

Synthesis, Characterization and Thermal Stability Study of Styrene-based Ionomers I) Programmed Heating Experiments (10 °C/min to 500 °C)

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ABSTRACT: Ionomers are generally described by copolymers having either acrylic or methacrylic acid as one component and the other component is mostly either ethylene or styrene. The objective of this research was to study the thermal behaviour and stability of ionomers of styrene with some alkali metal acrylates. These materials have been synthesized by neutralization of the respective copolymer containing 40 mole percent acrylic acid with sodium and potassium hydroxides in acetone medium. The copolymer of styrene-acrylic acid was made by solution polymerization in methanol using 2,2'-azobisbutyronitrile (AIBN) as initiator under nitrogen blanket at 60 °C. Copolymer composition was calculated from the monomer feed concentration. The ionomer samples were characterized using FTIR technique. Thermal behaviour of the ionomers has been studied under programmed heating in dynamic nitrogen atmosphere by using differential thermal analysis (DTA) and thermogravimetry (TG) and in vacuo using thermal volatilization analysis (TVA) techniques supported by product analysis. The thermal behaviour of the sodium and potassium salts of styrene-acrylic acid copolymer is found to be rather similar. Infrared spectroscopy, mass spectrometry and GC-MS techniques were used to examine the degradation products from TVA degradation. Quantitative measurements of the main product fractions under normal TVA conditions have been made. It is found that the main decomposition of the styrene-acrylic acid salts copolymers starts at about 350 °C and reaches maximum at 450 °C.

KEY WORDS: Thermal Volatilization Analysis(TVA), Subambient TVA, Degradation products, Thermal stability, Styrene-based ionomers, Onset & main decomposition temperatures.

INTRODUCTION

The word ionomer is usually used to describe ionic polymers which are constructed from a hydrocarbon backbone containing some pendant carboxylic acid groups which are neutralized either partially or

completely to form salts. Ionomers are generally prepared from copolymers having either acrylic or methacrylic acid as one component. The other component is mostly either ethylene or styrene. The most important

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commercial ionomers are copolymers of ethylene with small amounts of salt units. The description "ionomer" can also be broadly applied to other copolymers containing both salt monomers and covalently bonded monomer unit. These materials have seen expansive growth in recent years.

The thermal degradation behaviour of polymers and copolymers containing acrylic and methacrylic acid salt units has received much less attention than that devoted to the corresponding ester polymers from these acids.

Whether present in a homopolymer or copolymer chain, however, these ionic salt units can have a major effect on thermal behaviour.

The main features of the thermal stability and the mode of thermal degradation of the parent homopolymers such as polyacrylic acid and polystyrene with respect to the corresponding ionomers have been considered for many years.

The effect of different metal cations including alkaline, alkaline-earth and transition metal salts on the structure and physical and thermal properties of ethylene ionomers has been studied by Hirasawa, E. et al. [1]. They have shown that changes in the structure and properties are attributed to the strength of the ionic interactions and the valence of the cation.

Some properties of styrene-based ionomers containing alkali metal salts of acrylic or methacrylic acid have been investigated by Suchocka-Galas, K. [2]. The study has been conducted to examine the influence of the acidic content and nature (acrylic or methacrylic) and the nature of the alkali metal salts on the properties such as glass transition temperature of the ionomers.

McNeill and Alston [3] studied the thermal behaviour of polymers and copolymers containing acrylic and methacrylic acid salts. They have considered the patterns of degradation behaviour and mechanisms of such systems. They showed that degradation of the salts from these structures is depend both on the acid type and the nature of the metal ion involved.

Suchocka-Galas et al. [4] studied the thermal and thermooxidative degradation of copolymer of styrene-acrylic acid and their sodium salts. They have shown that thermal resistance is independent of the amount of introduced acid.

The thermal degradation of the copolymers of styrene-methacrylic acid and their sodium salts was

investigated by Suchocka-Galas [5], who reported that initial decomposition and the main decomposition temperatures of the ionomers remain almost constant, independently of the amount of MAA and NaMA introduced.

In the present study, the thermal behaviour of copolymers of styrene-acrylic acid salts (Na and K) have been investigated using DTA, TG and TVA [6] techniques.

It is found that the main decomposition temperature of the copolymer samples is higher than that of polystyrene [7-9] and the styrene acrylic acid copolymer [10] but less than the corresponding polyacrylic acid salts [11].

According to this, it seems that the thermal stability of the styrene-acrylic acid salt copolymers can be dependent on the amount of introduced salt units and the degree of neutralization of the styrene-acrylic acid copolymer by the respective bases which is inconsistent with those obtained by Suchocak-Galas [5].

A comparison of the results of this investigation with those of the earlier studies [3, 12-14] reveals some similarities to the products which can also be considered the similar routes of decomposition and mechanisms of degradation.

In this study some of the degradation products such as styrene, toluene, α -methyl styrene and benzene can be attributed to the degradation of the styrene chain units of the copolymers which are consistent to the results of different investigations [3, 12-14].

The volatile products of degradation such as carbon dioxide, carbon monoxide, styrene, multi-membered ring products, ketone groups and unsaturated products derived from break down of copolymers indicating chain and side chain scission reactions which are almost similar to the results of a series of studies [3, 14-16].

The presence of two monomers and short chain fragments of them in the cold ring fraction of TVA indicate that depolymerisation process occurs during the thermal degradation of styrene-acrylic acid salt copolymers [3,12].

EXPERIMENTAL

Materials

Styrene (Prolabo, 99.8wt%, France) was washed twice with equal amounts of a 10% solution of sodium hydroxide to remove inhibitor, then washed with distilled water and dried over calcium sulphate, calcium hydride

Table 1 : Copolymerisation & composition data for ST/AA copolymer.

ST/AA copolymer No.	Copolymerization data						Composition data				
	ST*		AA**		Methanol (ml)	Initiator (g)	Time (hr)	Conversion (%)	Mole% AA in monomer feed	Mole% AA in copolymer	Conversion (%)
(ml)	(g)	(ml)	(g)								
1	150	136.4	40	38.5	150	0.5	1.5	5.5	30	40	5.5

*Styrene monomer

** Acrylic acid monomer

and molecular sieves successively in a refrigerator. The styrene monomer was distilled under vacuum and degassed immediately prior to use. Acrylic acid (Hopkin and Williams Ltd, >99wt%, UK.) was distilled and used freshly. AIBN (BDH Chemicals Ltd, UK.) was recrystallized from methanol and used as initiator. Sodium hydroxide (BDH Chemicals Ltd, 98%, UK.) and potassium hydroxide (Fisons plc, A.R. grade, 85%, UK.) were used.

Preparation of ionomer samples

Styrene-acrylic acid copolymer (40 mole% acrylic acid)

The copolymer was made by solution polymerization in methanol. In a three-necked flask equipped with mechanical stirrer, condenser, thermometer and nitrogen inlet, dry methanol was introduced while the temperature was maintained between 0 and 5 °C under a gentle stream of oxygen-free nitrogen gas. Styrene and acrylic acid monomers were added gradually and the solution was left for 30 minutes under nitrogen flow to remove any dissolved oxygen. After addition of AIBN as initiator, polymerization was carried out under a blanket of nitrogen at 60 °C in a thermostated bath for at least one and half hr. The resulting solution was removed and the copolymer was precipitated in distilled water. The resulting white solid was filtered, washed with distilled water and dried under vacuum at 50 °C for 48 hr.

The mole fraction of acrylic acid in the monomer feed was calculated from weights of styrene and acrylic acid used. Copolymer composition was calculated from the monomer feed concentrations using the common method [17] and characterized using FTIR technique in which data were consistent with those obtained by Urban et al. [18], who studied the structure of styrene-acrylic acid copolymer using the same technique.

The copolymerization and composition data are summarized in table 1 and the respective FTIR spectrum has given in Fig. 1.

Neutralisation

Appropriate amount of the styrene-acrylic acid copolymer containing 40 mole% acrylic acid was dissolved in acetone (solution of 10%) and then titrated with a standard solution of the respective hydroxides (sodium & potassium hydroxides) in methanol (0.5 M) with phenolphthalein as indicator. Blank titration of acetone was performed. The neutralization solution was precipitated into 5 volumes of rapidly stirred acetone and the white solid copolymer was isolated and dried under vacuum at 40 °C for 72 hr.

Characterisation of copolymer samples

The copolymer was characterized by FTIR spectroscopy. The FTIR spectra of the sodium and potassium acrylate-styrene copolymer samples given in Fig. 2.

The main bands of interest are those arising at about 1610-1500 and 1430-1300 cm^{-1} due to conversion of carboxyl groups to carboxylates. There is significant indication of carboxylate formation, as shown in Figs. 2 and 3. The disappearance of bands at 1760 and 1700 cm^{-1} due to nonbonded and hydrogen-bonded carbonyl groups is consistent with the formation of the salts. Since FTIR spectra show the absorptions due to carboxyl groups have decreased but not completely disappeared, this indicates that some unreacted acrylic acid units are present in the copolymer samples.

Gas chromatography (GC)

A Perkin-Elmer F33 instrument with FID detector and 6 ft column (6 ft x 0.25 in outside diameter coiled glass) of 15% FFPA on GCQ 80-100 mesh and a 6 ft column of chromosorb 103 were used.

GC-Mass spectrometry (GC-MS)

A Perkin-Elmer Sigma 3 chromatograph interfaced to a Kratos MS 30 mass spectrometer and a high resolution Kratos DS 902S mass spectrometer with a DS 90 data

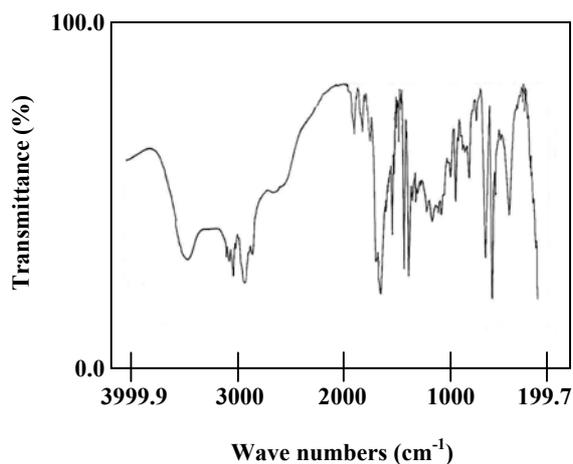


Fig. 1 : FTIR spectrum of styrene-acrylic acid copolymer.

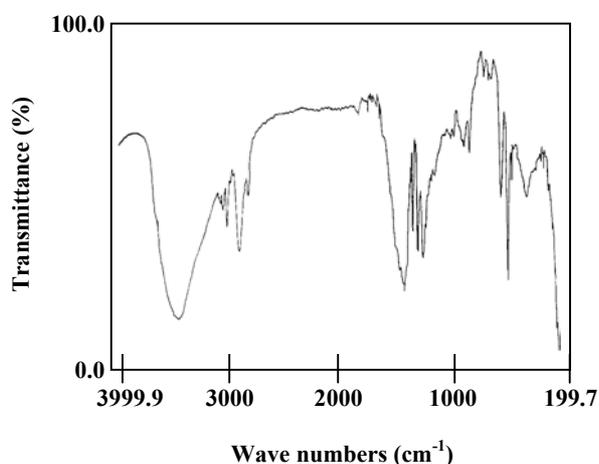


Fig. 2 : FTIR spectrum of the styrene-acrylic acid salt copolymers: ST/NaA copolymer.

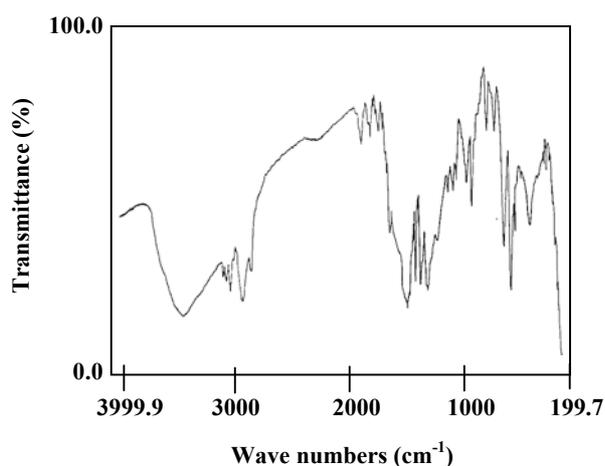


Fig. 3 : FTIR spectrum of the styrene-acrylic acid salt copolymers: ST/KA copolymer.

handling system were used. The column was a 15 m capillary column with DB-5(5% phenyl methyl silicone). Other instrumental conditions were as follows: injector temperature, 250 °C; voltage, 70 eV; initial column temperature, 50 °C for 5 minutes then programmed at 3 °C/min to 170 °C.

FTIR spectroscopy

Infrared spectra were obtained on a Philips PU 9800 FTIR, Perkin-Elmer 983 with P.E. 3600 data system and Perkin-Elmer 257 grating spectrometers.

Spectra of copolymer and involatile residue of degradation products were run as KBr discs. Cold ring fraction spectra were obtained by dissolution in suitable solvent and casting a film onto a salt plate (NaCl disc). Gas cells were used to obtain spectra of gaseous degradation products at room temperature.

Thermogravimetry (TG)

TG and DTG curves were obtained by using a DU Pont model 990 thermoanalyser with model 951 thermobalance. Samples of 3 mg were degraded from room temperature up to 500 °C in dynamic nitrogen (60 ml/min) at 10 °C/min.

Differential thermal analysis (DTA)

DTA curves were also recorded on the Du Pont thermoanalyser, using 10 mg samples in dynamic nitrogen (80 ml/min) under the same programmed heating conditions as for TG.

Thermal volatilization analysis (TVA)

The ionomer samples were examined as 70 mg powder samples under continuous evacuation in a TVA apparatus of the type described by McNeill [6]. Using the system, the degradation products were separated into non-condensable gases, condensable gas and liquid fraction, cold ring fraction of products volatile at degradation temperature but not at room temperature, and involatile residue. The condensable fraction was further separated by subambient TVA (SATVA) [19] before identification of the substances present.

RESULTS AND DISCUSSION

Thermogravimetry

The TG and DTG curves for both copolymer samples obtained under dynamic nitrogen atmosphere at 10

Table 2 : DTA, TG and DTG data for styrene-acrylic acid salt copolymer sample.

Copolymer samples	DTG		TG		DTA		
	Peak temp., °C	Temp. range, °C	Wt% loss for stage	Total Wt loss in the range	Peak temp., °C	Temp. range, °C	Thermal effect
ST/NaA	—	25-350	19		370*	355-375	Endo
				83			
	420	350-500	64		417	374-450	Endo
ST/KA	—	25-350	11.5		370**	355-375	Endo
				80.5			
	420	350-500	69		412	375-450	Endo

* A weak peak

** Shoulder

°C/min heating rate, are shown in Fig. 4 indicating a single stage decomposition above 400 °C with T_{max} at about 420 °C. The TG curves show that the weight losses to 200 °C are 15 and 8% for ST/NaA and ST/KA ionomers, respectively, due to the loss of water which both absorb from the atmosphere. Total weight loss at 500 °C is about 82% for both copolymers. The results show clearly that these copolymers are more stable than polystyrene and less stable than the corresponding salt homopolymers. Data are summarized in table 2.

Differential Thermal Analysis

The DTA curves, Fig. 5, for both ionomers are obtained under nitrogen atmosphere in the range 25-485 °C. The endothermic effect at about 370 °C prior to the main decomposition may possibly be due to dehydration and decarboxylation of acrylic acid units left unreacted during neutralization of acrylic acid/styrene copolymer with the respective bases. The DTA data are consistent with TG. The corresponding data are given in table 2.

Thermal volatilization analysis

The copolymer samples were of the order of 60-70 mg and in the form of a powder. All analyses were performed using a TVA system [6]. The TVA curves obtained for the ionomers are shown in Fig. 6

The main decomposition appears in the temperature range from 400 to 480 °C having T_{max} at about 435 °C. TVA shows two stages clearly for Na salt and in both samples the products differ at higher temperature. It is to be observed, however, that the T_{max} temperature of the major peak for the both copolymer samples lies between

that of polystyrene and the corresponding poly(acrylic acid) salts.

In addition, the ionomers have a peak on their TVA curves below 250 °C which is probably due to the release of precipitant or water taken up by them. There is not much difference in thermal behaviour of these copolymer samples on the basis of the TVA data. In degradation above 275 ° and 355 °C, the volatile material produced consist of substances non-condensable at liquid nitrogen trap (-196 °C) for sodium and potassium salts, respectively.

Gravimetric data, table 3, were obtained under normal TVA conditions using the same experimental approaches [20,21].

Subambient thermal volatilization analysis (SATVA)

Condensable volatile degradation products from the copolymer samples degraded to 500 °C using the TVA technique, collected in a liquid nitrogen trap in the vacuum system, were fractionated by the SATVA method [19].

Product analysis

Infrared spectroscopy, mass spectrometry and GC-MS techniques were used to examine the degradation products. The liquid fraction of the SATVA separation was subjected to GC-MS.

1) Residue

Metal carbonate is the main component in the involatile fraction. The corresponding IR spectra are illustrated in Fig. 7.

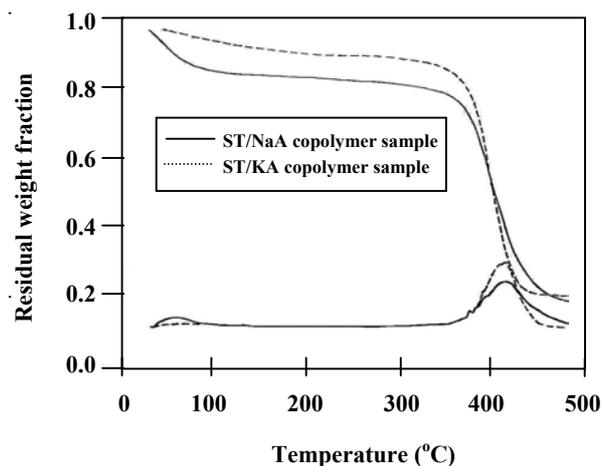


Fig.4 : TG and DTG curves (dynamic nitrogen atmosphere, heating rate $10^{\circ}\text{C}/\text{min}$) for ST/AA salt copolymer samples.

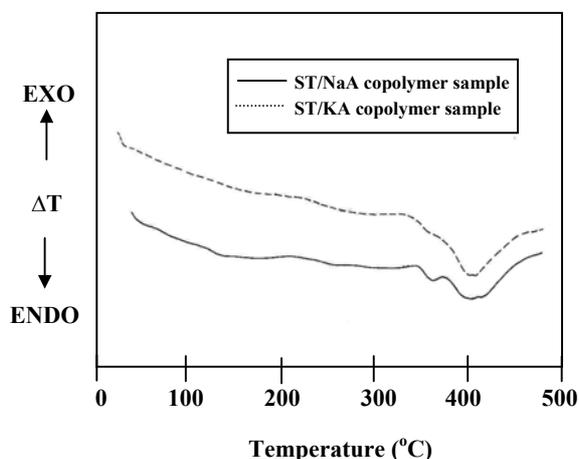


Fig. 5 : DTA curves (dynamic nitrogen atmosphere, heating rate $10^{\circ}\text{C}/\text{min}$) for ST/AA salt copolymer samples.

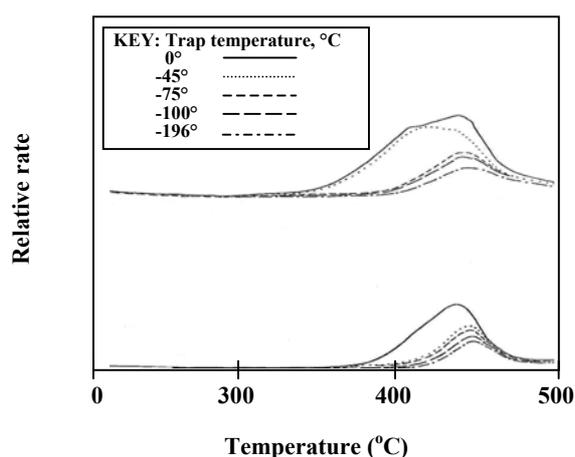


Fig. 6 : TVA curves (vacuum, heating rate $10^{\circ}\text{C}/\text{min}$) for styrene-acrylic acid copolymer samples. above : ST/NaA copolymer, below : ST/KA copolymer.

2) Cold ring fraction

IR spectra of the cold ring fractions are consistent with the presence of short chain fragments of the respective copolymer. The spectra of the CRF contain features of both polystyrene and the metal polyacrylates. These show different significant bands, Fig. 8, in the $3100\text{-}2850$, $2000\text{-}1600$, $1600\text{-}1500\text{ cm}^{-1}$ regions and a group of bands below 900 cm^{-1} which are produced by aromatic ring systems related as a main component. The characteristic bands in the $1610\text{-}1550$ and $1430\text{-}1350\text{ cm}^{-1}$ range produced by carboxylate ions (-COO^-) are due to the antisymmetrical and symmetrical stretching of carbonyl group. The characteristic bands at 1805 , 1760 (shoulder) and 1030 cm^{-1} , due to anhydride structures, imply that some acrylic acid units are left unreacted in the chain after the neutralization process.

The cold ring fractions tended to separate into two parts, an upper soluble in dichloromethane (CH_2Cl_2) giving an ir spectrum (film cast on NaCl disc) rather similar to styrene based compound and a lower, insoluble part giving a spectrum (KBr disc) closely resembling that of the acrylate salts. The spectra are shown in Figs. 9 and 10.

The presence of short chain fragments of polystyrene, such as dimer, trimer and tetramer (trace) together with one and two units (trace) of each type were also confirmed by mass spectrometry in the cold ring fractions. Products identified for the CRF of styrene-potassium acrylate copolymer sample are listed in order of importance in table 4.

3) Non-condensables as gaseous products

Methane and carbon monoxide were established as non-condensables.

4) Condensable gases

The condensable gaseous products were identified by IR and MS consisted of carbon dioxide and acetone as major products together with small amounts of ethylene, propene, 1-butene, acrolein, acetaldehyde, methyl ethyl ketone, benzene, toluene, cyclopentene and cyclopentadiene.

5) Condensable as liquid fraction

The IR spectra of liquid fractions from degradation of the ionomer samples are clearly indicative of styrene as

Table 3 : TVA data for degradation of styrene-acrylic acid salt copolymer samples containing 40 mole% salt units.

Ionomers	Initial temp. for non-condensable gases, °C	T _{max} °C	Wt% residue at about 500 °C	Wt% CRF at about 500 °C	Wt% of condensable volatile products at about 500 °C (including CO ₂)	Wt% of CO ₂
ST/NaA	275	435	13.2	21.5	65.3	7.6
ST/KA	355	435	16.5	23.7	59.8	8.3

Table 4 : Products identified in the cold ring fraction from degradation of ST/KA copolymer under TVA conditions to 500 °C.

Product	m/e
CH ₂ = CH - COOK	110
$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{O}=\text{C} \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \backslash \quad / \\ \quad \quad \quad \text{O} \end{array}$	128
$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 = \text{C} - \text{CH}_2 \\ \quad \quad \\ \text{O}=\text{C} \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \backslash \quad / \\ \quad \quad \quad \text{O} \end{array}$	126
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH} = \text{CH} \\ \quad \quad \quad \\ \text{C}_6\text{H}_5 \quad \quad \quad \text{C}_6\text{H}_5 \end{array}$	208
(styrene dimer)	
$\begin{array}{c} \text{CH}_2 = \text{C} - \text{CH}_2 - \text{CH}_2 \\ \quad \quad \quad \\ \text{COOK} \quad \quad \text{COOK} \end{array}$	220
(salt dimer)	
$\begin{array}{c} \text{CH}_2 = \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_2 \\ \quad \quad \quad \quad \quad \quad \\ \text{O}=\text{C} \quad \quad \quad \text{C}=\text{O} \quad \quad \quad \text{COOK} \\ \quad \quad \quad \backslash \quad / \\ \quad \quad \quad \text{O} \end{array}$	236
Previous saturated sample	238
$\begin{array}{c} \text{CH}_2 = \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ \quad \quad \quad \quad \quad \quad \\ \text{O}=\text{C} \quad \quad \quad \text{C}=\text{O} \quad \quad \quad \text{COOK} \\ \quad \quad \quad \backslash \quad / \\ \quad \quad \quad \text{O} \end{array}$	250
Previous saturated sample	252
$\begin{array}{c} \text{CH}_2 = \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_2 \\ \quad \quad \quad \quad \quad \quad \\ \text{C}_6\text{H}_5 \quad \quad \quad \text{C}_6\text{H}_5 \quad \quad \quad \text{C}_6\text{H}_5 \end{array}$	312
(styrene trimer)	
$\begin{array}{c} \text{CH}_2 = \text{C} - \text{CH}_2 - \text{CH}_2 \\ \quad \quad \quad \\ \text{C}_6\text{H}_5 \quad \quad \quad \text{COOK} \end{array}$	214
(mixed dimer)	
$\begin{array}{c} \text{CH}_2 = \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_2 \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \\ \text{COOK} \quad \quad \quad \text{C}_6\text{H}_5 \quad \quad \quad \text{COOK} \quad \quad \quad \text{C}_6\text{H}_5 \end{array}$	428
(two units of each type)	

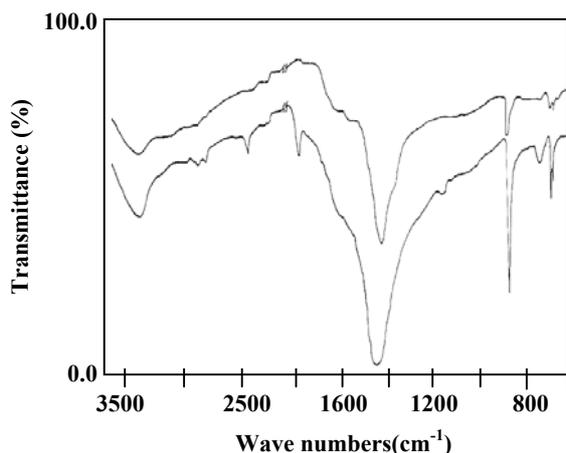


Fig. 7 : IR spectra of residues of styrene-acrylic acid salt copolymer samples. above : ST/NaA copolymer, below : ST/KA copolymer.

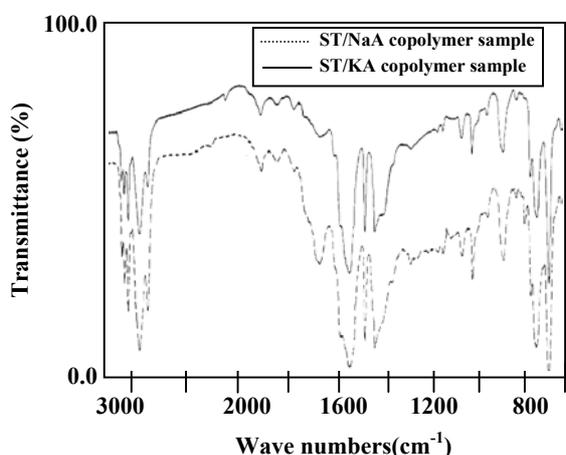


Fig. 8 : IR spectra of the cold ring fraction of styrene-acrylic acid salt copolymer samples.

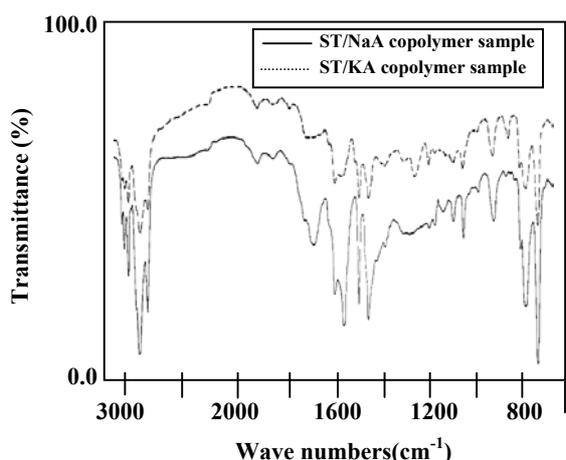


Fig. 9 : IR spectra of upper part of the cold ring fraction of styrene-acrylic acid salt copolymer samples.

principal component together with different kinds of styrene based compounds, Fig. 11.

These fractions were subjected to GC-MS and the corresponding chromatograms are reproduced in Figs. 12 and 13. It is observed that toluene, α -methyl styrene and methyl ethyl ketone are the volatile products next in importance to styrene. The products of degradation of the styrene-acrylic acid salt copolymers (Na and K) to 500 °C under TVA conditions are listed in tables 5 and 6.

Mechanism of degradation

The degradation mechanism of the alkali metal salts is explicable in terms of main chain and side group scission reactions, accompanied to a limited extent by intra-molecular transfer of the macroradicals. The presence of the ionic groups causes an increase in the thermal stability of the copolymer relative to the parent styrene-acrylic acid copolymer. The main features of the degradation of sodium and potassium salts of styrene-acrylic acid copolymer samples depend on composition and the distribution of the ionic groups along the chain.

At temperatures below 350 °C, dehydration and decarboxylation of the acrylic acid units left probably unreacted during neutralization of the styrene-acrylic acid copolymer accompanied by some chain scission can be proposed as main reactions (Scheme 1).

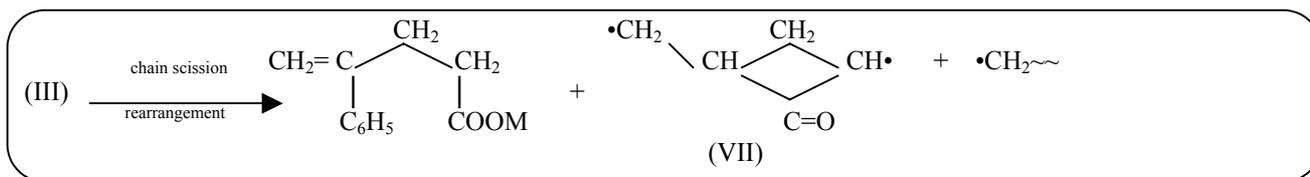
Further main chain and side chain group scission reactions followed by intra- and intermolecular transfer might be expected at temperatures higher than 350 °C, in leading to oligomer (dimer or trimer) of styrene and a little of the salt monomer together with mixed dimer or one and two units of each type (Scheme 2).

Macroradical (III) may undergo backbone scission and rearrangement (Scheme 3).

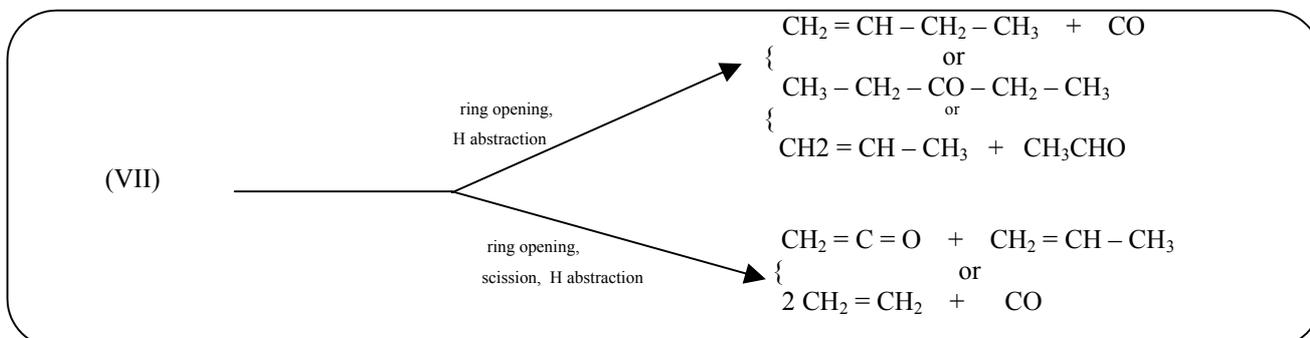
The intermediate species (VII) may also form from side group splitting and main chain scissions of neighbouring carboxylate groups along the backbone. Formation of a variety of degradation products including carbonyl containing products can be explained by further reactions of intermediates (Scheme 4).

Main and side group scissions from neighbouring carboxylate groups lead to the formation of metal carbonate, metal oxide, carbon dioxide and carbon monoxide, while secondary reactions of the backbone following several such scissions can also explain the formation of unsaturated hydrocarbons (Scheme 5).

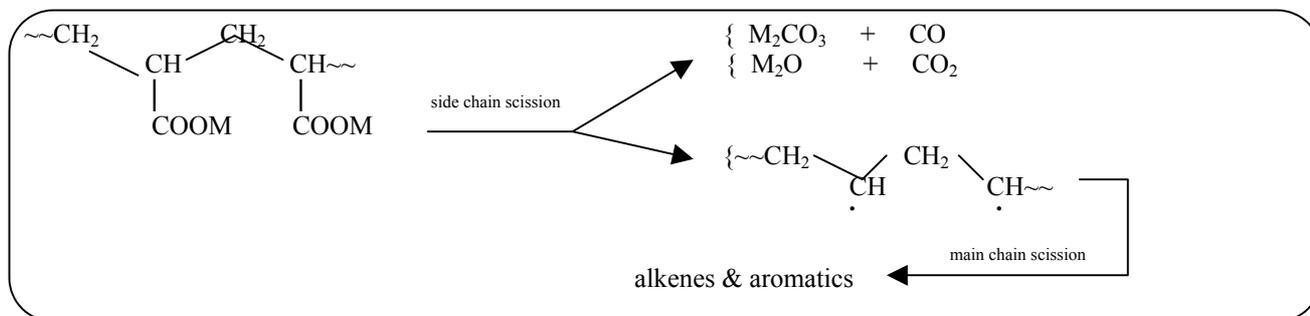
The minor products such α -methyl styrene, toluene



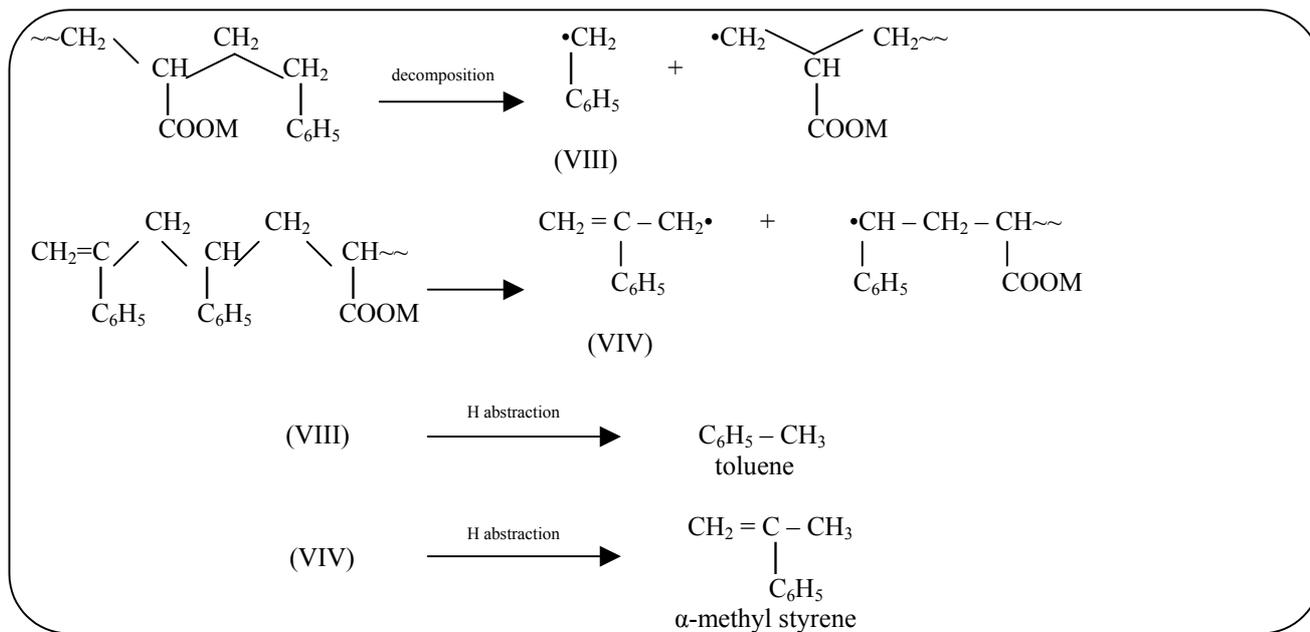
Scheme 3



Scheme 4



Scheme 5



Scheme 6

Table 5: Products of degradation of ST/NaA copolymer sample to 500 °C at 10 °C/min under TVA conditions.

Non-condensable products at -196 °C	Condensable volatile product at -196 °C		Cold ring fraction (light brown solid)	Residue (black)
	Gases	Liquid fraction		
IR	IR , MS	GC-MS	IR , MS	IR
CO CH ₄	CO ₂ * Acetone Ketene Toluene Propene Methyl ethyl ketone	styrene* toluene α-methyl styrene methyl ethyl ketone ethyl benzene xylene allyl benzene indane acetone cumene benzaldehyde n-propyl benzene 2-methyl propenyl benzene β-methyl styrene 2-methyl indane cyclopropyl benzene 4-phenyl-1-butene	Short chain fragments of polystyrene, such as dimer, trimer and also monomer and dimer of acrylic acid salt together with mixed dimer and anhydride structures.	Metal carbonate as a major product.

* As major products

Table 6: Products of degradation of ST/KA copolymer sample to 500 °C at 10 °C/min under TVA conditions.

Non-condensable products at -196 °C	Condensable volatile product at -196 °C		Cold ring fraction (light brown solid)	Residue (black)
	Gases	Liquid fraction		
IR	IR , MS	GC-MS	IR , MS	IR
CO CH ₄	CO ₂ * Acetone Ketene Toluene Propene Cyclopentene 1-butene Acetaldehyde Acrolein Benzene Cyclopentadiene Methanol**	styrene* toluene α-methyl styrene methyl ethyl ketone ethyl benzene 1-phenyl-2-butene allyl benzene indane benzene cumene 1-methyl indane n-propyl benzene 2-methyl propenyl benzene 2-methyl indane cyclopropyl benzene 4-phenyl-1-butene α-methyl dihydro naphthalene	Short chain fragments of polystyrene including dimer, trimer and traces of tetramer. Compounds with anhydride structures together with monomer and dimer of the metal acrylate and also one and two units (traces) of each type are also present.	Metal carbonate as a major product.

* As major products.

** Impurity from solvent

and the other styrene-based compounds results from the mechanisms as (Scheme 6).

CONCLUSIONS

Although the thermal behaviour of the sodium and potassium salts of styrene-acrylic acid copolymer is rather similar, there is significant difference from the parent acid copolymer on the basis of TVA, TG and DTA data.

The temperature of the maximum rate of evolution of volatile products from the major degradation process of the copolymer samples is markedly higher than that of polystyrene and the styrene-acrylic acid copolymer. This increase in stability results from the inhibition of the depolymerisation and chain transfer reactions of the styrene sequences blocked by acrylate units within the copolymers due to the presence of metal acrylate units randomly distributed in the chain. It seems that the

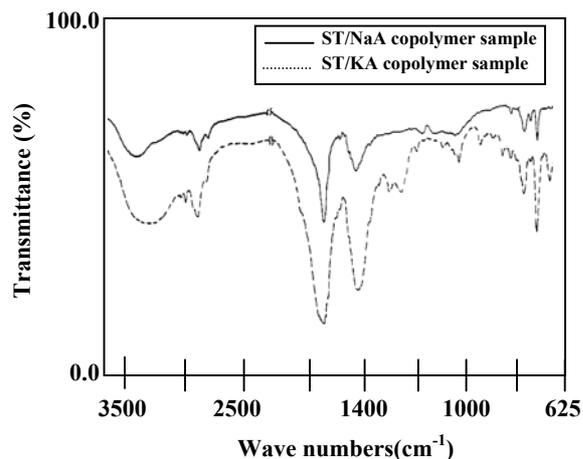


Fig. 10 : IR spectra of lower part of the cold ring fraction of styrene-acrylic acid salt copolymer samples.

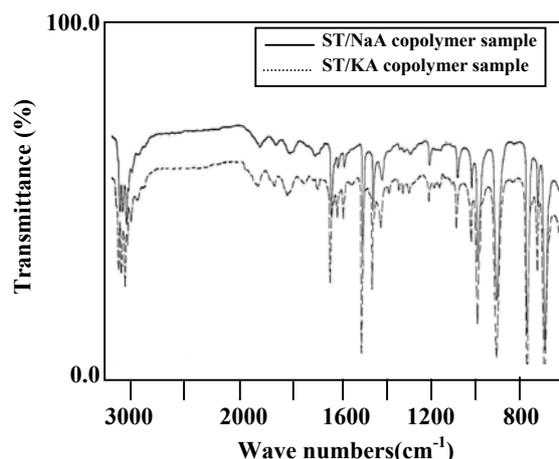


Fig. 11: Infrared spectra of liquid fractions of products separated by SATVA after degradation of styrene-acrylic acid copolymer samples to 500 °C by TVA.

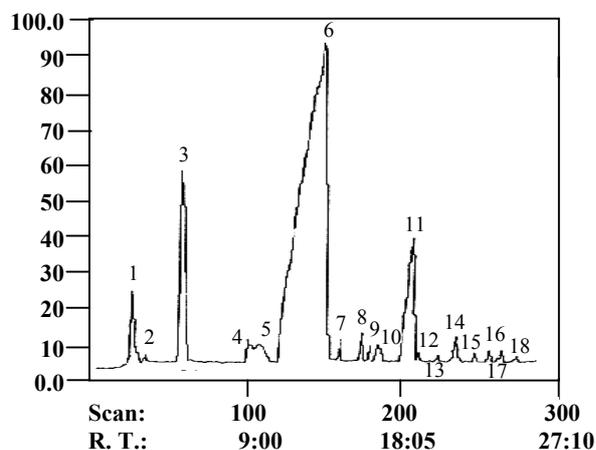


Fig. 12: GC-MS chromatogram of the liquid fraction of products separated by SATVA after degradation of ST/NaA copolymer to 500 °C by TVA.

Assignments: 1. methyl ethyl ketone and acetone, 2. benzene, 3. toluene, 4. ethyl benzene, 5. xylene, 6. styrene, 7. cumene, 8. allyl benzene, 9. *n*-propyl benzene, 10. benzaldehyde, 11. α -methyl styrene, 12. cyclopropyl benzene, 13. 1-methyl indane, 14. indane, 15. 4-phenyl-1-butene, 16. β -methyl benzene, 17. 2-methyl propenyl benzene, 18. 2-methyl indane.

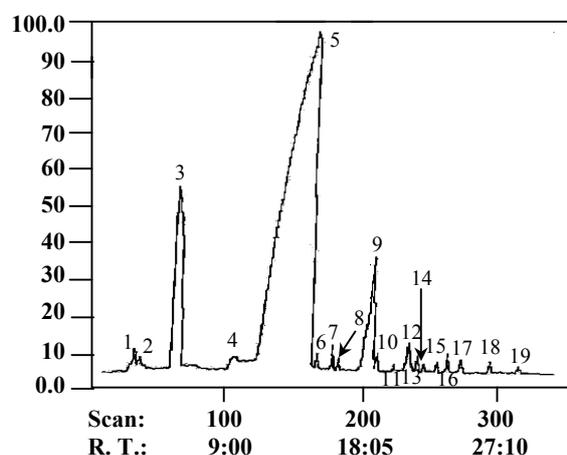


Fig. 13: GC-MS chromatogram of the liquid fraction of products separated by SATVA after degradation of ST/KA copolymer to 500 °C by TVA.

Assignments: 1. methyl ethyl ketone, 2. benzene, 3. toluene, 4. ethyl benzene, 5. styrene, 6. cumene, 7. allyl benzene, 8. *n*-propyl benzene, 9. α -methyl styrene, 10. cyclopropyl benzene, 11. 1-phenyl-2-butene, 12. indane, 13. unknown, 14. 4-phenyl-1-butene, 15. methyl benzene, 16. 2-methyl propenyl benzene, 17. 2-methyl indane, 18. 1-methyl indane, 19. α -methyl dihydronaphthalene.

thermal stability of these ionomer samples is dependent on the amount of introduced salt units and the degree of neutralization of the styrene-acrylic acid copolymer by the respective bases.

It is found that the main decomposition of the styrene-acrylic acid salts copolymer samples starts at about 350 °C and reaches maximum at 450 °C. At the temperatures below 350 °C, dehydration and decarboxylation of the

acrylic acid units left probably unreacted during neutralization process can be expected.

The presence of two monomers together with oligomer and mixed dimer in the cold ring fraction of TVA indicates that depolymerisation process occurs during the thermal degradation of the ionomers at temperatures higher than 350 °C.

Formation of a variety of degradation products

including metal carbonate or metal oxide as solid residue and carbon dioxide, carbon monoxide, methane, styrene-based compounds, carbonyl containing products and unsaturated hydrocarbons can be explained by reactions occur at temperatures higher than 350 °C.

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