

# Stability of Aqueous Solutions of Poly[(maleic acid)-*alt*-styrene] Sodium Salts in the Presence of Divalent Cations

V. JARM, S. SERTIĆ, and N. ŠEGUDOVIĆ\*

Ina-Industrija Nafta, Research and Development, 10000 Zagreb-Croatia, Savska cesta 41/X, Croatia

## SYNOPSIS

The influence of divalent salts ( $MgCl_2$ ,  $CaCl_2$ ,  $BaCl_2$ ) on precipitation of polyelectrolyte, poly[(maleic acid)-*alt*-styrene]sodium salts, NaMA/St, having two degrees of neutralization (100 mass %, 100NaMA/St and 50 mass % 50NaMA/St) from their aqueous solutions, has been investigated. The experiments were performed by variation of the copolymer concentration,  $c_p = 0.005$ – $0.04 M/L$ , salt concentration,  $c_s = 0.002$ – $0.4 M/L$ , and temperature,  $T$  298–333 K. The critical concentrations of salts,  $c_{sc}$ , used as a measure of solution stability, were determined from turbidimetric measurements, while viscosity and refractive index measurements were used to indicate the changes in dimensions and hydration of polyions, respectively. © 1995 John Wiley & Sons, Inc.

The solution of 100NaMA/St, is very sensitive to divalent cations, showing a drastic decrease of viscosity, low dehydration, and low  $c_{sc}$  values (approximately equivalent to  $c_p$ ) independent of  $T$ . More extended and hydrated macromolecules in aqueous solution of 50NaMA/St show a gradual decrease of viscosity, larger dehydration, and higher  $c_{sc}$  values ( $c_{sc} = 0.015$ – $0.5 M/L$  for  $c_p$  3 g/L at 298 K) which, however, decrease with the increase of  $c_p$  and  $T$ . The tendency of divalent cations to precipitate the copolymer follows the order  $Ba^{2+} > Ca^{2+} > Mg^{2+}$ . The stability of aqueous solution of sulfonated NaMA/St, having the same chain length, increases with the increase of degree of sulfonation.

## INTRODUCTION

The precipitation of synthetic polyelectrolytes from aqueous solutions containing multivalent cations decreases their efficiency as auxiliary agents in many applications. In aqueous solutions of polyelectrolytes abound with various interactions, a higher electrostatic potential of polyions attracts cations, causing

their contraction, dehydration, decrease in solubility, and precipitation. The mechanism of phase separation and precipitation of polyelectrolyte depends on a number of factors such as the chemical nature, configuration,  $M$ , MMD, and concentration of polymer; the type and concentration of small ions; the type of solvent; temperature; etc. Its complexity and difficulty to interpret in terms of known theoretical models is the main reason for only a few articles in the area of synthetic polyelectrolytes.

The precipitation with divalent cations has been examined in aqueous solutions of following polyacids and their salts: poly(acrylic acid),<sup>1,2</sup> poly(methacrylic acid),<sup>3</sup> copolymer of acrylamide and acrylic acid,<sup>4–6</sup> and polysulfostyrene.<sup>7–9</sup>

Although the sensitivity of aqueous solutions of alternating copolymers of maleic acid and styrene, MA/St, in the presence of divalent cations are known in practice, there are no many published results<sup>10</sup> about it. In our preliminary investigations,<sup>11</sup> the comparison of stability of aqueous solutions of sodium salts of alternating MA/St copolymers having various degree of neutralization in the presence of  $CaCl_2$  at 298 K has been made. The sodium salts of lower degree of neutralization (45–65%) showed a higher tolerance to  $CaCl_2$  than those of higher degree of neutralization (70–100%), due to more extended conformations and higher hydration of polyions of the former copolymers.

\* To whom correspondence should be addressed.

In continuation, the phase separation behavior of aqueous solution of two NaMA/St (full Na-salt and half Na-salt) were examined in dependence of the type and concentration of divalent cation salts ( $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ), concentration of copolymer ( $c_p = 1$  to  $10$  g/L) and temperature (298–333 K). For comparison, the stability of aqueous solutions of some sulfonated NaMA/St copolymers in the presence of salts has been investigated.

## EXPERIMENTAL

All chemicals used had a pro analysis grade of purity. Monomers and solvents were purified using conventional methods. Redistilled, demineralized water having the conductivity  $1.8 \mu\text{S}$  was used as a solvent in hydrolysis, neutralization of copolymers and in preparation of their aqueous solutions.

### Preparation of Copolymers

#### *Poly[(maleic anhydride)-alt-styrene], MA/St*

The starting MAn/St copolymer was synthesized<sup>12</sup> in 98% conversion by heterogeneous copolymerization of equimolar mixture of monomers in toluene at 348 K using 2,2-azobisisobutyronitrile as initiator. During separation copolymer was thoroughly washed with hot toluene, vacuum dried, reprecipitated from tetrahydrofuran solution with benzene, and dried in vacuum at 333 K to the constant weight. No additional fractionation was undertaken. This copolymer precursor shows a characteristic IR absorption of carbonyl groups at 1850  $\text{cm}^{-1}$ , contains 48.3 mass % of maleic anhydride, and has the intrinsic viscosities at 298 K: 0.548 dL/g (tetrahydrofuran) corresponding to  $M_v$  185,000 according to the D. C. Chow equation<sup>13</sup> and 0.626 dL/g (*N,N*-dimethylformamide + 0.05 M LiBr).

#### *Poly[(maleic acid)-alt-styrene], MA/St*

The polyacid MA/St was prepared by heating MAn/St in water (1 g in 100 mL) at 333 K for 24 h. After filtration of aqueous solution the solid polyacid was separated by a repeated dissolution and freeze-thaw vacuum evaporation and at the end by a vacuum drying at 313 K to the constant weight. The characteristic IR absorption of polyacid is at 1710  $\text{cm}^{-1}$ , and the intrinsic viscosities at 298 K: 0.351 dL/g (tetrahydrofuran) and 0.608 dL/g (DMF + 0.05 M LiBr).

#### *Poly[(maleic acid)-alt-styrene]sodium salt, NaMA/St*

Two sodium salts (100% neutralized sodium salt, 100NaMA/St and 50% neutralized sodium salt, 50NaMA/St) were prepared by heating of an aqueous solution of polyacid (1 g in 100 mL) with the calculated amount of NaOH (0.364 g; 0.182 g NaOH) dissolved in water at 333 K for 4 h. The filtered aqueous solution was evaporated in vacuum and the powdered NaMA/St dried in vacuum at 373 K to the constant weight. Dry salt was used for preparation of aqueous stock solutions. Intrinsic viscosities determined in 0.5 M NaCl at 298 K are: 0.567 dL/g for 100NaMA/St and 1.250 dL/g for 50NaMA/St.

#### *Poly[(maleic acid)-alt-(p-sulfostyrene, styrene)] (37.5% and 75 mass % p-sulfostyrene), MA/37SSStSt; MA/75SSStSt*

Two polyacids with different degrees of sulfonation were prepared employing the described procedure<sup>14,15</sup> for sulfonation of MAn/St homogeneously suspended in dichloroethane with sulfur trioxide/triethylphosphate at room temperature. The degree of sulfonation was calculated from sulfur content determined by the elementary analysis (ASTM 1551). The 100 mass % and 50 mass % neutralized sodium salts were prepared in aqueous solutions by the addition of calculated amounts of NaOH (per 1 g of MA/37SSStSt: 0.377 g and 0.188 g NaOH; and per 1 g of MA/75SSStSt: 0.391 and 0.195 g NaOH). After filtration of the aqueous solution of Na-salt, the solid salt was separated by a freeze-thaw vacuum evaporation and vacuum drying to the constant weight. Intrinsic viscosities of individual Na-salts determined in 0.5 M NaCl solutions at 298 K were: 0.464 dL/g for 100NaMA/37SSStSt; 1.054 dL/g for 50NaMA/37SSStSt; 0.426 dL/g for 100NaMA/75SSStSt; 0.972 dL/g for 50NaMA/75SSStSt.

### Turbidity Measurements

The turbidities were measured in essentially static "test tube" experiments using a combination of Zeiss tyndalometer and Pulfrich photometer with green filter. Measurements were carried out at copolymer concentrations  $c_p = 1, 1.5, 3, 5, 7,$  and  $10$  g/L and at temperatures ranging from 298 to 343 K. To each tube of the series of test tubes, containing the same concentration of copolymer, a gradually increased quantity of the solution of appropriate salt was added in such a way that the total volume of solution

was 10 mL. After a thorough mixing and staying for 20 min, turbidities of solutions were measured in the mentioned type of thermostated ( $\pm 0.5$  K) instrument. The readings of at least two runs for each concentration of salt,  $c_s$ , were reported as tyndalometric values, T.V.. The critical concentration of salt,  $c_{sc}$ , at which the precipitation began was determined as the intersection of tangents on the curve  $\log c_s$  vs. T.V.

### Viscosity Measurements

Viscosity measurements were performed at various temperatures in a modified Cannon-Fenske-type viscometer with flow times for water: 101.5 s at 298 K, 77 s at 313 K, 66 s at 323 K, and 57.5 s at 333 K. Intrinsic viscosities of copolymers were measured in a similar Cannon-Fenske viscometer with flow time for water 300.5 s at 298 K.

### Refractive Index Measurements

A Brice Phoenix Differential Refractometer Model BP-1000-V was employed for the measurement of relative refractive indexes of solvent,  $n_o$ , polymer solution,  $n_p$ , salt solution,  $n_s$ , and their mixture,  $n_{(p+s)}$ . Measurements were performed at 456 nm and 298 K. For calibration, sodium chloride solutions of known concentration and refractive index were used.<sup>16</sup> The polymer concentration was kept at 3 g/L, and concentration of added salts varied in the range of 0.003–0.20 M/L.

## RESULTS AND DISCUSSION

The water solubility of polyacid form of alternating MA/St copolymer is limited and increases with increasing the degree of neutralization.<sup>17–19</sup> Consequently, sodium salts of MA/St copolymer having the degree of neutralization lower than 25 mass % are insoluble, and those with degree of neutralization higher than 25 mass % are soluble in water.

Moreover, specific structural characteristics of alternating MA/St copolymer, such as the regular structure of main chain, the presence of two —COOH groups bonded on two neighboring carbon atoms of the main chain, and hydrophobicity of the alternating styrene unit may in certain circumstances initiate various interactions and influence the solution properties.<sup>20–22</sup>

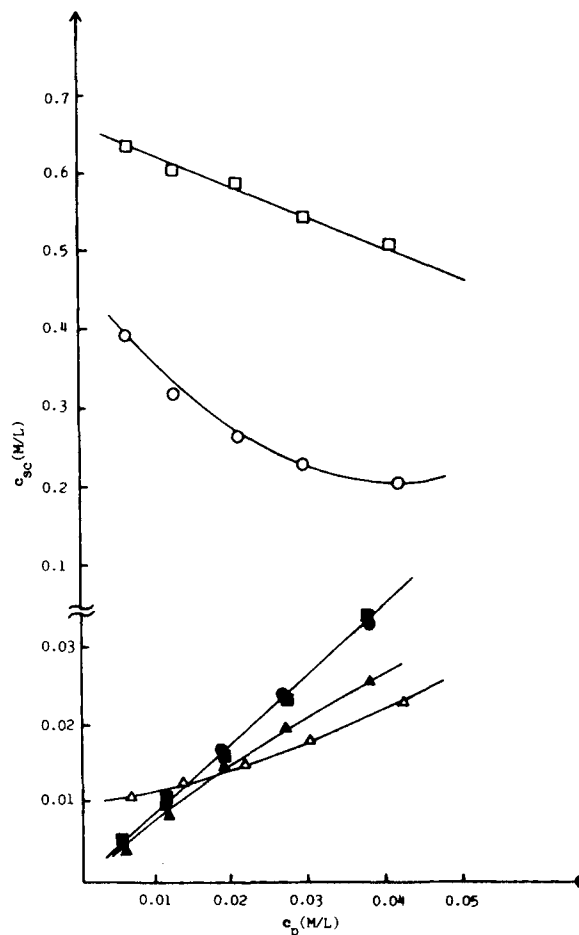
This investigation of the stability of aqueous solutions of NaMA/St copolymers in the presence of divalent cations were limited to two sodium salts

(full sodium salt, 100NaMA/St, and partially neutralized sodium salt, 50NaMA/St) the polyions of which differed in charge density, dimensions, and hydration.

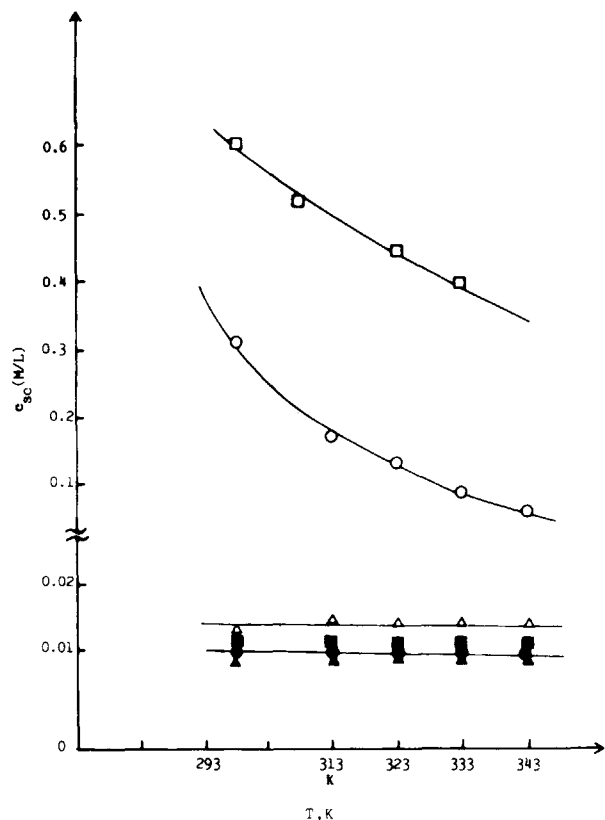
### Dependence of Critical Salts Concentrations on the Degree of Neutralization and Concentration of Copolymer

The stability of aqueous solutions of NaMA/St copolymers in the presence of divalent cation salts is expressed as a critical concentration of salt,  $c_{sc}$ , i.e. the minimum salt concentration at which the precipitation begins.

The change of critical concentration of salts ( $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ),  $c_{sc}$ , with increasing the concentration of polyions,  $c_p$ , and temperature for aqueous solutions of 100NaMA/St and 50NaMA/St copolymers are shown on Figures 1 and 2.



**Figure 1** Critical salt concentration,  $c_{sc}$ , vs. copolymer concentration,  $c_p$ , for aqueous solutions of: 100NaMA/St in the presence of ■  $\text{MgCl}_2$ , ●  $\text{CaCl}_2$ , and ▲  $\text{BaCl}_2$ ; 50NaMA/St in the presence of □  $\text{MgCl}_2$ , ○  $\text{CaCl}_2$ , and △  $\text{BaCl}_2$ .



**Figure 2** Critical salt concentration,  $c_{sc}$ , vs. temperature,  $T$ , for aqueous solutions ( $c_p = 3$  g/L) of 100NaMA/St in the presence of ■  $MgCl_2$ , ●  $CaCl_2$ , and ▲  $BaCl_2$ ; and 50NaMA/St in the presence of □  $MgCl_2$ , ○  $CaCl_2$ , and △  $BaCl_2$ .

The aqueous solution of 100NaMA/St is very sensitive to the presence of divalent cations ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ). Values of the critical salt concentration,  $c_{sc}$ , in these systems are low, they increase with increasing of  $c_p$  (Fig. 1), they are approximately equivalent to the  $c_p$ , and do not change with increasing temperature (Fig. 2).

More expanded polyions in an aqueous solution of partially neutralized copolymer, 50NaMA/St, tolerate considerably higher concentration of  $CaCl_2$  and  $MgCl_2$ , but not  $BaCl_2$ .

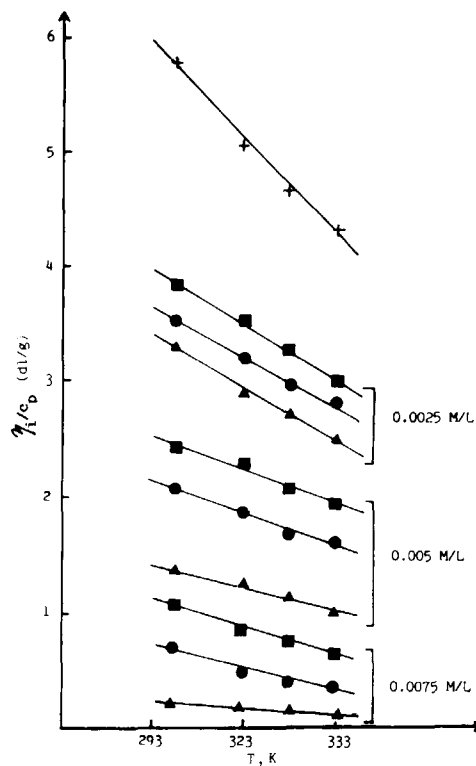
Relatively high  $c_{sc}$  values for  $MgCl_2$  and  $CaCl_2$  slowly decrease with increasing of  $c_p$  (Fig. 1), and markedly decrease with the increase of temperature (Fig. 2). The influence of the type and size of cation on the precipitation of copolymer is more pronounced in the solution of 50NaMA/St following the order:  $Ba^{2+} > Ca^{2+} > Mg^{2+}$ , while the behavior of  $Ca^{2+}$  and  $Mg^{2+}$  is similar,  $Ba^{2+}$ , with their low  $c_{sc}$  value independent of  $T$ , illustrating L-type precipitation.<sup>2</sup>

Application of the empirical equation proposed by Michaeli,<sup>3</sup> which connects  $c_{sc}$  and  $c_p$  ( $c_{sc} = bc_p - a$ , where  $a$  represents a fraction of free divalent cation and  $bc_p$  represents a fraction of cations bound to a single polyion) to investigated systems, the positive  $b$ -value was obtained for 100NaMA/St- $BaCl_2$ ; 50NaMA/St- $BaCl_2$ ; 100NaMA/St- $CaCl_2$  but a clearly negative  $b$ -value for 50NaMA/St- $CaCl_2$ , which meant a largely different phase separation behavior in the last system.

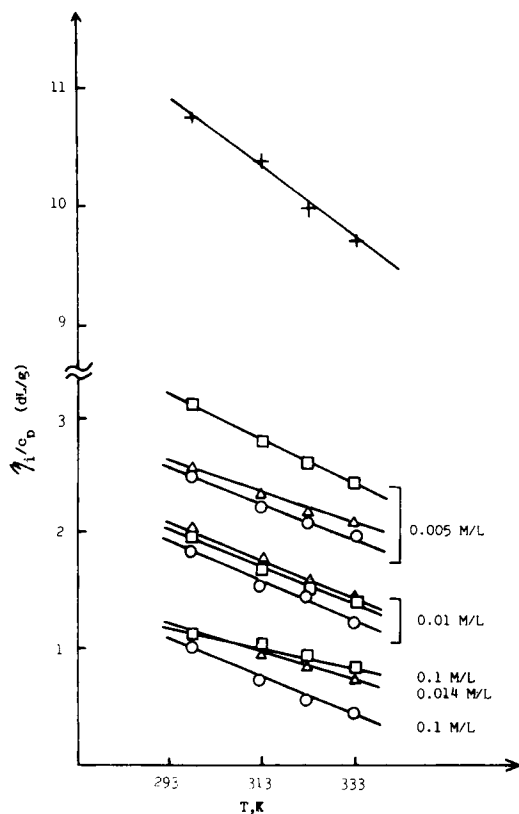
### Effect of Salts on Viscosity

Figures 3 and 4 present the dependence of reduced viscosity, of aqueous solutions of 100NaMA/St and 50NaMA/St on divalent salt concentration ( $MgCl_2$ ,  $CaCl_2$ ,  $BaCl_2$ ) and temperature (298 to 333 K). Generally, the reduced viscosity  $\eta_i/c_p$ , at constant temperature decrease with increasing the concentration of divalent salt, and at constant  $c_s$ , with increasing the temperature.

In salt-free copolymer solutions, the influence of temperature on the drop of  $\eta_i/c_p$  is stronger for 100NaMA/St (slope) than for 50NaMA/St, be-



**Figure 3** Reduced viscosity,  $\eta_i/c_p$ , vs. temperature,  $T$ , for aqueous solution of 100NaMA/St ( $c_p = 3$  g/L) × salt free and with various concentrations of ■  $MgCl_2$ , ●  $CaCl_2$ , and ▲  $BaCl_2$  indicated on curves.



**Figure 4** Reduced viscosity,  $\eta_i/c_p$ , vs. temperature,  $T$ , for aqueous solution of 50NaMA/St ( $c_p = 3$  g/L):  $\times$  salt free and with various concentrations of  $\square$  MgCl<sub>2</sub>,  $\circ$  CaCl<sub>2</sub>, and  $\Delta$  BaCl<sub>2</sub> indicated on curves.

cause the latter system is stabilized by the hydration of the —COOH groups.

Aqueous solutions of full sodium salt, 100NaMA/St, are more sensitive to the concentration and type of divalent cation than the solution of 50NaMA/St. The higher drop of  $\eta_i/c_p$  is caused by the cation of higher size and lower hydration shell in the following order:  $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ . For the contraction of more extended polyions of 50NaMA/St to the precipitation range, higher amounts of MgCl<sub>2</sub> and CaCl<sub>2</sub> but not of BaCl<sub>2</sub> are required.

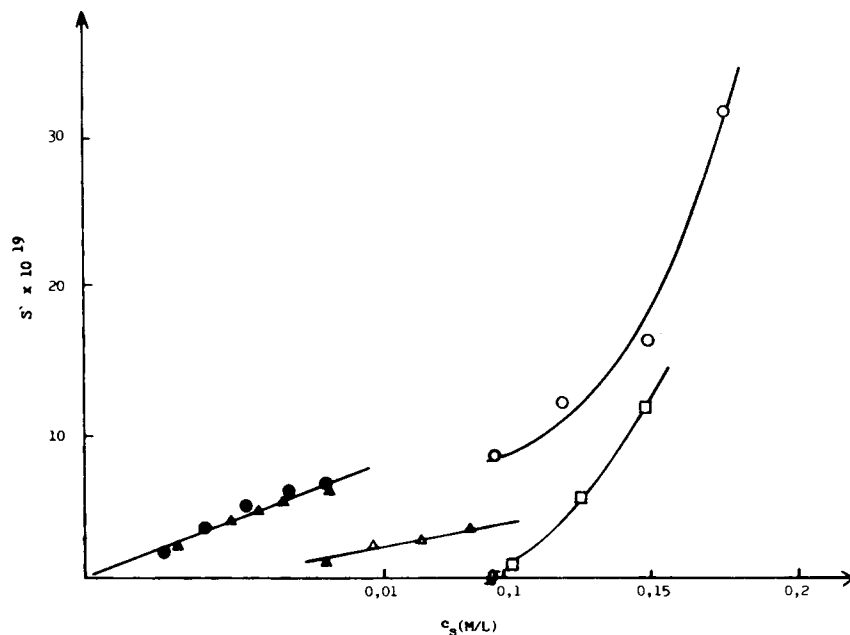
### Effect of Salts on Hydration

When a cation is bound to a carboxyl group on the polymer, the amount of water released is a result of ion binding. By measuring the refractive indices of solutions an estimate of the number of water molecules dehydrated by salts per unit volume of solutions,  $S'$ , was made using the following relationships:<sup>2</sup>

$$S' = - \frac{100 \rho_o}{11 M_o} \frac{6n_o N_A \Delta n}{(n_o^2 + 2)(n_o^2 - 1)}$$

$$\Delta n = (n_{(p+s)} - n_o) - (n_p - n_o) - (n_s - n_o)$$

where  $n_o$ ,  $n_s$ ,  $n_p$ , and  $n_{(p+s)}$  refer to refractive indices of water, salt solution, polyelectrolyte solution, and mixture of salt and polyelectrolyte, respectively,  $\rho_o$



**Figure 5** Dehydration of polyions,  $S'$ , in the presence of added divalent salts,  $c_s$  for aqueous solutions of: 100NaMa/St with  $\bullet$  CaCl<sub>2</sub> and  $\blacktriangle$  BaCl<sub>2</sub>; and 50NaMA/St with  $\square$  MgCl<sub>2</sub>,  $\circ$  CaCl<sub>2</sub>, and  $\Delta$  BaCl<sub>2</sub> ( $c_p = 3$  g/L).

and  $M_0$  density and molecular mass of water,  $N_A$  Avogadro's number.

The dependence of  $S'$  on concentration of salts,  $c_s$ , is presented in Figure 5. It is obvious that the amount of released water ( $S'$ ) depends on the degree of neutralization of polyelectrolyte and the cation species. Partially neutralized and more hydrated 50NaMA/St needs a higher  $c_s$  for releasing a higher amount of water than the fully neutralized 100NaMA/St. Here, again, appears a similar behavior of  $Mg^{2+}$  and  $Ca^{2+}$ , but different behavior of  $Ba^{2+}$ , probably due to differences in the size, hydrophobicity, and binding form<sup>2</sup> of  $Ba^{2+}$ .

### Stability of Aqueous Solutions of Sulfonated NaMA/St Copolymers

The comparison between the critical concentration of  $CaCl_2$  in aqueous solutions of sulfonated (37.5 mass % and 75 mass %) and nonsulfonated NaMA/St copolymers of two different degrees of neutralization (100 mass % and 50 mass %) and approximately the same chain length is shown in Table I.

The stability of aqueous solutions of copolymers ( $c_{sc}$  values) is directly proportional to the degree of sulfonation of copolymer and indirectly to the degree of neutralization. The  $c_{sc}$  values for a copolymer of a lower degree of sulfonation, 50NaMA/37SSSt, similarly to the nonsulfonated 50NaMA/St copolymer, decrease with the increasing  $c_p$  and temperature. On the contrary, an aqueous solution of copolymer of a higher degree of sulfonation, 50NaMA/75SSSt, does not show any sign of turbidity even in the presence of 235 g/L  $CaCl_2$ , and stays clear at higher  $c_p$  (1, 3, and 5 g/L) and higher temperature (298–365 K).

Such behavior is possibly a consequence of the formation of soluble Ca-sulfonate for which a certain

higher ratio of two functional groups<sup>14</sup> ( $-COOH/-SO_3H$ ) along the chain is required. Aqueous solutions of both sulfonated copolymers are very sensitive to the presence of  $BaCl_2$  and become turbid in the presence of 1 to 3 g/L  $BaCl_2$ .

### CONCLUSIONS

The behavior of aqueous solutions of alternating copolymers of maleic acid and styrene (100NaMA/St; 50NaMA/St) in the presence of divalent salts ( $MgCl_2$ ,  $CaCl_2$ ,  $BaCl_2$ ) is generally similar to the behavior of solutions of other synthetic polyelectrolytes.<sup>1-9</sup> The binding of divalent cations to polyanions causes their contraction, dehydration, decrease in solubility, and precipitation. The stability of solutions depends on the neutralization degree, the concentration of copolymer, concentration of salt, and on temperature.

Aqueous solutions of fully neutralized copolymer, 100NaMA/St are more sensitive to the presence of divalent salt, with low  $c_{sc}$  values (approximately equivalent to  $c_p$ ) independent of  $T$  and the type of cation (like the L-type precipitation).<sup>2</sup> The solutions of more extended and largely hydrated macromolecules of partially neutralized copolymer, 50NaMA/St, could stand a higher  $c_s$ . Their stability, however, decreases with the increase of  $c_p$  and temperature, because of higher intermolecular interactions and higher mobilities of macromolecules in such conditions. The influence of type and size of divalent cations on the instability of solutions follows the order:  $Ba^{2+} > Ca^{2+} > Mg^{2+}$ . The aqueous solutions of sulfonated NaMA/St show better stability to divalent cations than nonsulfonated NaMA/St, possibly because of a higher solubility of sulfo-salts and a different hydration sphere of sulfonated macromolecules.

**Table I Critical Concentrations of  $CaCl_2$  in Aqueous Solutions of 100 mass% and 50 mass% Neutralized Sodium Salts of Poly[(maleic acid)-*alt*-styrene] and Poly[(maleic acid)*alt*-(*p*-sulfostyrene, styrene)] Containing 37.5 and 75 mass% of *p*-Sulfostyrene**

Copolymer	X mass% <sup>a</sup>	$E^b$	$c_p$ , g/L	$c_p$ , equiv/L	$c_{sc}$ , g/L	$c_{sc}$ , equiv/L	$c_{sc}/c_n$
100NaMA/St	0	132.1	3	0.0227	1.14	0.0205	0.903
100NaMA/37SSSt,St	37.5	128.3	3	0.0234	1.40	0.0252	1.077
100NaMA/75SSSt,St	75	124.6	3	0.0241	3.35	0.0604	2.502
50NaMA/St	0	121	3	0.0250	3.53	0.0675	25.4
50NaMA/37SSSt,St	37.5	117.3	3	0.0260	27.5	2.297	89.7
50NaMA/75SSSt,St	75	113.5	3	0.0264	> 235	> 4.234	> 160

<sup>a</sup> Degree of sulfonation.

<sup>b</sup> Equivalent mass of the repeating unit.

$c_p$ —concentration of polyion in g/L and equiv/L;  $c_{sc}$ —critical concentration of salt in g/L and equiv/L.

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