

Some Properties of Styrene-Based Ionomers. I

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ABSTRACT: Some properties of styrene-based ionomers containing alkali metal salts of acrylic acid or methacrylic acid have been investigated. A study has been conducted to examine the influence of the acidic content and nature (acrylic or methacrylic) and the nature of the alkali metal salt on the glass transition temperature, density, melt index and activation energy of a flow of the styrene-based ionomers. The present studies have indicated that the temperature of glass transition (T_g) of sodium ionomers increases as the sodium content rises and the region of the glass transition broadens. The T_g 's of the styrene-acrylic acid (S-AA) ionomers do not depend on the nature of the alkali metal intro-

duced into the copolymer. The density of films rises with the content of acid or salt introduced to the polystyrene chain. The melt index of the investigated ionomers depends on the amount and type of the introduced acid and salt as well as on the molecular weight of the initial copolymer. The energy of activation of the flow is independent of the polymer molecular weight; however, the energy of activation of flow of the ionomers increases with larger ionic radii of the introduced alkali metal. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 55–62, 2003

Key words: glass transition; density; activation energy

INTRODUCTION

Considerable attention has been given to the study of ionomers. The primary reason for the great interest in these materials lies in the major changes that can be achieved in the properties and morphology of a polymer by introducing ions. Among the dramatic effects usually observed are increases in modulus, in glass transition temperature, and in viscosity.

Eisenberg¹ reviewed the effect of ions on the temperature of glass transition (T_g) of ionomers based mainly on styrene,² butadiene,³ ethyl acrylate,⁴ and ethylene.⁵ It has been shown^{1–6} that the T_g of the ionomer is considerably higher than that of the polymer before the introduction of ions. Although no meaningful correlation has yet been found, the effect seems to become more pronounced as the T_g of the host material decreases. Recently Eisenberg and Kim⁷ stated that three effects — copolymerization, crosslinking and filler — could be the causes that lead to an increase in T_g for ionomers.

Only a few studies have measured the density of styrene ionomers. Yano et al⁸ measured density as a function of degree of neutralization of styrene ionomers containing 4.4 mol % methacrylic acid (MA) neutralized by copper. They showed that the density of ionomers increases with a growing degree of neutralization from 1.046 to 1.074 g/ml over the range of

7–79% neutralization. Above this degree of neutralization, the density levels off up to 139% neutralization, beyond which no data were given.

Eisenberg et al^{7,9–11} looked at the densities of completely neutralized S-co-MNa copolymers of 0–9 mol % ion content. They observed an appreciable change in slope at around 6 mol % on a plot of the dependence of the density on the content of sodium methacrylate, which they attributed to the onset of clustering in these materials.

Weiss et al¹² measured the densities of styrene-co-(sodium styrene sulfonate) copolymers and sodium sulfonated polystyrene as a function of concentration and observed an increase in density with content of sulfonate.

The effects of incorporating ionic groups into polymers are evident in melt flow behavior. Although entangled polymers already have viscosities and relaxation times which are quite large by small molecule standards, adding ionic associations can further increase these properties by several orders of magnitude. In many cases, these increases are undesirable, as they can make the materials difficult to process into complex shapes. At the same time, these ionic associations open up the possibility of producing ionic thermoplastic elastomers, i.e., at room temperature, the materials behave as if crosslinks are present, while a weakening of the associations at elevated temperatures permits melt processing.

Studies of melt rheology are often conducted by means of capillary rheometers. A melt indexer is similar to a capillary rheometer, albeit the capillary is very short. The melt index (MI) is the mass of polymer

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which flows through a die of standard dimensions for a specified period of time at a constant temperature under a specified stress. This quality is thus inversely related to melt viscosity, but since the flow field is unlikely to be fully developed by the die's exit, the melt index reflects both a material's viscosity and elasticity. Melt index measurements are the most readily available, but the least informative, rheology parameters and are principally useful in demonstrating gross differences among materials.

Ide et al¹³ found that the MI of S-MA ionomers neutralized with sodium was dependent on the degree of neutralization, the content of methacrylic acid and the limiting viscosity number (LVN) of the initial copolymer. They also indicated that the activation energies of flow for copolymers and ionomers have almost the same values. However, Nicolajev and Galperin¹⁴ indicated that the activation energies for ionomers were higher than for the initial S-MA copolymers.

Schade et al¹⁵ observed a reduction of the MI in relation to the initial copolymers of styrene ionomers based on copolymers of S-MA containing sodium and magnesium ions.

The documented rheological studies of ionomers based on ethylene,¹⁶ propylene,¹⁷ and styrene^{18,19} also indicated an enhancement of melt viscosity and activation energy of viscous flow of these ionomers with an increase in the content of salt. These observations are a consequence of intermolecular interactions between salt groups for the metal salt derivatives.

In our earlier articles,²⁰⁻²⁴ we indicated that the state of ion aggregation in ionomers based on styrene-acrylic acid copolymers depends on the amount and the type of the introduced ions of alkali metals and on the placement of ions either at random or in more ordered configurations, such as short blocks along the main chain backbone.

In spite of the extensive studies of the properties of styrene-based ionomers, such properties as density and melt index (MI) have only been investigated as properties of secondary importance and only for ionomers based on styrene-methacrylic acid copolymers.⁸⁻¹⁵ There are no studies of these properties for ionomers based on styrene-acrylic acid copolymers.

This article reports our results of studies of some properties of a series of copolymers of styrene (S) and acrylic acid (AA) or methacrylic acid (MA) and their alkali metal salts. Specifically we have varied the amount and nature of acid (acrylic or methacrylic) introduced to the polystyrene (PS) chain, the amount and nature of alkali metal salt and finally the overall polymer molecular weight. The effect of these different variables on the T_g , density (d), MI and activation energy of flow (E) has been investigated.

EXPERIMENTAL

The copolymers of S and AA or S and MA were obtained in bulk using benzoyl peroxide as the initiator at 353K.^{25,26} The time of polymerization was chosen so as to achieve a conversion between 15 and 20%. Suitable ionomers were then obtained by titrating (under N_2) a 3–5% solution in benzene (for AA content of about 5 mol %, a 9 : 1 v/v mixture of benzene and methanol was used) by a standard solution of alkali metal hydroxide in methanol.²⁰⁻²⁵ Some of these solutions were freeze-dried, and the others were used to obtain films by evaporation of the solvent at room temperature. All polymers were dried to a constant weight at 323K in vacuum. The number-average (M_n) and weight-average (M_w) molecular weights were determined by gel-permeation chromatography using tetrahydrofuran (THF) as an eluent. The limiting viscosity numbers (LVN) of the initial copolymers were determined in THF at $298 \pm 0.1K$.

The T_g 's of the polymers were measured with a Perkin-Elmer DSC-2 differential scanning calorimeter. Samples of about 8.0 ± 0.1 mg were encapsulated in sealed aluminum pans and then dried in vacuum at 403K for 30 min.

Differential scanning calorimetry (DSC) measurements were performed the next day in the following sequence. First, a DSC-scan of each sample was recorded during heating (10K/min) from 220K up to $T_g + 50K$. Then the sample was quenched by rapid cooling to 220K and rescanned at 10K/min. The glass transition was determined by applying the mid-point method to the data collected from the second scan. The experimental error in T_g was $\pm 2K$, as measured by duplicate measurements.

The density (d) of the polymer films were measured by flotation.²⁷

The melt index (MI) was determined on the melt indexer, performed in accordance with recommended standard PN-71/C-89292. The measurements were made at 473K, under a load of 49N (5kg). The mass of the flow out polymer was determined with an accuracy within ± 0.1 mg, and time of the cutting off within ± 0.1 s.

All measurements were made under the same conditions. MI was calculated according to the following equation¹⁴:

$$MI = \frac{600xm}{t} \quad (1)$$

where MI is the melt index (g/10 min), m is the average weight of the extruded sections of the polymer (g), and t is the time of extrusion of one section (s). For the determination of the activation energy of flow we measured MI in the range of 473–523K. Based on these data, the energy of activation of flow was calcu-

TABLE I
Glass Transition Data for Copolymers of S and AA and Their Sodium Salts

Polymer	T_g (K)		Temperature Range of the Glass Transition for Sodium Ionomers (K)
	Copolymer	Ionomer	
PS	373	-	-
S - AA(3.9)	381	389	11
S - AA(5.2)	384	394	15
S - AA(6.4)	388	400	20
S - AA(11.7)	395	410	32
S - AA(14.1)	399	441	42

lated by applying the least squares method to the logarithmic form of the following equation:

$$\eta = B \times e^{E/RT} \quad (2)$$

where η is the viscosity, B is a constant, E is the activation energy of flow, R is the ideal gas constant, and T is the absolute temperature.

The materials are labeled with a number in parentheses, which gives the concentration of AA, MA, or the appropriate salt comonomer in mol %. For example, S-ANa(3.9) is a copolymer of S and sodium acrylate (ANa) in which 3.9 mol % of the comonomer units correspond to ANa.

RESULTS AND DISCUSSION

Glass transition temperature

For all investigated ionomers, DSC thermograms show only one glass transition.

The DSC-results for the copolymers of S and AA and their alkali metal salts are presented in Tables I and II.

The results shown in Tables I and II confirm the results of previous studies: the increase in glass transition temperature is much larger in the neutralized form than in the acidic form of the ionomer,¹⁻⁷ and this increase does not depend on the alkali metal used.²⁹⁻³²

For the sodium ionized copolymer, the increase in T_g as a function of ion content was linear (dT_g/dc

= 4.21 K/mol %) up to about 6 mol % sodium and was higher than that of the acidic form ($dT_g/dc = 1.85$ mol %). Above that, however, the increase for the ionomers was much more rapid ($dT_g/dc = 5.37$ K/mol %), which is consistent with that normally observed for the other ionomers. Note that the increase was about 3.24 times higher than would be expected from a simple linear combination of the pure homopolymer glass transitions for the ionomers. The exact reasons for the increase in T_g are currently unknown. Eisenberg and Kim⁷ suggested that all three effects – copolymerization, crosslinking and filler can lead to an increase in the T_g of the investigated ionomers.

Two glass transitions that are commonly found in dynamic mechanical thermal analysis (DMTA) experiments.²⁹ However, only one was found here, which is unsurprising because DSC is much less sensitive than DMTA.^{7,33} Also, the breadth of the glass transitions are broader as the sodium content increases, as explicitly described for Nafion ionomers³⁴ and depicted in Figure 1 of Reference 29.

Density

The density (d) of copolymers of S and AA and their cesium and sodium salts are presented in Table III. These data indicate that density increases with increases in the content of AA introduced to the polystyrene chain. The observed rise in the density compared to PS is connected to the changes in composition and the more dense packing of the copolymer macromolecules as a result of hydrogen bond formation.

TABLE II
Glass Transition Data for Ionomers Containing 5.2 mol % and 11.7 mol % of Salt Units

Cation	R_{cationic} (Å)	5.2 mol %		11.7 mol %	
		T_g (K)	Temperature Range Glass Transition (K)	T_g (K)	Temperature Range Glass Transition (K)
H ⁺	-	384	-	395	-
Li ⁺	0.60	394	14	410	32
Na ⁺	0.95	394	15	410	32
K ⁺	1.33	395	16	408	29
Cs ⁺	1.69	395	14	408	28

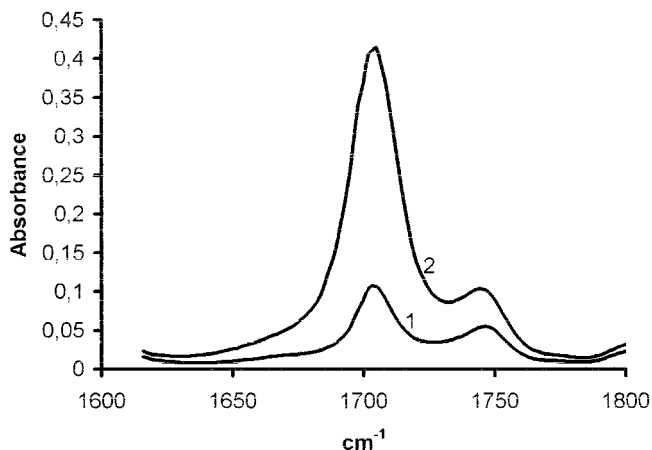


Figure 1 FTIR spectra of styrene-acrylic acid copolymers in the region 1600–1800 cm^{-1} . (1) S-AA (3.9); (2) S-AA (11.7).

We can see that the higher content of AA in the copolymer favors the formation of a larger number of hydrogen bonds, which causes more dense packing of macromolecules and increase in the density.

It can be proved by the FTIR spectra of S-AA copolymers. We can see that the band intensity at $\sim 1704 \text{ cm}^{-1}$ (Fig. 1), which is assigned to the dimerized carbonyl stretching vibrations, increases with the increasing content of AA introduced to the copolymer. The band intensity at $\sim 2640 \text{ cm}^{-1}$ (Fig. 2), which is attributed to the characteristic stretching vibration of the hydrogen bonded OH group, also increases.

As shown in Table III, the introduction of cesium ions into the copolymer causes further increase in the density. The increased content of AC introduced to the polystyrene chain further increases the density of ionomers.

Knowing the chemical composition of the investigated ionomers and the density of cesium polyacrylate (2 g/ml)³⁵ and the density of our polystyrene ($1,044 \text{ g/ml}$), we calculated the density of our ionomers containing cesium ions. These results are presented in Table III. The calculated values of density are lower than the measured ones. These data may indicate that the effects of composition alone are insufficient to

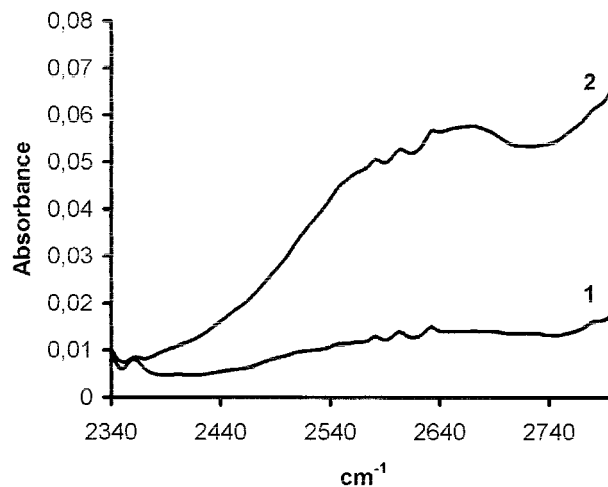


Figure 2 FTIR spectra of styrene-acrylic acid copolymers in the region 2340–2740 cm^{-1} . (1) S-AA (3.8); (2) S-AA (11.7).

explain the effect of ions on the density of ionomers. These results may indicate that composition effects and electrostatic interactions after the introduction of cesium ions, which caused the aggregation of ionic groups, have an appreciable effect on the density of the investigated ionomers.

The data presented in Table III indicate that, as in the case of ionomers containing cesium ions, the density of ionomers containing sodium increases with the rise in content of introduced sodium ions.

The increase in the density of styrene ionomers based on copolymers of styrene-methacrylic acid with increasing degrees of neutralization over the range of 7–79% neutralization have been observed by Yano et al.⁸

In an earlier discussion of clustering in ionomers Eisenberg^{9–11} showed that a plot of the density of styrene-sodium methacrylate copolymers as a function of carboxylate concentrations exhibits an appreciable change in slope around 6 mol %, which he attributed to the onset of clustering in these materials. He then calculated the fraction of ions in the clusters from the integrated intensities of the two dielectric peaks observed in the glass transition region¹⁰ and

TABLE III
Density of Copolymers of S - AA and Their Cesium (S-ACs) and Sodium (S-ANa) Salts

Polymer	Density, d ($\text{kg/m}^3 \times 10^3$)			
	S - AA	S - ACs Exp.	S - ACs Calc.	S - ANa
PS	1.044	-	-	-
S - AA(3.9)	1.082	1.118	1.081	1.085
S - AA(5.2)	1.090	1.138	1.093	1.093
S - AA(6.4)	1.095	1.144	1.105	1.098
S - AA(11.7)	1.100	1.221	1.156	1.121
S - AA(14.1)	1.101	1.254	1.178	1.127

TABLE IV
Density of Ionomers Containig 5.2 mol % and 11.7 mol % of Salt Units

Cation	Molecular weight (g/mol)	Density, d ($\text{kg/m}^3 \times 10^3$)	
		5.2 mol %	11.7 mol %
H ⁺	1.008	1.090	1.100
Li ⁺	6.941	1.092	1.109
Na ⁺	22.990	1.093	1.121
K ⁺	39.102	1.121	1.134
Cs ⁺	132.905	1.138	1.221

showed that the density varied linearly with this variable. From this and other results, Eisenberg concluded that the clusters dominate the properties of ionomers. He therefore suggested that the density of the ionomers is extremely sensitive to the morphology of the ionic aggregation.

However, recently Eisenberg⁷ discussed the same results regarding the density of styrene ionomers containing 9 mol % sodium methacrylate, and he indicated that the best fit second order polynomial to describe the data is

$$\text{Density (g/ml)} = 1.057 + 6.53 \times 10^{-5}x + 3.85 \times 10^{-4}x^2$$

where x is the mole percent of ions.

Weiss et al,¹² measuring the densities of styrene-co-sodium styrene sulfonate copolymers and sodium sulfonated polystyrene, observed an increase in density with an increase in the content of sulfonate. They obtained linear data and, contrary to Eisenberg's results for styrene-sodium methacrylate, neither of the two sulfonate ionomer system exhibited a change in the slope of the density-concentration curve. They suggested that this result may be a consequence of differences in ion association between sulfonate and carboxylate ionomers.

Our results agree with the results of Weiss et al¹² and, contrary to Eisenberg's results for styrene-sodium methacrylate, exhibit no change in the slope of the density-concentration curve. Such results may indicate that, independent of the type of ionic groups present (carboxylate or sulfonate), the aggregation of

these groups contributes to the increase in density of the investigated ionomers.

Table IV presents the density for ionomers based on copolymers S-AA(5.2) and S-AA(11.7) with different alkali metal ions. The densities of salts of these copolymers are higher than those of the acid and increase with the molecular weight of the ions of alkali metal introduced to the copolymer. This increase is larger for ionomers containing a higher content of salt.

Melt index and energy of activation of flow

The melt viscosity of ionomers depends on the nature and content of acid or metal cation, molecular weight and molecular weight distribution.³⁶

Table V presents the dependence of MI on molecular weight. These results, obtained from sodium ionomers, indicate that copolymers containing almost the same amount of AA or MA but of different molecular weight have higher MI values for copolymers and ionomers of lower molecular weights.

It is possible to explain²⁸ that macromolecules of lower \bar{M}_w , or lower number of segments, flow more easily because they lose less energy needed for the displacement of the segments of macromolecules. These data may indicate how great a significance the molecular weight bears on the flow of the polymers.

Table VI presents values of MI and E for copolymers of S and AA and of the obtained sodium ionomers. These data indicate that MI decreases and E increases with the increase in AA content in the copolymer. The diminution of MI and the increase in E with higher contents of introduced acid, as well as increase in the

TABLE V
Dependence of MI on Molecular Weight

Copolymer	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	\bar{M}_w/\bar{M}_n	MI (g/10min)	
				Copolymer	Ionomer
S - AA(3.9)	34.9	107.5	3.08	26.1	2.3
S - AA(3.9)	127.7	305.0	2.39	4.4	0.3
S - MA(3.9)	32.9	86.4	2.63	37.2	3.1
S - MA(3.4)	120.1	267.7	2.23	6.5	1.6

TABLE VI
The influence of Content of Introduced AA on the MI and E of Initial Copolymers and Obtained Ionomers

Polymer	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n	MI (g/10min)		E (kJ/mol)	
				Copolymer	Ionomer	Copolymer	Ionomer
PS	514.0	203.0	2.53	1.5	-	147.0	-
S - AA(3.9)	305.0	127.7	2.39	4.4	0.3	151.0	161.6
S - AA(5.2)	386.0	206.8	1.87	3.9	0.1	122.9	129.3
S - AA(6.4)	423.0	203.0	2.08	2.7	n.p.	151.4	-
S - AA(11.7)	571.0	269.0	2.12	1.9	n.p.	161.0	-
S - AA(14.1)	580.0	273.0	2.12	1.6	n.p.	176.6	-

n.p. - no flow at these conditions

density, may be explained by the formation of hydrogen bonds among the carboxylic groups, which increase with the increase in the content of AA in the copolymer and form stronger interactions, which increase E .

The substitution of H^+ ions in the carboxylic group by Na^+ ions causes a further decrease in MI and an increased E of ionomers in relation to the initial copolymers. In the case of ionomers containing about 6 mol % and more sodium acrylate (ANa), the polymers do not flow under conditions of determination of MI. This perhaps indicates that introduction of higher content of sodium ions causes such strong electrostatic interactions, which contribute to the aggregation of ions, that it prohibits the flow of the polymer.

The data presented in Table VI may also confirm our earlier statement, that at approximately 6 mol % ANa in our ionomers signals the onset of clustering.

The diminution of MI values of copolymers of S and MA and their salts containing primarily sodium and potassium ions was observed earlier¹⁵⁻¹⁷, but there were no measurements of MI of S and AA copolymers and of the ionomers obtained.

The data presented in Table VII indicate that copolymers and sodium ionomers obtained, containing almost the same content of AA or MA and having the same molecular weight, make up the higher values of MI in the case of copolymers and ionomers containing MA.

We also can see that values of E for these copolymers and sodium ionomers are lower than those of

copolymers S-AA and ionomers of similar composition.

Such dependence indicates that, in the case of styrene-methacrylic acid copolymers and the obtained sodium ionomers, interactions of segments with environment are weaker than in the case of styrene-acrylic acid copolymers. The presence of a methyl group on the α -carbon probably explains the weaker interactions of hydrogen bonds in the case of copolymers. Reduced flow of these ionomers may be generated by stronger interactions of ionic aggregates, which can form crosslinks or may act as fillers. We earlier indicated that, in the case of styrene ionomers based on acrylates, larger ionic aggregates are formed than in the case of these based on methacrylates.²⁴

These data experimentally confirm the dependence of E on the composition of polymer segment.²⁸

On the basis of our results we suggest that the copolymers and styrene ionomers based on MA have better flow properties (higher MI and lower E) than those based on AA.

Our results contradict those of Kim et al,²⁹ which suggested that for the acrylate ionomers the samples start to flow at lower temperatures than the methacrylates. Such dependence may be due to the fact that acrylate ionomers in that study had considerably lower average molecular weight (\bar{M}_n) of 100,000 than that of methacrylate, 500,000. Our results indicate how great a significance the molecular weight bears on the flow of the polymers.

TABLE VII
Influence of the Type of Acid on Melt Index and "Energy Activation of Flow"

Polymer	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	\bar{M}_w / \bar{M}_n	MI (g/10min)		E (kJ/mol)	
				Copolymer	Ionomer	Copolymer	Ionomer
S - AA(3.9)	107.5	34.9	3.08	26.1	2.3	153.0	161.1
S -MA(3.9)	86.4	32.9	2.63	37.2	3.1	116.4	133.7
S - AA(3.9)	305.0	127.7	2.39	4.4	0.3	150.1	161.6
S -MA(3.4)	267.7	120.1	2.23	6.5	1.6	105.9	162.0

TABLE VIII
Influence of Molecular Weight on E of Initial Copolymers and Sodium Ionomers

Polymer	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n	E (kJ/mol)
S - AA(3.9)	107.5	34.9	3.08	153.0
S - AA(3.9)	305.0	127.7	2.39	151.0
S - ANa(3.9)	107.5	34.9	3.08	161.1
S - ANa(3.9)	305.0	127.7	2.39	161.6
S - MA(3.9)	86.4	32.9	2.63	116.4
S - MA(3.4)	267.7	120.1	2.23	105.9

These data (Table VIII) indicate that copolymers containing almost the same content of AA or MA or their sodium salts, but of different molecular weight, have almost the same values of E . These results confirm the dependence earlier obtained for PS.³⁷

It is known²⁸ that the energy of activation of flow determines the interactions of segments with environment. Therefore, its value is independent of the number of segments in the macromolecule (i.e. on molecular weight), and only depends on the size and composition of the polymer segment.

The data presented in Table VIII also indicate that values of E obtained for sodium ionomers are higher than those obtained for the initial copolymers. The increase in E in relation to the copolymer may be explained by the crosslinking effect after introduction of ions and their aggregation.

An increase in E of ionomers was observed earlier for ionomers based on S-MA copolymers by Galperin and Nikolajev¹⁴ and Plochocka and Wojnarowski.³⁸ However, Ide et al,¹³ while investigating the same ionomers, did not observe the increase in E of ionomers.

Also Weiss and Agrawal,¹⁷ investigating melt rheology of ionomers based on propylene-acrylic acid copolymer, and Iwakura and Fujimura,¹⁹ investigating the rheological properties of molten blends of PS and styrene ionomers have observed the increase in E .

The next table (Table IX) presents the influence of the nature of the introduced alkali metal on the activation energy of flow for ionomers containing 5.2 mol % of salt.

These data indicate that substitution of hydrogen ions in the copolymers by ions of alkali metals causes

the increase in E of the ionomer relative to the initial copolymer. We can see that maximum value of E correspond to ionomers containing Li^+ ions. This may be ascribed to the forces between lithium cations and carboxylate groups, which are covalent in nature, which was confirmed by far-IR investigations.^{39,40}

The increase in E with the ionic radius of the alkali metal used confirms the dependence of E on the chemical composition of the polymer segment.

CONCLUSIONS

The present studies indicate that T_g of sodium ionomers becomes higher and the region of the glass transition becomes broader as the ANa content increases. The T_g values of salts of copolymers S-AA are independent of the nature of alkali metal introduced into the copolymer.

The density increases with the content of introduced AA to the polystyrene chain. Substitution of H^+ ions by alkali cations increases the density further; the density is higher with higher molecular weight of the alkali metal.

The melt index of the investigated ionomers depends on the amount and type of introduced acid or salt and on the molecular weight of initial copolymer. An increase in the content of acid introduced to the copolymer decreases the MI. Introduction of ions of alkali metals to the copolymer causes further diminution of MI.

The energy of activation of flow is independent of the molecular weight but increases with an increase in alkali metal ionic radius.

Copolymers and styrene ionomers containing methacrylic acid have better flow properties (higher MI and lower E) than those containing acrylic acid.

TABLE IX

Influence of the Nature of Introduced Alkali Metal on the activation energy of flow for Ionomers Containing 5.2 mol % of salt

Cation	Ionic radius (Å)	E (K)(kJ/mol)
H^+	-	122.9
Li^+	0.60	240.3
Na^+	0.95	129.3
K^+	1.33	152.1
Cs^+	1.69	228.5

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