

High-Temperature Continuous Bulk Copolymerization of Styrene and Acrylic Acid: Thermal Behavior of the Reactants

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SYNOPSIS

The behavior of the monomers: styrene (St) and acrylic acid (AA) during the process of thermally initiated bulk copolymerization realized in a continuous stirred tank reactor (CSTR) is discussed in this work, on the basis of results obtained from experimental work carried out by the authors and data available from literature. GPC, GC, IR, and NMR techniques were used to examine the volatile oligomers released from the raw St-AA polymers. The mechanism of the thermal initiation of polymerization in the system under investigation is also discussed. Polymer degradation reactions in the vicinity of the ceiling temperature T_c , chain transfer reactions, and secondary reactions of carboxylic groups in high temperatures have also been considered. The behavior of the St-AA polymers during derivatographic tests in the temperature range: ambient–400°C, conducted in atmospheric air, was also evaluated. Experimental conditions, in which deep destruction of the product during the copolymerization process could be avoided, were established. Knowledge of these conditions is important from a practical point of view.

INTRODUCTION

High-temperature continuous polymerization of vinyl monomers applied for the production of reactive polymers of low molecular weight or oligomers^{1–4} is commercially very effective. These processes make it possible to synthesize polymers having the following characteristics:

- molecular weights M_n mostly in the range of several hundred up to ca. 20,000
- beneficial molecular weight distribution ($M_w/M_n < 3.0$)
- uniform copolymer composition
- high conversion and productivity

Low molecular weight polymers such as St-AA copolymers are widely applied.⁵ Coatings (high solids, polishes, etc.), flocculants, dispersants, and plasticizers are some of the most frequent applications.

In spite of large practical importance of the products of high-temperature polymerization, our knowledge of the behavior of the reactants in the CSTR is unsatisfactory. The synthesis of St-AA low molecular weight copolymers at high temperatures has been widely investigated at the McMaster Institute for Polymer Production Technology.^{2,6–12}

The present paper focuses on the investigation of the reactants, i.e., monomers, oligomers (reactive and neutral byproducts), and polymeric products (thermal degradation, side reactions of carboxylic groups) in CSTR. Using derivatographic measurements, the behavior of hot raw copolymers in oxidative conditions was evaluated. Experimental conditions making possible the synthesis of copolymers and avoiding deep destruction changes were determined.

EXPERIMENTAL

Polymer Synthesis

All polymer samples were synthesized in bulk in the CSTR. The volume of reactor was either 1.400 cm³ or 400 cm³; the conditions of syntheses are given in

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Table I. No special treatment of technical grade monomers was applied prior to syntheses. St was obtained from Aldrich Chemical Co. (Milwaukee, WI) and AA from Rohm and Haas Canada Inc. (Toronto, Ontario, Canada). The syntheses were carried out after degassing of the monomer feed and purging it twice with nitrogen. The other details connected with the experiments were published earlier.^{7,11}

Polymer Characterization

GPC Analysis

Styragel column systems applied in polymer evaluation: GPC I: μ -Styragel 10⁴ + ultra Styragel 10³ + μ -Styragel 500 + ultra Styragel 100; and GPC II: μ -Styragel 500 + ultra Styragel 100, both in THF. Preliminary GPC data on St-AA copolymers have been published.^{9,10}

GC Analysis

High-temperature gas chromatography was applied using 5% SE-54 on the Chromosorb GAW-DMCS column (GC instrument: HP model 5880A, temperature gradient: 130°C through 3 min; gradient 2°C/min up to 144°C, 144°C through 1 min; gradient 10°C/min up to 290°C, 290°C through 6 min).

Copolymer Composition

Two procedures of carboxylic group titration were used in measurement:

1. The first procedure was based on direct titration of COOH groups with 0.1N solution

of aqueous NaOH in the presence of bromothymol blue indicator. Dry polymer samples (ca. 1–2 mmol COOH groups), precipitated from methanol-dichloromethane solvent system (according to Ref. 10) dissolved in dioxane were used for analyses.

2. The second procedure used in determining COOH groups in St-AA copolymers was based on the neutralization of carboxyl groups in an excess of 0.1N NaOH solution, bringing the whole solution to boil under a condenser for 2 h. Residual alkali was titrated with 0.1N HCl using phenolphthalein as an indicator. Methanol-dichloromethane solvent systems were applied for polymer dissolution.¹²

Infrared spectra for selected St-AA polymers were measured on KBr pellets using a Nicolet FTIR instrument.

Derivatography

Investigations of St-AA copolymers were carried out in an atmosphere of air, at temperatures ranging from room temperature to 400°C. Temperature rate: 6°C/min. Instrument: MOM Paulik-Paulik-Erdey Derivatograph, type 102, Budapest, Hungary.

RESULTS AND DISCUSSION

In the case of high-temperature polymerization of St-AA monomers, the following reactions that influence the molecular weight, molecular weight dis-

Table I Experimental Conditions of Styrene-Acrylic Acid Copolymerization

Reactor Type ^a	Monomer Feed (St/AA) (mol %)	Synthesis Temp (°C)	Residence Time, R_T (min)	Run or Polymer Description
I ^a	15/85	270	60	106
	35/65	270	60	105
	50/50	278	60	104
	65/35	270	60	107
	100/0	270, 280	60, 30	109A, 109B, 103
II ^b	8/92	270	30	175B ^c
	20/80	255	30	194C
	35/65	250	30	177B
	50/50	270	30	182C
	50/50	270	10	183C
	65/35	270	10	184F
	100/0	300	30	202B

^a CSTR volume 1400 cm³.

^b CSTR volume 400 cm³.

^c Chemically initiated (0.2 mol % *tert*-butylhydroperoxide).

tribution, and copolymer chain structure are especially important⁷:

- initiation of the copolymerization process,
- thermal degradation and chain transfer reactions,
- side reactions of carboxylic groups.

The Thermal Polymerization Mechanism

Mayo's mechanism of thermal initiation of St polymerization,¹³ as outlined by Kirchner and Riederle,¹⁴ should play a significant role in the copolymerization of St and AA at high temperatures. The Mayo mechanism involves a Diels-Alder reaction between two styrene molecules (refer to Fig. 1(A) and Refs. 7 and 14) as well as a further reaction with the next monomer molecule. This produces two monoradicals: monomeric and dimeric. These radicals initiate the propagation of styrene polymer. The intermediate Diels-Alder adduct, together with the monomer molecule, creates cyclic trimers; cyclic dimers are formed independently [Fig. 1(A)].

In the case of the thermal polymerization of the AA monomer, the situation is not as clear as in the well-established case of St. This is because the thermal polymerization of St has been applied in industry for a long time, whereas trials of high-temperature polymerization of AA are recent.

There is very little literature available on the thermal polymerization of AA (or its salts) in bulk.

Results given in Ref. 15 are interesting in the context of this discussion. The thermal initiation of sodium acrylate (AA-Na) polymerization in bulk (solid-state polymerization) was investigated by Indian authors.¹⁵ The findings are as follows:

- The initiation process has a radical character (activation energy 28.8 kcal/mol).
- The formation of free radicals through the spontaneous dissociation of C-C or C-H bonds or by the opening of the double bonds. It guarantees the level of the activation energy.

Balcerowiak et al.¹⁶ ascertained that at the temperature of 280°C the bulk polymerization (thermal) of AA-Na takes place at a very low degree of polymerization. However, no details of the polymerization initiation mechanism were given.

Our attempt to polymerize continuously AA monomer in bulk in the CSTR was unsuccessful. The polymerization of AA in a water solution (40 wt % of AA, 250°C, 30 min residence time) led to a product containing many volatiles. The chromatogram of the polymerization product of AA, obtained under these conditions (Fig. 2), shows only very low molecular weight oligomers. It may be concluded that dimers, trimers, and tetramers are the major products of the synthesis. St homopolymerization has a different course, and chains of substantially higher molecular weight are created, as is evident in Figure 2.

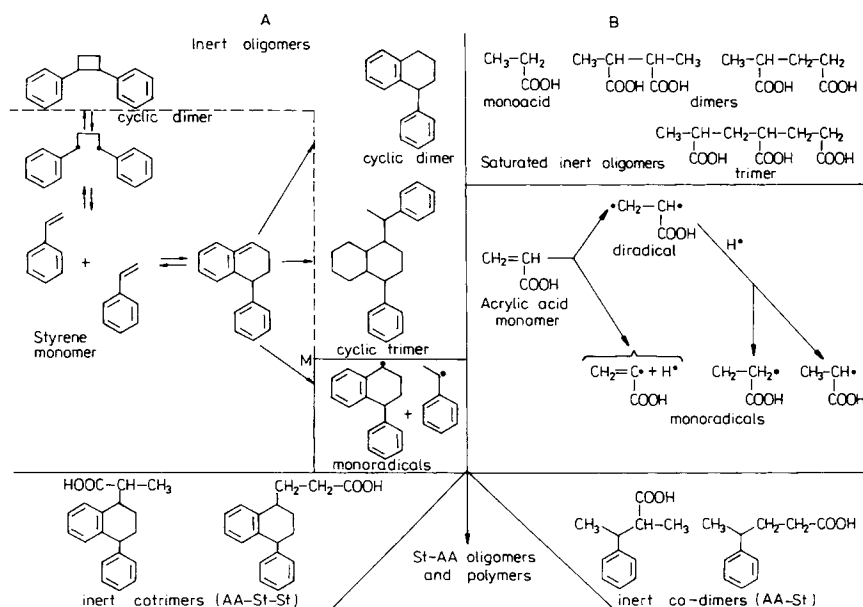


Figure 1 Mechanism of the thermal initiation of St polymerization (A) and AA oligomerization (B).

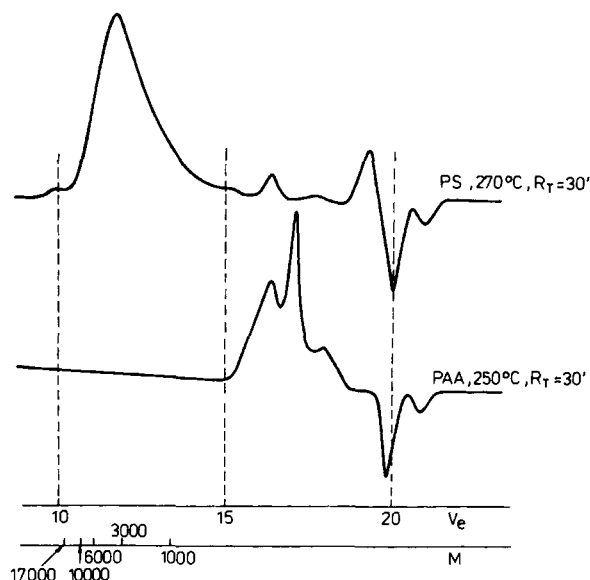


Figure 2 GPC traces of the thermal homopolymerization products of St (PS) and AA (PAA). II GPC system.

Low molecular weight oligomers such as styrene cyclic dimers and trimers [Fig. 1(A)] are the main undesired byproducts of the thermally initiated St polymerization or copolymerization processes. They are created at the initiation stage [Fig. 1(A)]. Anticipated oligomeric inactive products created during the initiation of AA thermal polymerization are shown in Figure 1(B).

The volatile St oligomers released from the PS samples were monitored using GPC (Fig. 3) and GC (Fig. 4) techniques. Figure 3 presents GPC chromatograms of the fractions obtained through vacuum distillation of the PS 103 sample.¹² They showed dimer, trimer, and tetramer peaks, partially

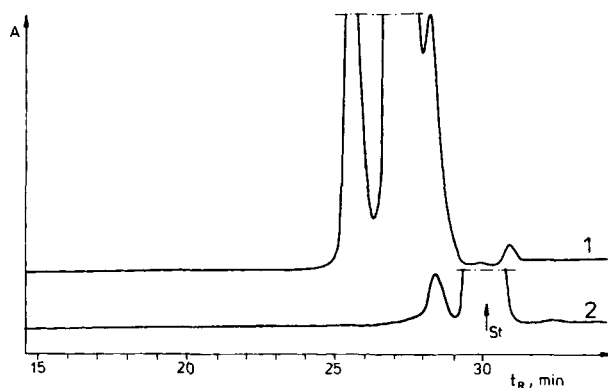


Figure 3 GPC chromatograms of the volatile fractions isolated from polystyrene sample 103 via vacuum distillation: (1) distillation receiver I (ambient temperature); (2) distillation receiver II (liquid nitrogen temperature). II GPC system.

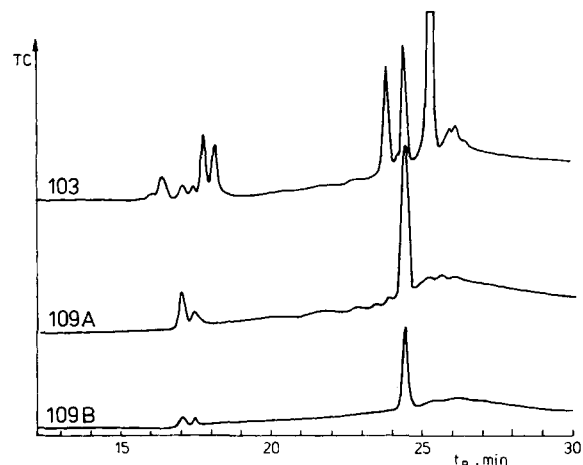


Figure 4 GC chromatograms of the volatile fractions of St homopolymers 103, 109A, and 109B. Conditions of syntheses in Table II.

separated. Two groups of peaks attributed to dimers (t_R 16.5–18.5 min) and trimers (t_R 24–25.5 min) of St are easily distinguished on GC chromatograms of PS samples (Fig. 4).

The intensive GC peak with t_R 24.5 min can be correlated with the cyclic trimer (1-phenyl-4-phenylethyltetraline) formed at the initiation stage of the St thermal polymerization^{7,13,14} Similarly, the dimer peaks with $t_R = 17.10$ and 17.50 min are most likely created by diphenylcyclobutan and 1-phenyltetraline.¹⁴ At higher polymerization temperatures and during longer residence times, one can observe other volatile species (refer to Table II and chromatograms in Fig. 4). They are created as a result of thermal degradation reactions and are discussed later. Such volatile byproducts appear on the GC chromatogram of the PS 103 sample (Fig. 4 and Table II) at t_R 25.3 min (trimer) or $t_R = 18$ –18.5 min (dimers). In general, these findings are in accordance with the results of other works.^{14,17,18}

Volatile oligomers isolated from two selected St-AA copolymer samples (106 and 182C) are shown in Figure 5 in the form of GPC chromatograms along with their corresponding polymeric parts. Figure 6 shows the UV spectra recorded in the peak maximum positions of the GPC chromatogram of the copolymer 182C sample's volatile part.

The share of volatile oligomers in St-AA raw copolymers rises with the increase of AA content in the monomer feed, temperature of synthesis, and residence time of the reactants. In industrial conditions, those volatile fractions of the copolymers containing oligomers of a low degree of polymerization ($P = 2$ –4), can be eliminated by vacuum degassing. GC chromatograms of the volatile parts of

Table II Gas Chromatographic Analysis of Volatile Oligomers in Styrene Polymerization Products

Polymer Sample	Temp/ R_T	Wt % of Oligomer with t_R (min)							
		t_R 16.10 (min) 16.43	17.10 17.50	17.81 18.15	Σ % Dimers	23.87 24.46	25.33	Σ % Trimers	Σ % Dimers + Trimers
103	280°C/60 min	0.06 0.31	0.16 0.10	0.56 0.55	1.74	1.00 1.22	3.63	5.85	7.59
109A	270°C/60 min	0 0	0.35 0.17	0 0	0.52	0.03 1.79	0	1.82	2.34
109B	270°C/30 min	0 0	0.09 0.18	0 0	0.27	0 1.44	0	1.44	1.71

the copolymers are not as discrete as are those of St oligomers (Fig. 7). Even in the case of the St-AA monomer feed polymerization product obtained from the monomer mixture of 35/65 mol %, one can easily distinguish St dimer peaks in the range $t_R = 17-17.5$ min. However, no St trimer peaks are observed in the copolymer. The absence of St trimer peaks in the copolymer GC chromatograms is due to high AA radical activity that suppresses the evolution of the intermediate St structure into an inactive cyclic trimer [Fig. 1(A)]. The intensity of the main St dimer peaks in the GC chromatograms

($t_R = 17-17.5$ min) decreases with the increase of the AA content in the monomer feed (Fig. 7). Certain new peaks appear in the GC chromatogram, e.g., near the $t_R = 22$ min (Fig. 7) caused most likely by inert St-AA codimers or cotrimers (see also Fig. 1).

Thermal Degradation and Chain Transfer Reactions

Considering the high temperature involved during polymerization (200–300°C) conducted in this study, one should take into account the ceiling tem-

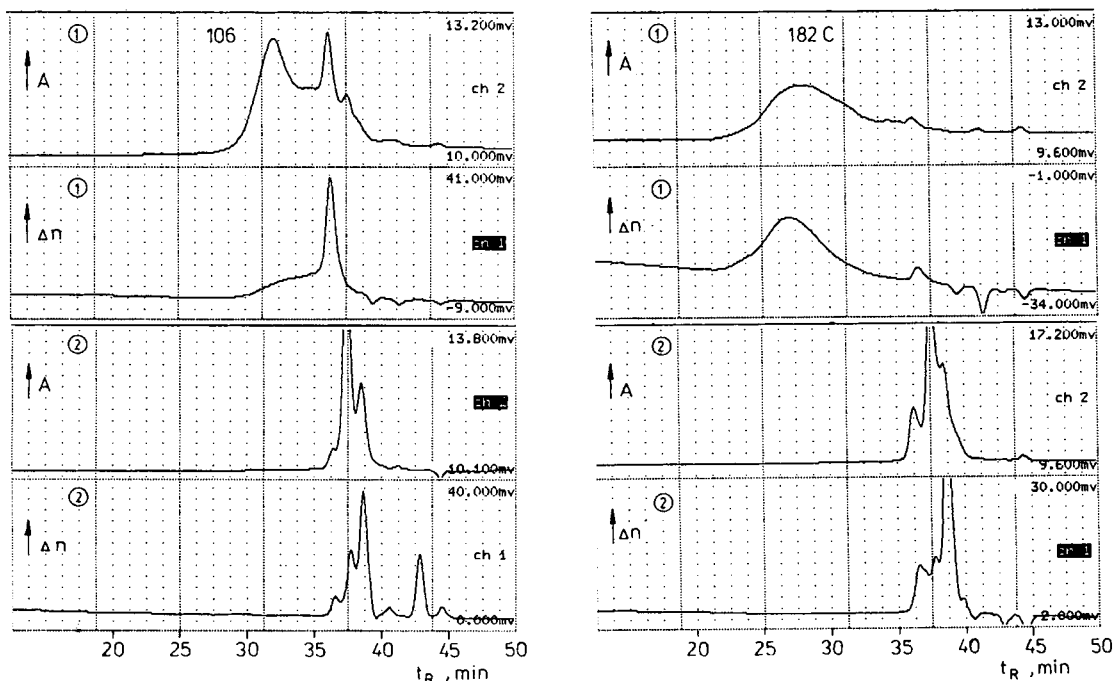


Figure 5 GPC chromatograms of the selected St-AA copolymers (1) after removing the volatile fractions via vacuum distillation and the chromatograms of the volatiles (2) from the distillation receiver I. Copolymers: 106 and 182C (see Table I). I GPC system, detection UV 250 nm (A) and refractive index (n).

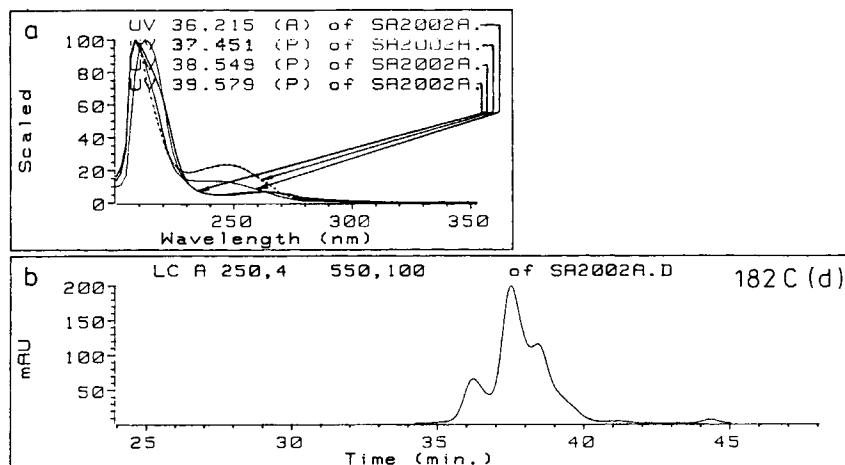


Figure 6 UV spectra (a) measured at the maximum peaks of GPC chromatogram (UV 250 nm) (b). Copolymer sample 182C, volatile part (see Table I).

perature, T_c , for a given polymer. T_c is a kind of "thermodynamic borderline" between polymer molecule propagation and depropagation (depolymerization). The ceiling temperature for PS is about 300°C. The T_c value for PAA is not known because the side reactions of carboxylic groups does not allow its reliable evaluation. An increase in pressure (which takes place during St-AA synthesis in the CSTR) can also influence T_c .¹⁹

In the range of temperatures applied in CSTR, random chain scission and unzipping should be considered for St-AA copolymers.⁷ The course of PS degradation at high temperatures has been well in-

vestigated and is adequately described in the literature (see, e.g., Refs. 18 and 20–23). The decrease in the average polymer molecular weight and the polydispersity index (M_w/M_n tends to 1.7) is a consequence of PS thermal degradation. There has been very few publications about the homolytic scission of the acrylic-based polymer chains. Therefore, the work of Gunawan and Haken²⁴ seems to be valuable although they investigated the thermal degradation of poly(methyl acrylate). The above authors²⁴ identified a series of saturated and unsaturated oligomers of methyl acrylate in the products of the polymer degradation. The main products of degradation in pyrolysis gas chromatography conditions²⁴ were unsaturated (i.e., conjugated triene and mono-unsaturated trimers) and saturated trimers (total content of trimers ca. 75% in comparison with a total dimer content of ca. 11%). We can expect a similar result in the case of PAA degradation. Proton NMR spectra of selected oligomers isolated from the raw polymers through vacuum distillation indicate the presence of saturated and as well as unsaturated compounds in the samples.¹²

Previous investigation of St thermal homopolymerization^{20,25} showed that the transfer of the chain to molecules of low molecular weight, other than styrene monomer, had occurred to a significant extent, thus influencing molecular weight development.²⁰ Therefore, one can see that the intermediate products as well as byproducts of low molecular weight created during thermal copolymerization of St and AA and degradation processes of macromolecules in CSTR are responsible for molecular weight and molecular weight distribution. The influence of each chain transfer agent is not known.

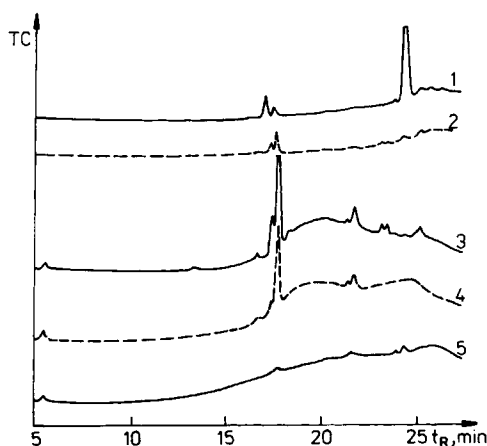


Figure 7 GC chromatograms of the volatile oligomers present in the St-AA thermal copolymerization products (270°C, $R_T = 60$ min): (1) St homopolymer 109 A; (2) copolymer 107; and in the lowest molecular weight fractions¹² of the following copolymers: (3) 104; (4) 105; (5) 106. Description of the samples in Table I.

Side Reactions of Carboxylic Group

Substantial changes in the structure of the polymer chain, due to carboxylic group side reactions, may take place at high temperatures. These side reactions comprise anhydride formation, decarboxylation, and deep destruction of the polymer chain.

According to some authors, PAA forms intramolecular glutaric anhydride structures or intermolecular butyric structures at high temperatures.²⁶⁻²⁹ This happens also in relatively mild conditions, for instance, during the drying of PAA samples at 125°C.²⁹ A similar situation was observed during heat treatment of AA copolymers.³⁰ The above-mentioned investigations³⁰ show that the process of PAA anhydridization begins at ca. 130°C and peaks at ca. 170°C.

During the heating of PAA in air in the temperature range 150–275°C, Gaugh and Kottle discovered the presence of anhydride structures after 5 min of heating. The higher the temperature, the lower was the content of anhydride structures in the polymer.²⁶ Anhydride groups were absent at temperatures above 275°C; however, using the IR method, intensive ketone bands and unsaturated bonds were identified²⁶; carbon dioxide was the main volatile component above 275°C. If the thermal conditions are more severe (275–350°C), then the proportion of cyclic ketone structures (IR band 1150 cm⁻¹) and unsaturated bonds (IR band 1650 cm⁻¹) is greater.²⁶ The maximum rate of decarboxylation was observed at ca. 225–230°C.^{29,30}

Very slight IR bands in the range 1625–1650 cm⁻¹

for PAA (sample 155B) and the richest in AA copolymer (sample 175B) were found (Fig. 8). This may be attributed to the anhydride (1620 cm⁻¹) and/or to cyclic ketone structures (1650 cm⁻¹). It should be mentioned, however, that no explicit evidence of deeper destruction of COOH groups in the St-AA copolymers, as can be determined by IR measurements, was found.

The results of copolymer composition determination could be interpreted as follows: Certain anhydride groups present in St-AA copolymers do not undergo neutralization through titration with alkaline solution during direct analysis of the copolymers.¹² The level of anhydride groups is proportional to the AA unit content in the copolymer. Detailed discussion of these results is carried out in Ref. 12.

Thermal Stability of St-AA Copolymer

The first qualitative information about St-AA polymer destruction during high-temperature syntheses can be drawn from visual examination of the raw polymer exiting the CSTR. The higher the temperature of synthesis, the longer is the residence time of the reactants, and the higher the AA content in the monomer feed, the more intensive is the color of the bulk polymer product. It was found that destructive reactions played a negligible role in the changing of the polymer color at temperatures of up to ca. 230°C in the range of R_T values investigated (see Table I).

Thermal stability tests of St-AA copolymers were carried out in oxidative conditions. Thermal gravi-

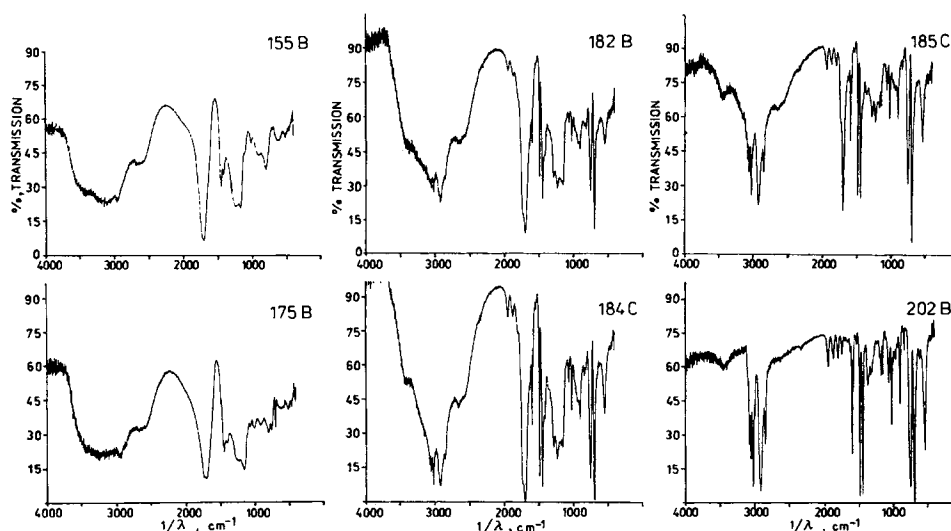


Figure 8 Selected IR spectra of St-AA polymers. AA homopolymer (155B), copolymers from the monomer feed mixtures, in AA mol %: 92 (175B), 50 (182B), 35 (184C), 15 (185C), and St homopolymer (202B).

Table III Thermal Stability of Styrene–Acrylic Acid Polymers

No.	Polymer Sample Description	Copolymer Composition AA (mol %)	Mass Losses at Temperature (wt %)			
			200°C	250°C	300°C	350°C
1.	156C	100	29	49	62	73
2.	175B	76	13	43	57	73
3.	194C	75	9	37	55	80
4.	177B	60	11	29	48	80
5.	183C	44	3	11	19	47
6.	184F	30	6	10	16	39
7.	185F	14	3	4	9	30
8.	202B	0	0	1	5	28

metric behavior of both the homopolymers, as well as a range of St–AA copolymers, is presented in Figure 9. The higher content of AA in the copolymer, the lower its thermal stability in oxidative conditions. The polymers under investigation roughly constitute two groups: less thermally stable (samples 1–4) containing above ca. 50 mol % of AA and more stable (samples 5–8), richer in St units as is evident from Figure 9. Loss of mass of each particular poly-

mer during its heating at the rate of 6°C/min to temperatures of up to 200, 250, 300, and 350°C, respectively, is shown in Table III.

CONCLUSIONS

The results of the investigations carried out may be summarized as follows:

1. Thermal initiation of high-temperature copolymerization of St and AA is initiated mainly by St radicals, according to the Mayo mechanism; thermal initiation of AA polymerization leads exclusively to low molecular weight oligomers.
2. Except for residual monomers, saturated cyclic and linear oligomers as well as unsaturated oligomers of 2–4 degrees of polymerization are the major volatiles in the raw products of St–AA copolymerization in the CSTR.
3. Beside thermal degradation reactions, secondary reactions of carboxylic groups such as anhydridization, decarboxylation, and deep destruction play an important role in the process of high-temperature St–AA copolymerization (> 230°C), thus influencing the physicochemical properties of the product.
4. The following experimental conditions of the process of St–AA thermal copolymerization were determined to minimize undesired changes in the copolymer product—temperature: < 270°C; residence time: < 30 min; content of AA in monomer feed: < 30 mol %.
5. The thermal stability of St–AA copolymers in oxidative conditions depends on the chemical composition of the copolymer. Copolymers containing more than ca. 50 mol %

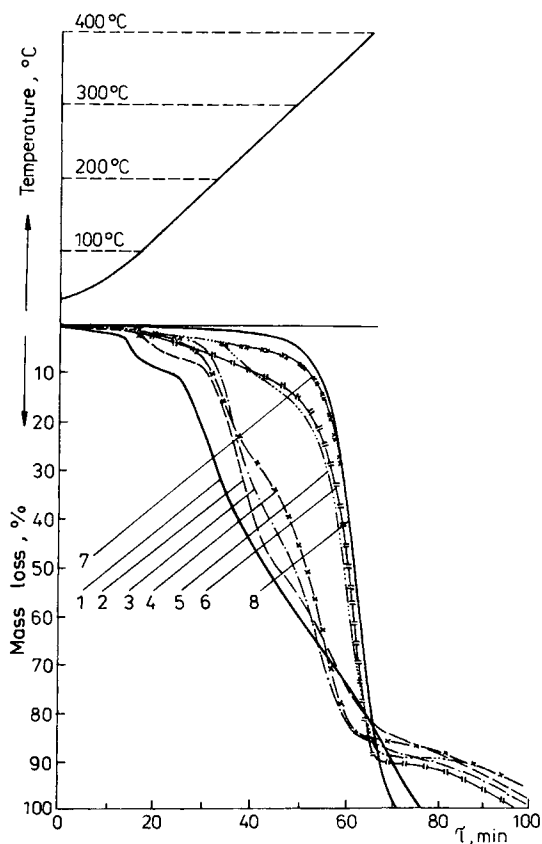


Figure 9 St–AA copolymer mass losses during derivatographic tests. Description of the curves in Table III.

AA are distinctly less stable at elevated temperatures than are those richer in St content.

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Received June 13, 1990

Accepted June 13, 1990