High-temperature continuous bulk copolymerization of styrene and acrylic acid
Determination of monomer conversions

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Dedicated to Ing. D. Berek, CSc., in honour of his 50th birthday

The content of residual monomers in styrene—acrylic acid copolymers of low relative molecular mass was quantitatively determined. These copolymers were produced by high-temperature (200 to 300 °C) continuous bulk copolymerization. Gas chromatography yielded the styrene content in the product, while liquid chromatography yielded the acrylic acid content. Problems associated with the analyses are discussed, as well as the influence of process variables such as temperature, residence time, monomer feed composition on conversion of the monomers. In addition an influence of the reaction conditions on the copolymer molecular mass and chemical composition is evaluated.

Проведено количественное определение остаточных мономеров в низкомолекулярных сополимерах стирола с акриловой кислотой. Эти сополимеры были получены в результате континуальной сополимеризации в массе при высокой температуре (200—300 °C). С помощью газовой хроматографии было определено содержание стирола в продукте, а с помощью жидкостной хроматографии содержание акриловой кислоты. Обсуждаются вопросы, связанные с проведением анализов, а также влияние переменных параметров, таких как температура, продолжительность процесса, состав мономерного сырья, на конверсию мономеров. Кроме того, оценивается влияние условий реакции на молекулярную массу сополимера и его химический состав.

High-temperature continuous bulk copolymerization of vinyl monomers is one of the most cost-effective methods for producing reactive oligomers. Processes of this type [1—4] can yield low molecular mass polymers or copolymers with narrow molecular mass distributions and high conversions, while maintaining negligible drifts in composition. Such oligomers have been used over the last few years for various applications [5], *e. g.* high solids coatings,

adhesives, finishes, and dispersants. On the other hand, an application of those materials in coating industry as high solids coatings allows to reduce production costs and is important from ecological point of view because it eliminates or minimizes air pollution with volatile organic solvents.

Bulk copolymerization of styrene and acrylic acid at high temperature in a continuous stirred tank reactor (CSTR) is being studied at the Institute for Polymer Production Technology, McMaster University [2, 6—10]. This paper describes the characterization of low molecular mass styrene—acrylic acid (St—AA) copolymers in terms of the conversion of each of the monomeric components. Copolymers were produced at different temperature levels, residence times, and monomer feed compositions. General discussion about influence of the synthesis parameters on polymer product properties is also inserted. The results will be utilized for mathematical modelling of this process [10].

Experimental

Polymer synthesis and sampling procedure

Technical grade monomers were utilized without further pretreatment. Styrene was obtained from Aldrich (Milwaukee, USA) and acrylic acid from Rohm & Hass (Toronto, Canada).

General description of polymer syntheses conditions is given in Table 1 whereas molecular mass and compositional characteristics for selected polymer samples are collected in Tables 2A—C.

Samples were collected by placing a wide-mouthed 25 cm^3 sample vial at the exit of the CSTR. The vials containing a known mass of solvent (tetrahydrofuran (THF) or methanol) were cooled in a refrigerator (*ca.* − 15 °C) prior to sampling. Typically about 1 to 2 g raw polymer was collected to 10 g of the solvent. Since the product emerged as a hot viscous liquid, a part of the volatiles could vaporize at the reactor exit and was not included in the sample. The above procedure was applied for most polymer sampling. Other more elaborate approaches included the use of glass tubes and condensers [11].

Determination of styrene content by gas chromatography

Preparation for GC involved the following steps. Fresh reactor samples were immediately dissolved in THF as described earlier. Between sampling and analysis the sample solutions were stored at about − 15 °C. From these solutions several to about 1000 mg, depending on the expected styrene content, were transferred to 1.5 cm^3 vials. About 10 mg of toluene was added to each as an internal standard. Finally, THF was added until each vial contained about 1400 mg of solution.

Table 1

Description of polymerization conditions

Polymer sample	Monomer feed				Temperature of synthesis	Nominal R_T
	Mole fraction		Mass fraction			
	St	AA	St	AA	°C	min
176B	0.15	0.85	0.199	0.801	250	30
194A—194D	0.20	0.80	0.265	0.735	210—270	30
193A, 193B	0.25	0.75	0.325	0.675	195, 270	30
178A—178C 177C	0.35	0.65	0.431	0.569	270	15, 30
177A					230	30
182A—182C 183B	0.50	0.50	0.591	0.409	230—270	30, 15
184A—184G	0.65	0.35	0.728	0.272	250, 270	30, 15
198A	0.70	0.30	0.771	0.229	250	30
190A	0.75	0.25	0.813	0.187	230	30
195A, 195B	0.80	0.20	0.852	0.147	230, 250	30
185B—185F	0.85	0.15	0.891	0.109	250—300	30
196A—196C	0.90	0.10	0.929	0.071	250	30
187B, 187D 192A, 192B	0.92	0.08	0.943	0.057	230—300	30
188A, 201A	1.00	0	1.000	0	270	30

A stainless steel GC column filled with 10 % Carbowax 1500 on Chromosorb T had been shown to give satisfactory results for quantitative determinations of the styrene content in samples obtained from the reactor [7]. The column, purchased from Chromatographic Specialties (Brockville, Canada), had an internal diameter of 0.32 cm and a length of 304.8 cm. The carrier gas was helium, and used at a pressure of 5.6×10^5 Pa. A thermal conductivity detector was employed at (270.0 ± 0.5) °C. Samples were injected in 1 mm³ aliquots at 250 °C. The temperature program consisted of maintaining 75 °C for 5 min, raising the temperature by 10 °C per min to 145 °C, and maintaining this temperature for further 3 min. A Varian Vista 6000 Gas Chromatograph with autosampler model 8000 and Varian 4270 printer/integrator performed the analyses.

Determination of acrylic acid content by liquid chromatography

Trials to apply gas chromatography for acrylic acid (AA) determination were unsuccessful probably because of fast AA polymerization at injection temperature (250 °C). Liquid chromatography on chemically modified silica gel column: Partisil PAC was applied for AA measurements.

Fresh reactor samples immediately dissolved in THF or methanol as described earlier, were stored at about -15 °C. From these samples 1 to 4 drops, depending on the

expected AA content, were mixed with 20 cm³ of the LC mobile phase. The mobile phase was added slowly to this solution to prevent vigorous precipitation in the form of small porous spheres. Instead a membrane of polymer formed on the liquid surface, from which the AA could be more readily extracted. To avoid plugging of the LC column, the mixed solution was filtered through a 0.2 μm syringe mouthed Milipore filter.

Conditions of the LC analyses were based on the work of *Brown* [12]. A Varian 5000 Liquid Chromatograph was equipped with an autosampler, type 8000 as well as a Varian CDS 401 recorder/plotter. The Partisil PAC 10 column from Whatman (Clifton, USA) consisted of silica with amino—cyano groups on the surface, and was protected by a proprietary guard column from the same supplier. The mobile phase was 0.01 mass % orthophosphoric acid in deionized water, applied at a flow rate of 0.8 cm³ min⁻¹ into which 20 mm³ samples were injected. An ultraviolet detector operated at $\lambda = 215$ nm.

Results and discussion

Styrene analyses

A typical gas chromatogram is shown in Fig. 1. Calibration had been accomplished by using a set of standard solutions which covered a range of styrene concentrations. The resulting areas under the appropriate peaks were then linearly regressed on these concentrations.
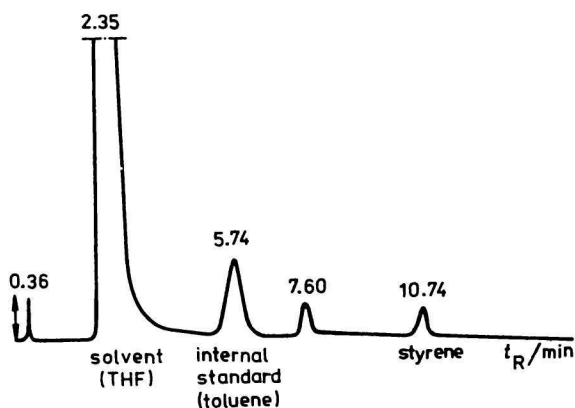

Fig. 1. An example of styrene determination by gas chromatography (Carbowax 1500 on Chromosorb T). Sample 185C.

More than 300 analyses were performed on the same column without significant deterioration of its characteristics. Judging from this experience, the column is likely to serve well for analyses of similar polymers. Evaluated precision of St determination was ± 5 %.

Acrylic acid analyses

Brown had applied a flow rate of $4.0 \text{ cm}^3 \text{ min}^{-1}$ and had no guard column installed [12]. When the same procedure was followed, a steady increase in the pressure over the column was observed with time. The problem was alleviated by reducing the flow rate to $0.8 \text{ cm}^3 \text{ min}^{-1}$ and installing the guard column. A typical chromatogram is shown in Fig. 2.
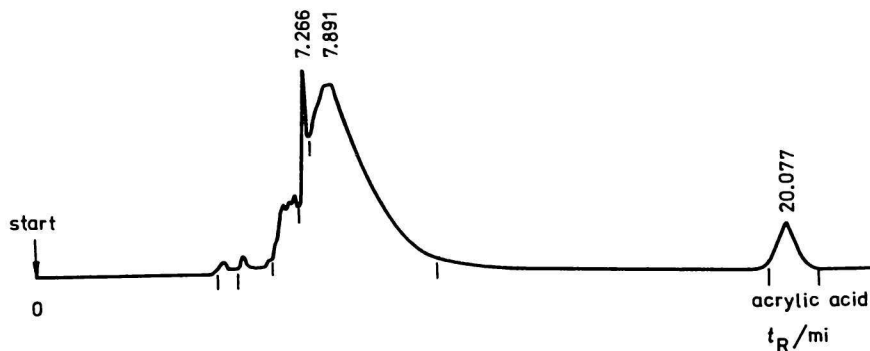

Fig. 2. An example of acrylic acid determination using liquid chromatographic column Partisil PAC. Sample 192A.

The LC column was calibrated in the same fashion as the GC column, as described earlier. The lowest detectability was about 0.5 ppm.

Over the course of about 250 h of analyses the initial calibration shifted as indicated by a drop of retention time t_R from 25.5 min to about 15 min and a decrease of area under the peaks of the calibrational standards (Figs. 3a and 3b). Since these calibrational standards had been intermittently used between sample analyses, it was possible to track these calibrational changes with changes in real time [11]. The cause was attributed to irreversible interactions between the carboxylic groups of the oligomeric samples and the surface of the stationary phase. Solutes containing polycarboxylic compounds such as maleic acid or acrylic acid oligomers had exhibited relatively long retention times, or were not eluted at all [13]. Precision of AA determination was *ca.* $\pm 13 \%$.

Influence of process variables

Since it was possible to obtain conversion for each of the monomers, the influence of the studied process variables could be evaluated as follows:
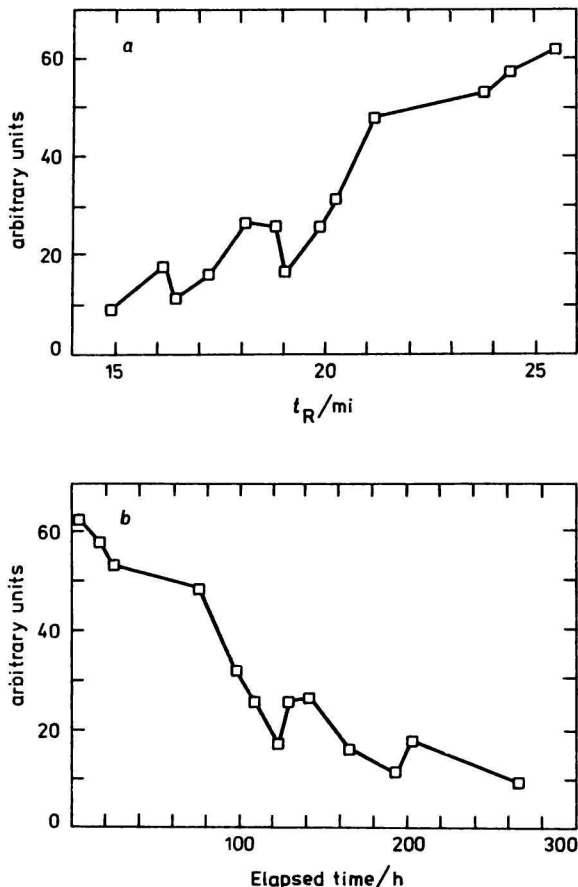
Fig. 3. Variation of Partisil PAC column characteristics with elapsed time of using.
a) Area under acrylic acid peak as a function of retention time; *b*) area under acrylic acid peak as a function of elapsed time of continuous work of the column.

1. As the polymerization temperature was increased from 200 to 300 °C, the conversion of St (Fig. 4) and that of AA (Fig. 5) increased as well. For any particular set of experimental conditions the conversion of St was higher than that of AA. This was expected considering that styrene has a significant rate of polymerization by thermal initiation above 230 °C [14]. However, a greater amount of AA in the feed resulted in lowering the St conversion as well (Fig. 5).

Fig. 5. Acrylic acid conversion α(AA) as a function of monomer feed composition w(St) and polymerization temperature. Denotation as in Fig. 4.
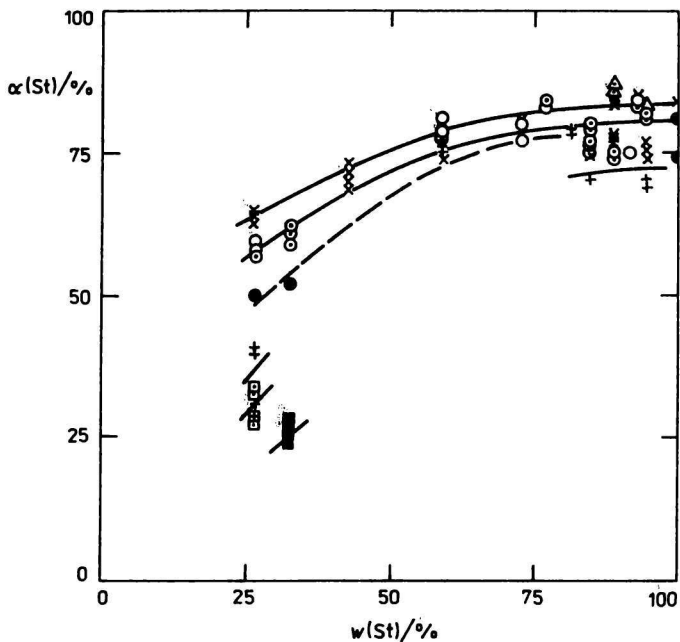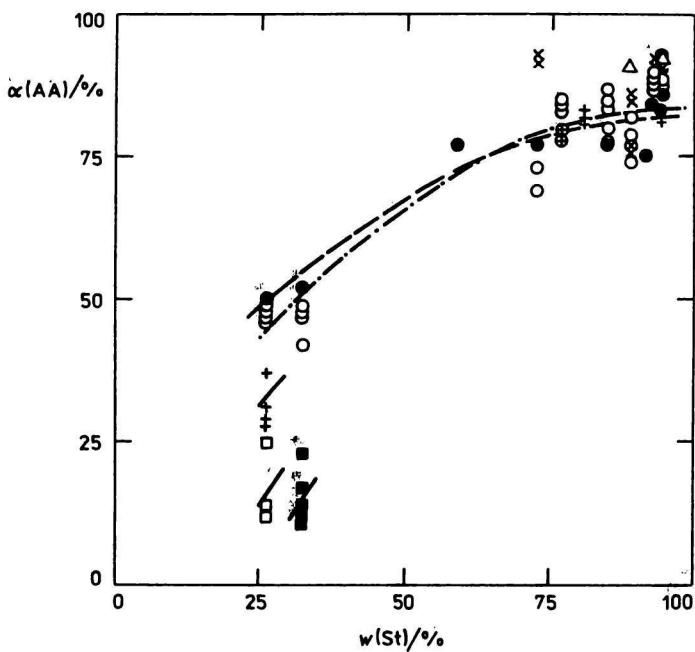
Fig. 4. Styrene conversion α(St) as a function of monomer feed composition w(St) and polymeriza-tion temperature. $\times$ 270 °C, $\bigcirc$ 250 °C, $+$ 230 °C, $\triangle$ 300 °C, $\square$ 210 °C, $\blacksquare$ 195 °C. $\bullet$ and dashed line — total conversion of monomers at 250 °C. Constant nominal R_T = 30 min.

2. Conversion of St was increased with longer residence times R_T in the CSTR. For example, there was a consistent difference of about 2 % between 15 and 30 min at 270 °C (Fig. 6). Additional experiments at a residence time of 7.5 min indicated slightly lower conversions than those either at 15 or 30 min. Due to this rather small difference in conversion it may be more economical to run the reactor at lower residence times despite the slightly higher levels of residual monomers in the product stream.
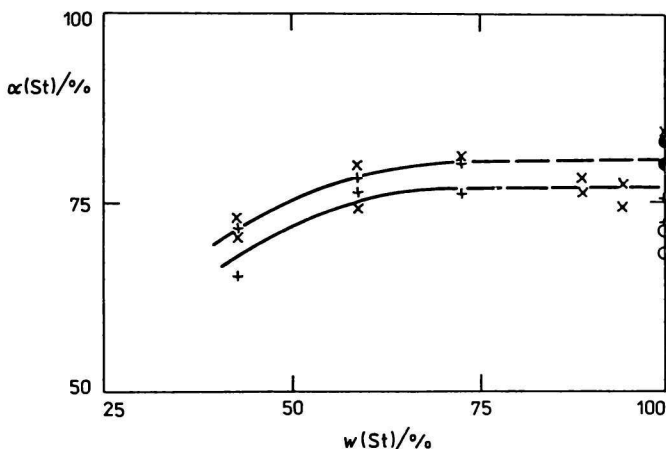

Fig. 6. Styrene conversion a(St) as a function of monomer feed composition w(St) and residence time R_T of reactants in CSTR. Temperature 270 °C. R_T/min: ● 45, × 30, + 15, ○ 7.5.

3. Total conversion, as measured by the conversion of both monomers, exceeded 70 % when more than *ca.* 40 mass % of the feed stream was St and the polymerization temperature was greater than 250 °C (Figs. 4 and 5).

Sampling procedure

Variability of the results was due to a number of factors, but the largest influence was attributed to the difficulty in obtaining a representative sample from the two-phase flow exiting the reactor. Efforts to improve the sampling method focussed on collecting the volatiles which flashed off the reactor exit [11]. For example, one method involved capturing the volatiles and passing them through a condenser. The volatile components of the product stream could thus be collected separately. However, improved sampling such as this was achieved at the expense of constructing sophisticated apparatus and having to spend the time to operate it.

Table 2
Influence of polymerization variables on polymer product characteristics
A. Temperature of synthesis[a]

Sample	Polymerization temperature °C	$\overline{M}_w{}^b$ (GPC)	$\overline{M}_n{}^b$ (GPC)
194A	210	2100	1500
194B	230	2000	1450
194C	255	1900	1400
194D	270	1150	850
196A	230	52000	16000
196B	250	37000	18000
196C	270	18000	6700

B. Residence time[c]

Sample	$\frac{R_T}{min}$	$\overline{M}_w{}^b$	$\overline{M}_n{}^b$	Copolymer composition Mole fraction St	AA
178C	15	1800	1200	0.449	0.551
177C	30	1900	1300	0.468	0.532
178A	45	2040	1300	0.507	0.493
184E	15	18500	7400	0.680	0.320
184B	30	14000	6100	0.672	0.328
184G	4	1700	1060	—	—

C. Monomer feed composition[a]

Sample	Monomer feed Mole fraction St	AA	$\overline{M}_w{}^b$	$\overline{M}_n{}^b$	Copolymer composition Mole fraction St	AA
194B	0.20	0.80[d]	2000	1430	—	—
177A	0.35	0.65[d]	2400	1330	0.484	0.516
182A	0.50	0.50[d]	4800	2250	0.645	0.355
195A	0.80	0.20[d]	40000	11000	0.814	0.186
196A	0.90	0.10[d]	52000	16000	—	—
176B	0.15	0.85[e]	1670	1380	0.413	0.587
182C	0.50	0.50[e]	2130	1500	0.486	0.514
184C	0.65	0.35[e]	14000	6100	0.697	0.303
196C	0.90	0.10[e]	18000	6700	0.901	0.099
201A	1.00	0[e]	20000	8300	1.000	0

a) Residence time R_T = 30 min, monomer feed composition as in Table 1.
b) GPC measurements were described in Ref. [8] and [9] (no correction on UV detector (250 nm) response as a function of $\overline{M}$ was made).
c) Polymerization temperature 270 °C, d) 230 °C, e) 280 °C.

Influence of the copolymerization conditions on copolymer product characteristics

It seems useful to summarize in here an influence of polymerization conditions on St—AA copolymer characteristics although molecular mass analysis by GPC and compositional analysis of the copolymers were given independently in Ref. [8, 9] and [15, 16], respectively.

Tables 2A—C show an influence of polymerization temperature, residence time of the reactants, and monomer feed composition, respectively, on average molecular masses. In Tables 2B and 2C one can find data about relation between experimental variables and St—AA copolymer composition.

Following conclusions may be drawn from data in Table 2 for thermally initiated bulk St—AA copolymerizations:

The higher polymerization temperature the lower molecular mass averages of the polymer product. Decreasing of $\overline{M}$ with temperature is especially evident in cases of $\overline{M}_w$ values.

Longer residence time of the reactants in CSTR causes generally decreasing in $\overline{M}_n$ values. That effect is more pronounced for St—AA systems richer in St monomer (Table 2B). Some destructive and secondary reactions of carboxylic groups at high temperatures and long R_T are probably responsible for unclear tendency of $\overline{M}_w$ values (Table 2B). Discussion of thermal behaviour of both St and AA monomers as well as the polymers is given in Ref. [15].

The higher St monomer content in St—AA monomer feed the higher are average molecular masses of the copolymer products (Table 2C).

Copolymer composition measurements done by direct titration of carboxylic groups in copolymers in dioxane solutions show that the longer are R_T values the lower is carboxylic group content in copolymers (Table 2B).

Similarly evident is an influence of the monomer feed composition on the copolymer composition reflecting differences in reactivity ratios of both the monomers [8], in spite of some surprising results in particular cases (compare data for samples 182A and 182C from Table 2C).

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