

Bulk copolymerization of styrene and acrylonitrile: Experimental kinetics and mathematical modelling

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The kinetics of styrene-acrylonitrile bulk copolymerization have been experimentally investigated over a wide range of conditions. The effects of temperature, and initiator and of comonomer concentrations on rate of polymerization and on copolymer properties including chain microstructure and molecular weight averages are reported. A mathematical model which uses the free volume theory to account for diffusion controlled termination and propagation reactions is developed. The model is capable of predicting the conversion, composition and sequence length development up to limiting conversions.

(Keywords: styrene-acrylonitrile; copolymerization; gel-effect; free volume theory; kinetics)

INTRODUCTION

Despite a number of experimental investigations on the copolymerization of styrene-acrylonitrile¹⁻³ there is limited information available on its kinetics. Most research has focussed on the evaluation of reactivity ratios and initial rates of polymerization using low conversion data, although some evaluations of termination rate constants and solvent effects have been reported^{4,5}. There have been no comprehensive studies on the kinetic modelling of styrene-acrylonitrile (SAN) throughout the entire course of polymerization and over a range of temperatures, initiator concentrations and comonomer compositions. In this paper we present the results of such an extensive experimental study on the bulk copolymerization of SAN⁶. We will also develop a comprehensive kinetic model capable of predicting the development of conversion, copolymer composition, and number average sequence length with time. The development and implementation of the analytical techniques required for the characterization of the SAN copolymers are described elsewhere^{6,8,9}.

EXPERIMENTAL

Reagents

The initiator: 2,2' azobisisobutyronitrile (AIBN) was recrystallized twice from absolute methanol. The monomers styrene and acrylonitrile industrial grade were distilled under vacuum and stored at -5°C until used. Tetrahydrofuran (THF) industrial grade was distilled under vacuum from cuprous chloride and stored under nitrogen. All other solvents used in the course of various analyses were used directly without further purification.

Polymerization procedure

Polymerizations were carried out in standard 25.4 cm long glass ampoules of two different diameters: 10 mm

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outer diameter and 13 mm outer diameter for the two conversion ranges, low conversions $<30\%$ and high conversions $>30\%$, respectively. These two surface-to-volume ratios are sufficiently large to ensure isothermal polymerization ($\pm 0.2^{\circ}\text{C}$), and to provide sufficient polymer samples for characterization.

Design of experiments

For the selection (design) of experimental conditions, several approaches are possible, depending on the objectives of the design. In this particular case, given the scarcity of published experimental data, it was decided to run a factorial design on the variables that are known to affect primarily the molecular weight and production rate (i.e. temperature and initiator concentration) and to use a range of compositions at each of these factorial points. The experimental conditions are summarized in *Table 1*.

ANALYTICAL METHODS

Conversion and average composition

Conversions were determined gravimetrically and by gas chromatography (g.c.). The copolymer compositions were determined by several methods; analysing the copolymer by infra-red spectroscopy (i.r.) and proton nuclear magnetic resonance (^1H n.m.r.), and by a mass balance on the residual monomer composition as measured with gas chromatography. I.r. spectra were obtained on a Beckman IR-5 from films cast from 10% W/V THF or CH_2Cl_2 solutions and from 0.05 g cm^{-3} solutions in CHCl_3 . Absorptions at the $-\text{C}\equiv\text{N}$ stretching band at approximately 2222 cm^{-1} ($4.5\ \mu\text{m}$) and at the band at approximately 1610 cm^{-1} ($6.3\ \mu\text{m}$) were used to measure the copolymer composition.

Molecular weight and sequence length

The development of techniques for molecular weight and sequence length characterization is detailed elsewhere^{6,8,9}. A brief outline is presented here. Weight average molecular weights were obtained by viscometry

Table 1 Experimental conditions

	$T_1 = 40^\circ\text{C}$	$T_2 = 60^\circ\text{C}$
	$[I]_1 = 0.01 \text{ M}$ $[I]_2 = 0.05 \text{ M}$	$[I]_1 = 0.01 \text{ M}$ $[I]_2 = 0.05 \text{ M}$
Mol fraction of styrene in feed	0.1 0.2 0.3 0.4	0.5 0.6 0.7 0.8 0.9
Experimental range	Conversion < 0.2	0 < Conversion < 1

using the Mark-Houwink parameters reported by Lange and Baumann^{9,10} and determined in our laboratories^{6,7}. Viscosity measurements were carried out using Cannon Ubbelohde viscometers (capillary diameters of 0.26 and 0.305 mm). The solvents used were DMF at 20°C and THF at 25°C. The intrinsic viscosities were estimated from Huggin's equation.

Molecular weight distributions for selected samples were determined by size exclusion chromatography (s.e.c.), based on the universal calibration procedure. Measurements were done at room temperature with THF as the mobile phase. The column combination used was a set of five 1.22 m Stryagel columns (10^6 , 10^5 , 10^4 , 10^3 , 500 Å) from Waters Scientific. A u.v. detector and a differential refractometer were used to determine copolymer composition as a function of molecular size. Axial dispersion corrections and molecular weight calculations are described in refs. 6 and 8.

Sequence lengths were obtained using a high resolution Fourier transform proton n.m.r.⁶ The assignment of the resonance bands was verified using ¹³C n.m.r. and by comparison with those assignments reported by Shaefer¹¹ and Pichot and Pahn⁵.

RESULTS

Reproducibility

The reproducibility and consistency of the experimental results were verified by replication and by the determination of the same polymer property using a variety of techniques⁶. Reproducibility of the conversion histories accounts for two kinds of errors: measurement errors and sampling errors. The uncertainties related to the preparation of reactants were minimized by preparing sufficiently large quantities so that weighing errors were negligible. The initial monomer compositions were verified by g.c. prior to filling of the ampoules. Figure 1 shows the agreement between conversions obtained gravimetrically and by g.c. The reproducibility of conversion measurement was, in general, better than 2%, although errors of about 2% were possible during extreme gel effect conditions (i.e. high polymerization rates).

The reproducibility of composition data (mole%) was verified routinely as part of the conversion replication measurements. The standard deviation for residual monomer fraction analysis on the same sample was, in general, smaller than 1%. The i.r. and n.m.r. replications indicate errors of up to 5% depending on the concentration of acrylonitrile and the purity of the polymer samples. The error associated with the intrinsic viscosity measurements is of the order of $\pm 0.5\%$ which translates into $\pm 3.0\%$ for the weight average molecular weights, assuming that the Mark-Houwink parameters are correct.

The reproducibility of size exclusion chromatograms was tested in the usual way by measuring the standard deviation of the normalized heights for replicate injections¹². Reproducibility was observed to be excellent at the central portions of the chromatograms and to deteriorate towards the tails, particularly the low molecular weight tail. The reproducibility of the molecular weight averages depends, of course, on the significance of the tails in the calculations of the respective moments. For the samples investigated, the reproducibility of the number and weight average molecular weight was between 5 and 10% for the same sample.

Conversion and composition histories

The bulk copolymerization of styrene-acrylonitrile is a homogeneous process throughout most of the conversion range for styrene-rich copolymers ($f_{10} \geq 0.5$) and for low conversion acrylonitrile-rich copolymers ($0.5 \geq f_{10} \geq 0.10$). The polymerization is initiated readily by light, by azo and peroxy compounds, or, in general, by any source of free radicals. Therefore, care must be taken to avoid prolonged exposure to light, particularly once the ampoules have been degassed. Once initiated, the polymerization proceeds rapidly through what is believed to be mainly a cross-propagation reaction. As the viscosity of the mixture increases, regions of hard and soft polymer in the ampoules become evident. These regions are clearly distinguishable towards the end of the reaction. If the fraction of acrylonitrile is increased ($f_{10} < 0.5$), then the hard transparent regions turn into a white solid very much like polyacrylonitrile indicating, therefore, that these regions are due to the heterogeneity of at least the composition distribution and also due to the poor distribution of monomer in the reacting mixture arising from the lack of mixing within the ampoules. The copolymers and the data obtained from the ampoule experiments are probably more representative of a suspension polymerization than of a well-mixed bulk polymerization process. The dissolution of the reacting mixture in DMF and the subsequent precipitation in me-

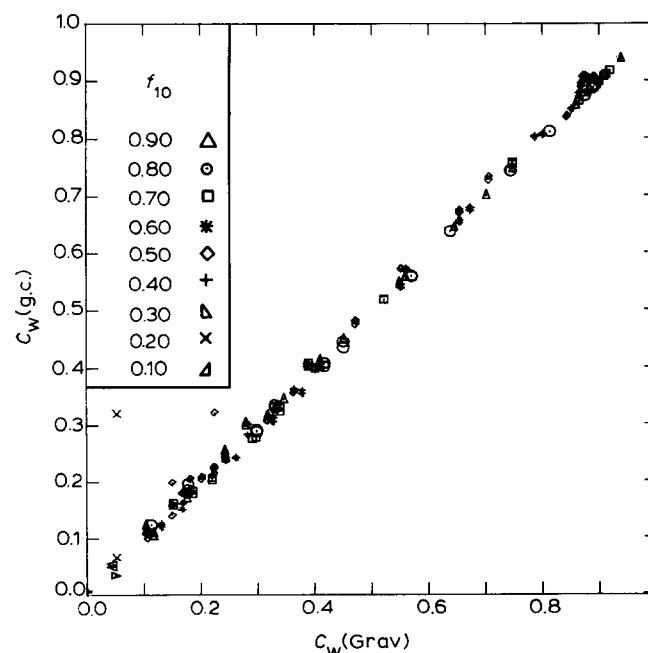


Figure 1 Comparison of conversion histories obtained gravimetrically and by gas chromatography for several feed compositions

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