was applied to estimate activation energies (E_a) and the pre-exponential factors (A). Calculated activation energies in the SDR were found to be smaller than corresponding batch values.

Keywords: Spinning disc reactor; Kinetics; Styrene polymerisation; Process intensification

1. Introduction

Free radical polymerisation technique is widely used by industry for polymerisation of styrene, acrylics, vinyls and a host of commercially important monomers. Due to increasing market competitiveness there is a growing need for industry to develop novel polymer processes that improve product quality, reduce processing time and make the process more responsive to market needs whilst improving energy efficiency and inherent safety of the process.

In order to address the above issues, the Process Intensification Group at Newcastle has been developing radical step-change reactor technology for polymerisation processes [1]. One such technology is the spinning disc reactor (SDR), which takes advantage of the thin highly sheared films that can be generated when a liquid is introduced over a rotating disc surface. Previous studies have demonstrated that these thin highly unstable films can generate extremely high transport rates [2,3], provide micro mixing [4] and are suitable for performing both exo and endothermic reactions.

SDR has been succesfully used to perform a range of polymerisation reactions including condensation polymerisation between a dibasic acid and a dihydric alcohol [5], free radical styrene and methyl methacrylate (MMA) bulk polymerisations [1,6], butyl acrylate (BAc) photopolymerisation [7] and styrene cationic polymerisation [8]. Generally, higher polymerisation rates are achieved in the SDR than in batch processes and the polymers produced in the SDR have tighter molecular weight distribution (MWD) (hence better quality) in comparison to their batch reaction counterparts. Other processes where the improved mixing and heat and mass transfer rates of the SDR have been succesfully exploited include precipitation of barium sulphate [9] and calcium carbonate [10], crystallisation of adipic acid [11] and organic catalytic reactions [12].

To understand and explain the phenomenon taking place on the surface of the spinning disc reactor we conducted a study of the kinetics and mechanisms of rapid free radical polymerisations in spinning disc reactors jointly with the Polymer Centre in the Chemistry Department of Sheffield University. We believe that understanding the kinetics and the reaction mechanisms that take place in a SDR will significantly influence the manner in which the future polymer processes are designed and operated. In our view it will provide an opportunity for flexible, mobile plants encouraging distributed manufacturing as it has been demonstrated that the foot print of the plant will be significantly reduced.

2. Experimental procedures

2.1. Polymerisation in conventional batch reactors

Batch styrene polymerisations were studied in a 250 cm^3 agitated vessel for a range of monomer concentrations [M],

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Nomenclature

A	Pre-exponential factor
E_a	Activation energy
f	Initiator efficiency
$[I]$	Initiator concentration
k_d	Initiator decomposition rate constant
k_P	Propagation rate constant
k_t	Termination rate constant
$[M]$	Monomer concentration
M_n	Number-average polymer molecular weight
M_w	Mass-average polymer molecular weight
PDI	Polydispersity index

initiator concentrations $[I]$, operating temperatures (T) and agitator speeds. Benzoyl peroxide, BPO (Merck, with 25% water) was used as an initiator in styrene polymerisation. Initiator was re-crystallised from ethanol prior to reaction. Styrene monomer (99%) and Toluene as a solvent (99%) were purchased from Aldrich. Samples were taken every 5 min for the first 20 min of reaction and every 10 min from then on and analysed using gel permeation chromatography (GPC) to assess conversion and molecular weight properties. GPC was calibrated using poly(styrene) standards obtained from Polymer Laboratories. Conversion was obtained using LC-GC software which was calibrated by samples of known monomer/polymer concentrations.

2.2. *Polymerisation in spinning disc reactor*

2.2.1. *Stage 1: pre-polymerisation*

Prior to being fed to an SDR, a pre-polymer mixture was prepared in a 250 cm^3 batch reactor as described above. Batch reaction was carried out until the desired initial conversion was achieved.

2.2.2. *Stage 2: SDR polymerisation*

A 300 mm diameter spinning disc reactor with a top surface made of brass and equipped with excellent heating and cooling facilities was used to study the free radical polymerisation of styrene. The pre-polymer mixture containing monomer, polymer and initiator in varying concentrations was fed to the centre of the disc by means of a gear pump. Centrifugal forces created by disc rotation force the liquid to flow over the disc surface in the form of a very thin, highly mixed film; after reaching the edge of the disc, the liquid gets thrown off the surface, hits the cold walls and gets collected for analysis.

The experiments were designed to enable assessing all kinetic parameters. The disc temperature (75–90 °C), monomer concentration $[M]$ (50–83%, w/w), initiator concentration $[I]$ (0.8–1.75%, w/w), disc rotational speed (500–1500 rpm), feed flow rate (4–9 cm^3/s) and pre-polymer (feed) conversion (10–54%) were varied. The conversion and molecular weight properties (M_n, M_w and polydispersity index, PDI) were obtained from GPC.

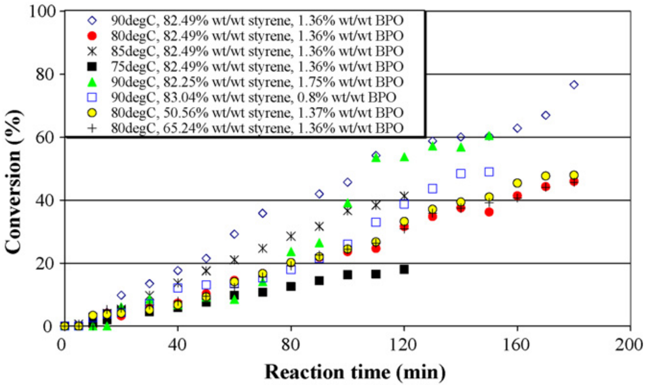

Fig. 1. Styrene polymerisation in a batch reactor: conversion profile.

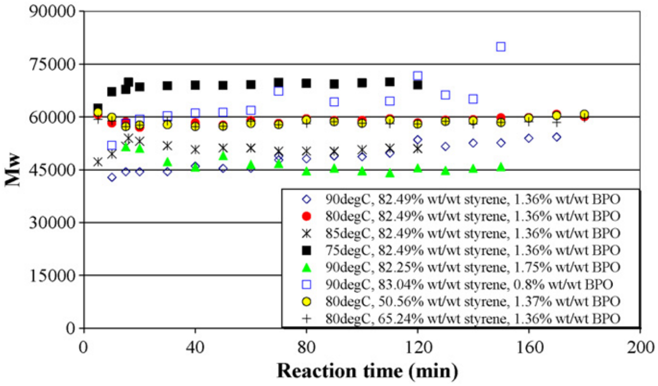

Fig. 2. Styrene polymerisation in a batch reactor: M_w profile.

3. Results and discussion

3.1. *Batch reactor*

Experimental results obtained in a batch reactor for styrene polymerisation can be seen in Fig. 1 in terms of conversion. In Figs. 2 and 3 molecular weight properties are presented in terms of M_w and PDI.

Obtained experimental data were employed in mechanistic model previously proposed [13,14] and model parameters were estimated. Software package used for both modelling and parameters estimations was gPROMS. In this study, parameters (i.e.

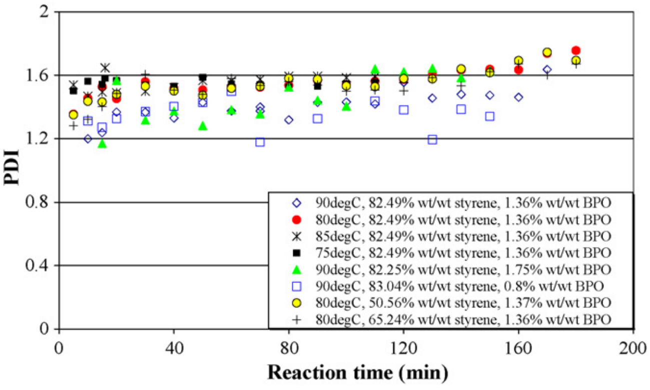

Fig. 3. Styrene polymerisation in a batch reactor: PDI profile.

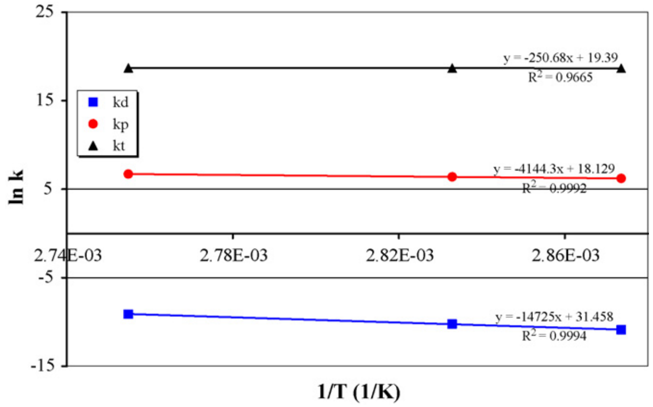

Fig. 4. Determination of activation energies for styrene polymerisation.

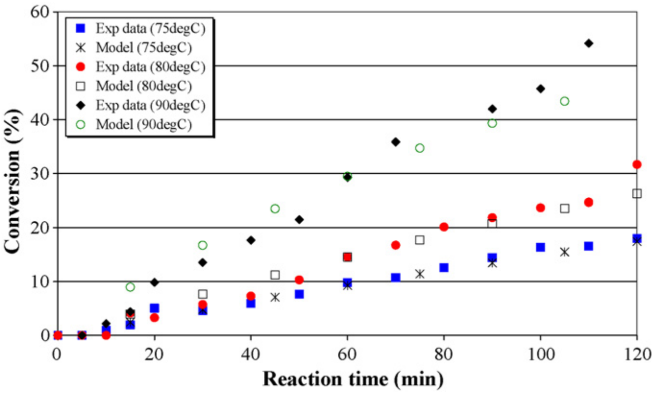

Fig. 5. Experimental and model conversion data for styrene polymerisation.

initiator efficiency *f*, initiator decomposition rate constant k_d, propagation rate constant k_P and termination rate constant k_t) were estimated by using constant variance model, as it was assumed that the measurement error of the variable does not depend on its magnitude [14].

Once parameters were estimated for experimental runs in a batch reactor carried out at different temperatures (75, 80 and 90 °C), the Arrhenius law was applied to estimate activation energies (E_a) and pre-exponential factors (*A*) as shown in Fig. 4.

Models for conversion, as shown in Fig. 5, and M_w and M_n, as shown in Fig. 6, illustrate close agreement (within the range of experimental error) with the acquired experimental data.

Table 1

Polymerisation rate constants and activation energies in batch ($f = 0.4$)

	k_d (s^{-1})	k_P ($dm^3\ mol^{-1}\ s^{-1}$)	k_t ($dm^3\ mol^{-1}\ s^{-1}$)
90 °C	1.10×10^{-4}	820	1.32×10^{8}
80 °C	3.60×10^{-5}	600	1.30×10^{8}
75 °C	1.90×10^{-5}	500	1.28×10^{8}
90 °C ($f = 0.8$) [14]	1.02×10^{-4}	927	1.23×10^{8}
	Decomposition	Propagation	Termination
A	4.59×10^{13}	7.47×10^{7}	2.64×10^{8}
E_a (kJ/mol)	122.4	34.46	2.084
A [15]	7.5×10^{13}	4.5×10^{6}	5.8×10^{7}
E_a [15] (kJ/mol)	124.2	30.53	7.95

Kinetic parameters for styrene polymerisation in the batch reactor are presented in Table 1. The rate constant values estimated in this study show close agreement with the values found in the literature [14].

3.2. Spinning disc reactor

SDR mechanistic model previously proposed is applied [14,16]. As the reaction time on a SDR is very short (several seconds) the steady state assumption cannot be applied. SDR model employed in this study accommodate this fact. Data obtained experimentally were used to estimate rate constants that will result in high increase of conversion over short residence time. Comparison was made with corresponding batch rate constants.

The polymerisation rate was much faster in the SDR than in the batch experiments and a maximum of approximately 10% change in conversion was achieved after one pass on the disc at 1500 rpm (i.e. approx. 2 s total residence time) (Fig. 7).

This is attributable to higher rate constants k_d and k_P in the SDR as indicated by values estimated in modelling studies (Table 2). Estimated values of k_t in both batch and SDR were approximately the same.

Employing estimated rate constants at different SDR temperatures (at disc speed of 1100 rpm, feed flow rate of 6 ml/s, and 30% pre-polymer conversion) activation energies in the SDR

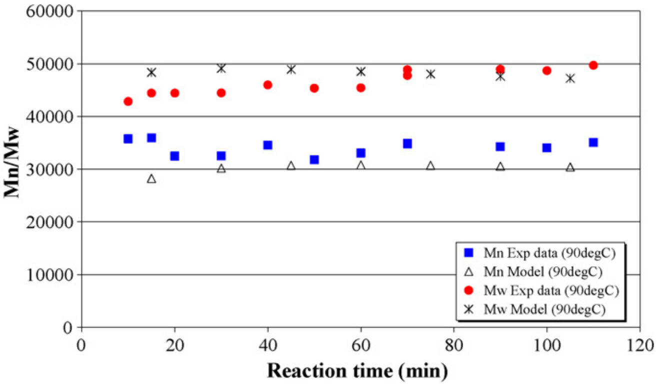

Fig. 6. Experimental and model M_n/M_w data for styrene polymerisation.

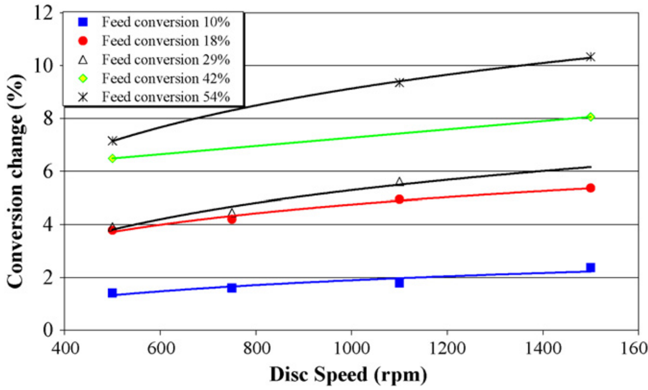

Fig. 7. Rotational speed influence on SDR kinetics for styrene polymerisation.

Table 2
Polymerisation rate constants k_d and k_P change at 90 °C

Temperature 90 °C	Run conditions	SDR rate constants	Corresponding batch rate constants
k_d (s^{-1}) k_P ($dm^3\ mol^{-1}\ s^{-1}$)	10% conv., 6 ml/s, 500 rpm	0.96×10^{-3} 8.20×10^{3}	1.19×10^{-4} 8.18×10^{2}
k_d (s^{-1}) k_P ($dm^3\ mol^{-1}\ s^{-1}$)	10% conv., 6 ml/s, 750 rpm	1.75×10^{-3} 9.00×10^{3}	1.19×10^{-4} 8.18×10^{2}
k_d (s^{-1}) k_P ($dm^3\ mol^{-1}\ s^{-1}$)	10% conv., 6 ml/s, 1100 rpm	3.00×10^{-3} 10.0×10^{3}	1.19×10^{-4} 8.18×10^{2}
k_d (s^{-1}) k_P ($dm^3\ mol^{-1}\ s^{-1}$)	10% conv., 6 ml/s, 1500 rpm	5.90×10^{-3} 11.5×10^{3}	1.19×10^{-4} 8.18×10^{2}

Table 3
Polymerisation rate constants in a batch reactor (at 90 °C) and SDR (at different temperatures)

	k_d (s^{-1})	k_P ($dm^3\ mol^{-1}\ s^{-1}$)	k_t ($dm^3\ mol^{-1}\ s^{-1}$)
Batch 90 °C	1.10×10^{-4}	820	1.32×10^{8}
SDR 90 °C	1.25×10^{-2}	1.20×10^{4}	1.32×10^{8}
SDR 80 °C	9.90×10^{-3}	9.80×10^{3}	1.32×10^{8}
SDR 75 °C	8.00×10^{-3}	8.00×10^{3}	1.32×10^{8}

are determined using the same method as for the batch process. Results of these studies are presented in Table 3. Activation energies were estimated as: $E_{ad} = 30.39$ kJ/mol; $E_{aP} = 27.48$ kJ/mol which are smaller than corresponding batch values.

4. Summary

In this study, we estimated kinetic parameters for both batch and SDR processes. Models for conversion, M_w and M_n, demonstrate close agreement with obtained experimental data.

Developed Arrhenius law equations for a batch process can be seen in Eqs. (1)–(3) for k_d, k_P and k_t, respectively.

$$k_d = 4.59 \times 10^{13}\, e^{(-122.4 \times 10^3/RT)} \tag{1}$$

$$k_P = 7.47 \times 10^{7}\, e^{(-34.46 \times 10^3/RT)} \tag{2}$$

$$k_t = 2.67 \times 10^{8}\, e^{(-2.084 \times 10^3/RT)} \tag{3}$$

Arrhenius law equations for SDR are presented in Eqs. (4)–(6) for k_d, k_P and k_t, respectively.

$$k_d = 2.88 \times 10^{2}\, e^{(-30.39 \times 10^3/RT)} \tag{4}$$

$$k_P = 1.10 \times 10^{8}\, e^{(-27.48 \times 10^3/RT)} \tag{5}$$

$$k_t = 2.67 \times 10^{8}\, e^{(-2.084 \times 10^3/RT)} \tag{6}$$

Initiator efficiency (f) in SDR systems is considered to be much greater than in batch systems. Whilst in latter f could have a value of approx. 0.4, f in the SDR film would be considered to be very close to 1 thus initiating more monomers into free radicals and increasing conversion.

Polystyrene with M_w of about 55,000 and M_n of about 35,000 was produced in one pass in the SDR from batch pre-polymerised feed. PDI of 1.5–1.6 was achieved in most experiments. Generally, small decreases in M_n and M_w of the polymer product were observed from SDR processing indicating that higher radical concentrations prevail on the disc than in stirred batch reactors [17]. This is in agreement with the higher fk_d estimated by the model.

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