Some Properties of Styrene-Based Ionomers II

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ABSTRACT: Some properties of styrene-based ionomers obtained from copolymers styrene (S) and acrylic acid (AA) or methacrylic acid (MA) obtained in emulsion containing alkali metal salts have been investigated. A study has been conducted to examine the influence of the acid content and nature (acrylic or methacrylic) and nature of alkali metal salt on the glass transition temperature, density, melt index, and activation energy of 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, but the increase is lower than in the case of the ionomers based on copolymers obtained in bulk.

The density of films rises with the content of alkali metal salt introduced to the polystyrene chain, and it is higher than in the case of the ionomers based on copolymers obtained in bulk containing almost the same content of alkali metal salts. Styrene ionomers containing alkali metal acrylates have higher densities than those containing alkali metal methacrylates. The melt index of the investigated ionomers depends on the amount and type of introduced acid and salt, as well as on the molecular weight of the initial copolymer. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 268–275, 2005

Key words: glass transition; density; melt index; activation energy; ionomers

INTRODUCTION

A series of studies on ion-containing polymers has shown that the presence of ions influences a very wide range of physical properties of the host polymer. Some of the properties that are affected drastically are the increases in moduli, in the glass transition temperatures, and in the melt viscosities.

It has been demonstrated that the properties and the state of ion aggregation in ionomers depend on the sample history[1] and on the placement of ions either at random or in more ordered configurations, such as short blocks along the main chain backbone.[2]

It is also known[3,4] that the major factor in determining the morphology and properties of the ionomers is the sequence distribution of the ionic groups along the chain.

Weiss et al.[5] indicated that some differences in the properties of the copolymers of styrene and sodium styrene sulfonate obtained in emulsion and in the sodium sulfonated polystyrene (SPS) may originate with differences in the sulfonate group distribution.

Brown and Taylor[6] suggested that the copolymers of styrene and acrylic acid or methacrylic acid obtained by copolymerization in emulsion are block copolymers.

However, later Switała[7] indicated that the copolymers of styrene and acrylic acid obtained from the emulsion containing more than ≈ 40 mol % of acrylic acid have a structure of blocks. The copolymers of S and AA containing a smaller number of AA may contain longer sequences of AA as a result of the greater solubility of AA in water than in S and of greater participation in copolymers of sequences formed in the water phase.

In our earlier papers[8–14] 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 method by which the initial copolymer was obtained.

We also indicated[15] that certain properties of the ionomers obtained from emulsion and bulk copolymers were different.

In our previous article[16] we reported the results of the influence of the amount and nature of the introduced acid (acrylic or methacrylic) to the polystyrene (PS) chain and the nature and amount of alkali metal salt on the glass transition temperature (T_g), density (d), melt index (MI), and activation energy of flow (E) of the investigated polymers.

Because the effect of the distribution of ionic groups on the resulting morphology and properties is an area in which a great deal of work has to be done, in this article we report our results of studies of some properties of the ionomers based on copolymers of styrene and acrylic acid or methacrylic acid obtained by copo-

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lymerization in emulsion. We would like to probe how some properties change when the ions are placed on the chain in more ordered configurations, such as longer sequences or short blocks.

EXPERIMENTAL

The copolymers of styrene (S) and acrylic acid (AA) or methacrylic acid (MA) were obtained by copolymerization in emulsion.[17]

Suitable ionomers were then obtained by titrating (under N_2) a 3–5% solution in benzene (for AA content *ca* 5 mol %, a 9 : 1 v/v mixture of benzene and methanol was employed) by standard solution of alkali metal hydroxide in methanol.[11,18] Some of the 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.

Number-average molecular weights, M_n, were determined on a 502 high speed membrane osmometer using solutions in toluene and tetrahydrofuran for the acid (unneutralized) samples at 298K. The limiting viscosity numbers (LVN) of the initial copolymers were determined in THF at 298K $\pm$ 0.1K

The T_gs of the polymers were measured with a Perkin–Elmer DSC-2 differential scanning calorimeter. Samples of about 8.0 $\pm$ 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 was measured by flotation.[19]

The melt index (MI) was determined on the melt indexer, performed in accordance with recommended standard PN-71/C-89,292. The measurements were made at 473K, under the load 49*N* (5kG). The mass of the flow out polymer was determined with an accuracy within $\pm$ 0.1 mg, and time of the cutting off within $\pm$ 0.1 s.

All measurements were made under the same conditions. MI was calculated according to the following equation:[20]

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

TABLE I
Characterization Data for the Polymers

Polymer	LVN (dl/g)	$M_n \times 10^{-3}$
PS	1.64	260[a]
S-b-AA(0.7)	2.34	460[b]
S-b-AA(2.3)	1.78	330[b]
S-b-AA(3.7)	2.56	320[b]
S-b-AA(5.3)	2.68	280[a]
S-b-AA(9.7)	2.00	390[a]
S-b-AA(14.6)	2.80	800[a]
S-b-MA(0.8)	1.48	320[b]
S-b-MA(3.6)	1.46	270[b]
S-b-MA(10.0)	2.08	190[a]

[a] In tetrahydrofuran.
[b] In toluene.

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 activation of flow was calculated by applying the least squares method to the logarithmic form of the following equation:

$$\eta = Be^{E/RT} \qquad (2)$$

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 %, and a letter b means that it is the ionomer based on the copolymer obtained in emulsion.

RESULTS AND DISCUSSION

The properties of the initial copolymers of S and AA or MA appear in Table I.

Glass transition temperature

For all investigated ionomers except for S-b-ANa(9.7), DSC thermograms show only one glass transition (Fig. 1).

The DSC results for copolymers of S and AA obtained in emulsion and their alkali metal salts are presented in Table II and in Figure 2.

The results shown in Table II and in Figure 2 partially confirm the results of our previous studies of these ionomers based on the S-AA copolymers obtained in bulk[16] and other studies[3,4,20–27]: the increase in the glass transition temperature is larger in the neutralized form than in the acid form of the ionomer (Fig. 2).
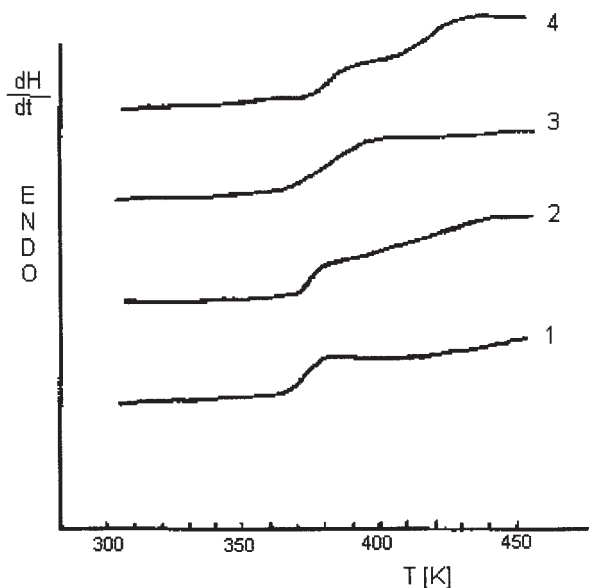
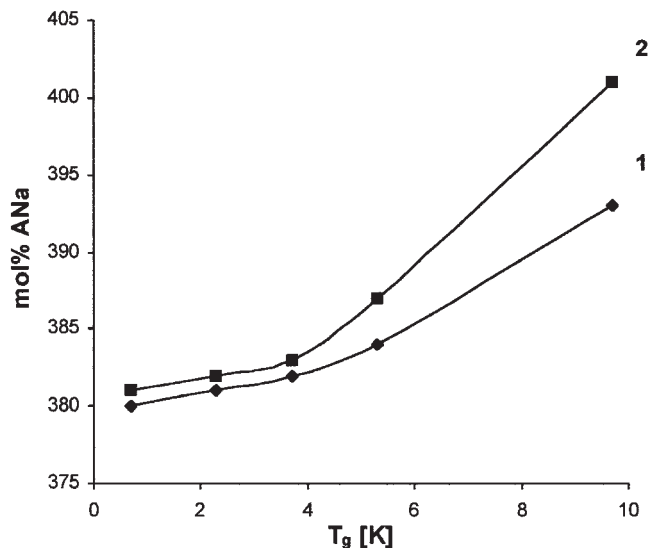**Figure 1** DSC thermograms for styrene-based ionomers with various mol % of ANa: (1) 2.3, (2) 3.7, (3) 5.3, (4) 9.7.

Figure 2 Dependence of T_g on the content of AA and ANa for the copolymers of S and AA or ANa: (1) S-b-AA, (2) S-b-ANa.

For the sodium ionized copolymer, as in the case of these ionomers obtained from copolymers received in bulk, the increase in T_g as a function of ion content was linear ($dT_g/dc = 1.70$ K/mol %) up to about 4 mol %, and it was higher than that for the acid form ($dT_g./dc = 1.37$ K/mol %), but it was also considerably lower than in the case of the ionomers obtained from copolymers received in bulk ($dT_g/dc = 4.21$ K/mol %).[16] This rise in T_g may be attributed to ion aggregation into small, tight multiplets.[9,28]

Above that, however, the increase of T_g for the ionomers was much more rapid ($dT_g/dc = 3.18$ K/mol %), which is consistent with the fact normally observed for the other styrene-based ionomers, but it was lower than the one observed for the same, earlier investigated ionomers based on copolymers obtained in bulk ($dT_g/dc = 5.37$ K/mol %).[16]

Such an increase in T_g is consistent with the one normally observed for the other ionomers, and it may be supposed that it indicates the onset of clustering.

TABLE II
The T_gS of Copolymers of S and AA and Their Sodium Ionomers

	T_g (K)	
Polymer	Copolymer	Ionomer
PS	378	—
S-b-AA(0.7)	380	381
S-b-AA(2.3)	381	382
S-b-AA(3.7)	382	383
S-b-AA(5.3)	384	387
S-b-AA(9.7)	393	T_g^1 401 T_g^h 429
S-b-AA(14.6)	398	—

Note that the increase was about 2.56 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 Kim[26] suggested that all three effects—copolymerization, crosslinking, and filler—can lead to an increase in the T_g of the investigated ionomers.

In the case of ionomer S-b-ANa(9.7) on the DSC thermogram (Fig. 1) were observed two heat capacity changes responsible for two T_gs: one at ca 401K (T_g^1) and the second at ca 429K (T_g^h). The transition at the lower temperature, T_g^1, may be attributed to the glass transition of the PS matrix containing a small amount of sodium ions that may aggregate into small, tight multiplets.[9,26,27,29,30] The high temperature transition, T_g^h, may be attributed to the glass transition of high-order aggregates or clusters.[9, 26,27,29,30]

Such multiple transitions were observed earlier by DSC in a number of cases, including a 40% neutralized poly(styrene-methacrylic acid) sample with acid comonomer content of 18 mol %,[29,30] the sulfonated-ethylene-propylene-ethylidiene norbornene (S-EPDM) system,[31] and the poly(ethyl acrylate-sodium acrylate) ionomer.[32] Recently, two glass transitions were detected in the styrene ionomers based on the sodium methacrylate for which dynamic mechanical data are also available.[33]

It was not possible to determine T_g for the sample S-b-ANa(14.6) because as the ion concentration of the samples increases, the thermal transitions become difficult to detect by the DSC method, probably due to the broadening of the distribution of the relaxation times in the transition regions.[29,30]

TABLE III
Density of Sodium Ionomers Based on S-b-AA Copolymers

Content of ANa (% mol)	Density, d (kg/m³ × 10³)
0	1.048
2.3	1.108
3.7	1.118
5.3	1.122
9.7	1.133
14.6	1.145

The use of the DSC for determining T_g of the ionomers rarely allows determining both glass transitions such as dynamic mechanical measurements, because the size requirement for the detection of the glass transitions appears to be different for these two methods.[26]

The lower values of T_g of the investigated ionomers based on S-AA copolymers obtained in emulsion than those obtained in bulk may be a consequence of different distribution of the carboxyl groups in the initial copolymers, higher molecular weight copolymers obtained in emulsion, and different molecular weight distribution.[7,34,35]

S-AA copolymers obtained in bulk have more or less randomly distributed carboxyl groups on the polymer chain. The copolymers obtained in emulsion may contain longer sequences of AA as a result of the greater solubility of AA in water than in S and of greater participation in copolymers of sequences formed in the water phase.[7]

Introduction of Na^+ ions into the copolymers in which carboxyl groups are randomly and homogeneously distributed on the polymer chain may cause more homogeneously distributed ionic interactions that reduce the chain mobility and produce a higher increase of T_g than in the case of the ionomers based on the S-AA copolymers obtained in emulsion.

Weiss et al.[5] also observed the higher increase of T_g in the case of the introduction of Na^+ ions into sulfonated PS than in the case of Na^+ ions in copolymer styrene-sodium styrene sulfonate, which is supposed to have the block structure. This dependence was related with the different distribution of ionic species along the polymer chain.

Density

The densities (d) of ionomers containing sodium ions based on S-AA copolymers obtained by copolymerization in emulsion are presented in Table III and in Figure 3.

This data indicates that density of the ionomers increases with the increase of content of sodium acrylate (ANa) introduced to the polystyrene chain. From
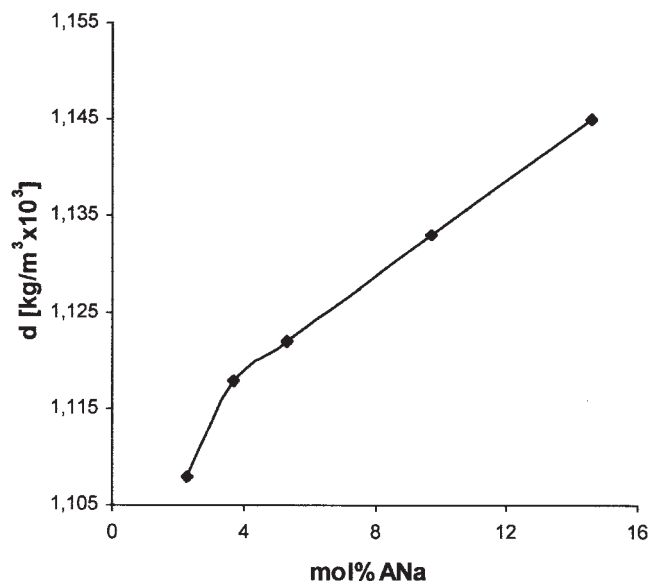

Figure 3 Dependence of density of S-b-ANa ionomers on the content of ANa.

Figure 3 it is also evident that the density of the investigated ionomers shows appreciable change in the slope at about 4 mol % of ionic groups as a function of ionic comonomer content. Similarly, as in the case of T_g, this change in the slope of the density may be attributed to the change in the state of ion aggregation.

This data (Table III) also indicates that the density of S-b-ANa ionomers is higher than in the case of the ionomers based on copolymers obtained in bulk[16] containing almost the same content of ANa (2.5 and 3.9 mol %).

We may suppose that these differences in behavior of the investigated ionomers obtained from emulsion and bulk copolymers probably may be a consequence of slightly different microstructure of the parent copolymers.[7]

We suppose that the copolymers obtained in emulsion have longer sequences of AA than in bulk.[7] This is a result of the higher solubility of AA in water than in styrene, and it may cause such interactions with Na^+ ions that may facilitate more dense packing of macromolecules.

TABLE IV
Density of Cesium Ionomers Based on S-b-AA Copolymers

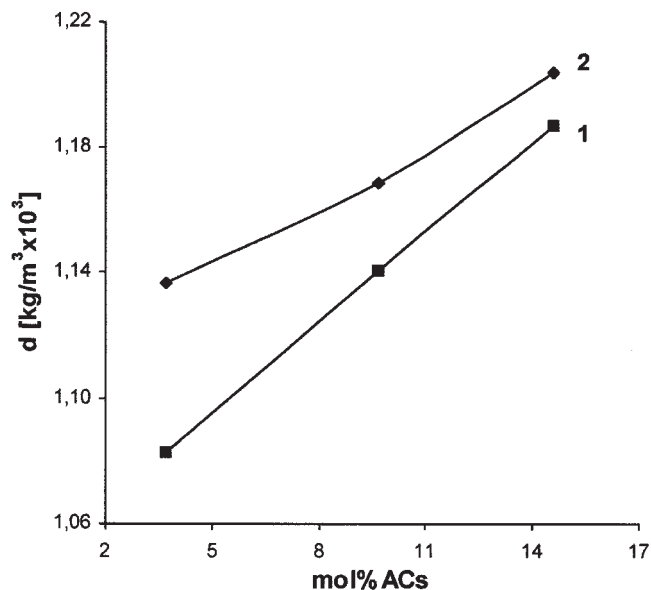| Content of ACs (% mol)	Density, d (kg/m³ × 10³)	
	Exp.	Calc.
3.7	1.137	1.083
9.7	1.169	1.141
14.6	1.204	1.187

Figure 4 Dependence of density of S-b-ACs on the content of ACs: (1) theoretical data, (2) experimental data.

We indicated earlier[15] that certain properties of the ionomers obtained from emulsion and bulk copolymers were different.

Table IV and Figure 4 show the density of the ionomers containing increasing content of cesium acrylate (ACs). Similarly as in the case of the ionomers containing Na^+ ions, the density increases with the rise in content of the introduced Cs^+ ions.

The investigated copolymers and ionomers were amorphous. Knowing the chemical composition of the investigated ionomers and the value of the density of cesium polyacrylate (PACs) – $d_{PACs} = 2g/mL$[36] and our $d_{PS} = 1.048$ g/mL, we calculated the density of our ionomers containing cesium ions. These results are presented in Table IV and in Figure 4.

The calculated values of the density (Fig. 4) are lower than the measured ones. This data may indicate that similarly as in the case of the ionomers based on copolymers obtained in bulk, the effects of composition alone are insufficient to explain the effect of ions on the density of the ionomers. These results may indicate that probably composition effects and electrostatic interactions after introduction of ions, which caused aggregation of ionic groups, probably have an appreciable effect on the density of the investigated ionomers.

Table V presents the density for the ionomers based on copolymer S-b-AA(3.7) with different alkali metal ions. The densities of salts of these copolymers are higher than those of acid and increase with the molecular weight of the ions of alkali metal introduced to the copolymer. Ionomers containing Li^+ ions have distinctive values among the studied polymers. It may be due to the fact that, as indicated by other au-

TABLE V
Density of Ionomers Containing 3.7 mol% of Salt Units

Cation	Molecular Weight (g/mol)	Density, d $(kg/m^3 \times 10^3)$
H^+	1.008	1.083
Li^+	6.941	1.124
Na^+	22.990	1.118
K^+	39.102	1.120
Cs^+	132.905	1.137

thors,[37,38] forces between lithium cations and anionic carboxylate groups are covalent in nature, which may cause more dense packing of macromolecules and increase in density.

Table VI presents the density of the ionomers containing almost the same amount of ACs, ANa and MCs, MNa.

These results indicate that ionomers containing cesium and sodium acrylate have higher density than ionomers based on sodium and cesium methacrylate.

This dependence may be caused by the difference in the nature of the ionic repeating unit, that is, the acrylate and methacrylate units, and these in turn differ only in the presence of a methyl group on the α - carbon of the ionic repeating unit. This methyl group makes approaching macromolecules of the polymer difficult, decreasing the density of packing of macromolecules, which causes lower density.

We indicated earlier[8] that our studies of the styrene based ionomers by means of far-i. r. containing almost the same content of acrylate and methacrylate also gave different spectra.

Our results of determination of the density presented in this work complete and broaden very unusual determinations this value of the styrene ionomers.[3]

Up to now only a few determinations of the density of styrene ionomers have been performed.

The increase in the density with the degree of neutralization by K^+ ions for the ionomers based on S-MA copolymers, containing 5 and 11 mol % of MA, was indicated earlier by Nicolajev and Galperin.[39]

Yano et al.[40] measured the density as a function of degree of neutralization of the styrene ionomers con-

TABLE VI
Density of Ionomers Containing Sodium and Cesium Salts of Copolymers of S-b-AA and S-b-MA

Polymer	Density, d $(kg/m^3 \times 10^3)$
S-b-ANa(9.7)	1.133
S-b-MNa(10.0)	1.119
S-b-ACs(9.7)	1.169
S-b-MNa(10.0)	1.157

TABLE VII
Dependence of MI on Molecular Weight

| Copolymer | $M_n \times 10^{-3}$ | MI (g/10 min) | |
		Copolymer	Ionomer
S-b-AA(5.3)	280	0.3	n.p.
S-b-AA(5.9)	170	0.5	n.p.
S-b-AA(5.5)	90	0.8	n.p.

taining 4.4 mol % methacrylic acid neutralized by copper. They showed that the density of the ionomers increases with the growth in the degree of neutralization from 1.046 to 1.074 g/mL over the range of 7–79% neutralization. In earlier discussion of clustering in styrene ionomers Eisenberg[28,41,42] showed that a plot of the density of styrene-sodium methacrylate copolymers as a function of carboxylate concentrations exhibits an appreciable change in slope at *ca* 6 mol %, which he attributed to the onset of clustering in these materials. Then he calculated the fraction of ions in the clusters from the integrated intensities of the two dielectric peaks observed in the glass transition region[41] and showed that the density varied linearly with this variable. From this and other results presented in his paper, Eisenberg concluded that the clusters dominate the properties of the ionomers. Thence, he suggested that the density of the ionomers is extremely sensitive to the morphology of the ionic aggregation.

However, recently Eisenberg[26] discussed the same results regarding the density of styrene ionomers containing 0–9 mol % of sodium methacrylate, and he indicated that the best-fit second order polynomial to describe the data is

Density(g/ml)

$$= 1.057 + 6.53 \times 10^{-5}X + 3.85 \times 10^{-4}X^2 \quad (3)$$

where X is the mol % of ions.

Weiss et al.,[5] measuring the densities of copolymers of styrene and sodium styrene sulfonate and sodium sulfonated polystyrene (SPS), observed an increase in density with an increase in the content of sulfonate.

They obtained linear data and, contrary to Eisenberg's earlier results for styrene-sodium methacrylate, neither of the two sulfonate ionomer systems exhibited a change in the slope of the density-concentration curve. They suggested that this result may be a consequence of differences in the ion association between sulfonate and carboxylate ionomers.

Our results of studies of the density of styrene based ionomers disagree with the results of Weiss et al.,[5] and as Eisenberg's results for styrene-sodium methacrylate, exhibit change in the slope of the density-concentration curve. These results also may confirm that the density of an ionomer is sensitive to the morphology of the ionic aggregation, as Eisenberg suggested.

Melt index and energy activation of flow

Table VII presents the dependence of MI on the molecular weight. These results indicate that copolymers obtained in emulsion containing almost the same amount of AA but of different molecular weight have higher MI than copolymers of lower molecular weights.[43] Obtained ionomers containing Na^+ ions don't flow under conditions of determination of MI.

It is possible to explain that macromolecules of lower M_n or lower number of segments flow easier because they lose less energy needed for the displacement of the segments of macromolecules.[20,43] This data may indicate how great a significance the molecular weight bears on the flow of the polymers.

Table VIII presents values of MI for copolymers S and AA or MA and obtained sodium ionomers. This data indicates that introduction of AA to the polystyrene chain doesn't really affect the MI of copolymers in the investigated range of composition. This may be probably caused by the fact that the influence of introduction of small amounts of AA to the PS chain is diminished by the changes of molecular weight of these copolymers, which, as shown above, have substantial influence on the values of MI.

In the case of copolymers containing MA, the increase of MI in relation to the MI of PS has been observed after introduction of this acid to the polysty-

TABLE VIII
Influence of Content of the Introduced AA or MA on the MI and E of the Initial Copolymers and Obtained Ionomers

| Polymer | $M_n \times 10^{-3}$ | MI (g/10 min) | | E (kJ/mol) | |
		Copolymer	Ionomer	Copolymer	Ionomer
PS	260	0.4	—	144.4	—
S-b-AA(0.7)	480	0.4	0.1	165.8	236.1
S-b-AA(2.3)	330	0.3	0.1	105.9	173.3
S-b-AA(3.7)	320	0.5	n.p.	139.2	—
S-b-AA(5.3)	280	0.3	n.p.	138.2	—
S-b-MA(0.8)	320	1.1	0.3	96.7	207.7
S-b-MA(3.6)	270	1.2	n.p.	136.3	—

rene chain, which may be caused by the decrease of LVN of these copolymers.

The substitution of H^+ ions in the carboxylic group by Na^+ ions causes further decrease of MI and increase of E of ionomers in relation to the initial copolymers.

In the case of ionomers containing *ca* 4 mol % and more sodium acrylate (ANa) and methacrylate (MNa), the polymers don't flow under conditions of determination of MI. This indicates that probably introduction of the higher content of sodium ions causes such strong electrostatic interactions, which contribute to the aggregation of ions, that they prohibit the flow of the polymer.

The data presented in Table VIII also may confirm our earlier statement on the basis of far-i. r. data[9] and the studies of T_g and the density of these ionomers, that at *ca* 4 mol % of ANa in our ionomers may be the onset of clustering.

The diminution of MI of copolymers of S and MA and their salts containing sodium and potassium ions was observed earlier,[39,44–46] but there were no measurements of MI of S and AA copolymers and obtained ionomers.

The increase in E in relation to the copolymer may be explained by the crosslinking effect after introduction of ions and their aggregation.

Increase in E of the ionomer was observed earlier for ionomers based on S-MA copolymers by Galperin and Nicolajev[39] and Plochocka and Wojnarowski.[46] However, Ide et al.,[45] investigating the same ionomers, did not observe the increase in E of the ionomers.

Also, Weiss and Agrawall[47] investigating melt rheology of the ionomers based on propylene-acrylic acid copolymer and Iwakura and Fujimura[48] investigating the rheological properties of molten blends of PS and styrene ionomers observed the increase in E.

CONCLUSIONS

The present studies indicate that T_g of sodium ionomers based on copolymers S and AA obtained in emulsion increases as ANa content in the ionomer increases, but the increase is lower than in the case of the ionomers based on copolymers obtained in bulk.

Density of S-b-ANa and S-b-ACs ionomers rises with the increase in content of acrylate introduced to the polystyrene chain, and it is higher than in the case of the ionomers based on copolymers obtained in bulk containing almost the same content of acrylate. The density is higher as the molecular weight of the alkali metal rises.

Ionomers containing sodium and cesium acrylate have higher density than styrene ionomers based on sodium and cesium methacrylate.

The melt index of the investigated ionomers depends on the amount and type of introduced acid or salt and on the molecular weight of the initial copolymer.

Introduction of the ions of alkali metals to the copolymers causes a diminution of MI of ionomers in relation to the MI of the initial copolymers. This diminution, however, is distinctly lower than the one observed for the same ionomers based on copolymers obtained in bulk.

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