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# THE EFFECT OF NATURE OF CATION ON THE RADICAL POLYMERIZATIONS OF CALCIUM, STRONTIUM AND BARIUM SALTS OF P-STYRENESULPHONIC ACID IN AQUEOUS SOLUTIONS

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**Abstract**—The kinetics of the homogeneous free radical polymerizations of divalent salts of styrenesulphonic acid (SSA) in water and water-salt solutions at 70° in the presence of ammonium persulphate has been investigated. It is shown that, for the concentration range from 0.12 to 0.3 mol/l for monomers, the initial rate of polymerization ($V_0$), the value of $k_p/k_t^{1/2}$, the kinetic order with respect to monomer and the average molecular weight of the resulting polymer increase in the series Ca–SSA < Sr–SSA < Ba–SSA. In every case the kinetic order with respect to initiator is 0.5. The effect of cation on $V_0$ is more significant for smaller values of ionic strength ($\mu$). With increasing $\mu$ the values of $V_0$ increase but the influence of cation radius on $V_0$ decreases; for large values of $\mu$, $V_0$ does not depend on the cation.

## INTRODUCTION

Water-soluble polyelectrolytes based on polystyrenesulphonic acid (PSSA) and its salts are of great practical value [1, 2] and are convenient model compounds for the investigation of properties of macromolecular systems [3, 4]. The kinetic peculiarities and the mechanism of free radical polymerization and copolymerization of monovalent salts of styrenesulphonic acid (SSA) in water–salt, water–dioxane, water–dimethyl sulphoxide (DMSO), DMSO–dioxane mixtures have been reviewed [5]. It has been shown that the kinetic parameters of the polymerization and copolymerization of ionogenic monomers and the properties of the resulting polymers (molecular weight, copolymer composition and compositional inhomogeneity) depend considerably on the nature of the medium. It is mainly connected with the influence of the reaction medium on the proportions of the different ion forms for ionogenic monomers and macroradicals and also on the effective ionic strength of the solution [5, 6]. This leads to change of character of electrostatic interactions in the reaction system and to change of the conformation of macroradicals, so influencing the reactivity of monomers and macroradicals.

The free radical polymerization of acidic water-soluble monomers depends on the nature of cation. The polymerization rate of various salts of acrylic and methacrylic acids in the crystalline state and in aqueous solutions [7–9] and also salts of *N*-vinylamidoamber acid in methanol solutions [10] depend significantly on the nature of cation. It has also been established that the copolymerization rate and reactivity ratios for acrylamide with acrylate and methacrylate salts, during aqueous copolymerization [11–14], and for methyl methacrylate with methacrylate salts, during copolymerization in methanol solutions [15], depend very closely on the nature of the cation. In this paper the free radical polymerizations of divalent salts of SSA (calcium, strontium and barium) in water and water–salt solutions were investigated.

## EXPERIMENTAL

Potassium salt of SSA (K–SSA) was purified by triple recrystallization from 93% ethanol. The purity was 98.9% by the mercury acetate addition method. Potassium salt of PSSA (K–PSSA) was prepared by polymerization of the monomer in aqueous solution at 50 in the presence of $(NH_4)_2S_2O_8$ under argon. The polymer was reprecipitated twice from water into acetone and then dried at 50° under reduced pressure to constant weight. The degree of polymerization was obtained by viscometry [16]. Aqueous solutions of K–SSA and K–PSSA were passed through a column of cation-exchange resin using KY 2 × 8 in the acid form. The resulting stock solutions were used to prepare other cationic forms by adding the carbonates (A.R.) and filtering off the unreacted carbonates. Ca-, Sr- and Ba-SSA stock solutions were analysed by complexometric titration. All solutions were kept in the cold. $(NH_4)_2S_2O_8$ was purified by two recrystallizations from water. Water was distilled twice. All other reagents were AnalaR grade.

The flask used for polymerization was equipped with glass stirrer, reflux condenser, thermometer, a helium sparging tube and a glass tubing nipple. The glass tubing nipple was closed with a rubber serum cap through which samples could be removed or initiator added with a hypodermic needle. A thermostatted water bath was used to control polymerization temperature. An aqueous solution of monomer was placed in the flask and purged with helium to remove dissolved $O_2$. Polymerization was started by adding $(NH_4)_2S_2O_8$ solution with a hypodermic syringe. Samples were withdrawn periodically by means of a hypodermic syringe and unsaturation determined by the polarographic method described previously [17].

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Polarographic measurements were made on a polarograph LP-60 (Czechoslovakia) at 25° with a dropping Hg cathode and the saturated calomel electrode. The capillary constants were: $m = 1.77$ mg/sec, $t = 4$ sec in water solution at $h = 75$ cm and $E = 0$. Before obtaining the polarograms, the solutions were deoxygenated (15 min) in a current of electrolytic $H_2$.

The viscosity measurements were made with an Ubbelohde capillary viscometer. Kinetic energy corrections were not significant ($<1\%$).

The polymerizations of Ca-, Sr- and Ba-SSA were carried out in water and water-salt solution at 70° in a He atmosphere in the presence of ammonium persulphate. It should be noted that the decomposition rate constant for persulphate is independent of ionic strength in acid solution [18]. In all cases polymerization was homogeneous; the spontaneous process was not observed. Kinetic data were obtained by a polarographic method, based on analysis of salts of SSA after their conversion into pseudonitrosite [17]. It has been shown that the components of the reaction mixture do not influence the analysis of monomers. Under experimental condition the pseudonitrosite of monomers gave excellent current-voltage curves (Fig. 1). Statistical analysis of the results showed that the error did not exceed 1.5% [19].

## RESULTS AND DISCUSSION

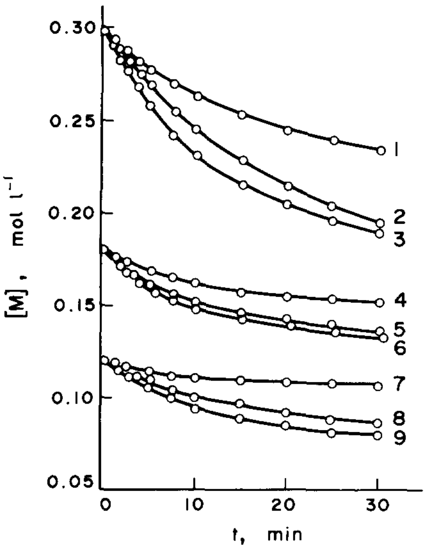

Fig. 2. Kinetic curves for the polymerization of Ca–SSA (1, 4, 7), Sr–SSA (2, 5, 8) and Ba–SSA (3, 6, 9) in water at 70°. $[M]_0$, mol/l = 0.3(1–3); 0.18(4–6); 0.12(7–9). $[I]_0 = 1.4 \times 10^{-3}$ mol/l.

Figure 2 shows the consumption of monomer, the data being obtained by the polarographic method. To define the kinetic orders with respect to monomer ($\alpha$) and initiator ($\beta$), the equation for the overall reaction rate was analysed

$$-\mathrm{d}[M]/\mathrm{d}t = \frac{k_p}{k_t^{1/2}}(2fk_d)^{1/2}[M]^{\alpha}[I]^{\beta},$$

where $[M]$ and $[I]$ are concentrations of monomer and initiator respectively; $k_p$, $k_t$, $k_d$—are rate constants of propagation, termination and decomposition of initiator respectively; $f$ is efficiency of initiation. On the base of the data of Fig. 2, the initial rates of polymerization ($V_0$) were deduced; bilogarithmic dependences of these rates on the concentrations of monomer (Fig. 3) and initiator were made. Figure 3 shows that a plot of lg $V_0$ vs lg $[M]$ is fairly linear over the range of concentrations examined. It indicates that the kinetic order with respect to monomer is only slightly sensitive to the characteristics of the polymerization [5] as the investigated range concentration of monomers is narrow. Fot all salts of SSA the rate of polymerization was proportional to (initiator concentration)$^{1/2}$ indicating that the chains were mutually terminated. Some parameters of the polymerization are presented in Table 1. The data show that $V_0$, the viscosity-average molecular weight ($\overline{M}_v$) and the kinetic order with respect to monomer increase in the series Ca-SSA < Sr-SSA < Ba-SSA. To explain the experimental data, the value of $k_p/k_t^{1/2}$ was obtained on the basis of the dependence $1/\overline{P} = \delta(V_0/[M]^2)$, where $\overline{P}$ is the number average degree of polymerization. The experimental plot of $1/\overline{P}$ vs $V_0/[M]^2$ is fairly linear and extrapolated to zero for different monomers (Fig. 4). It indicates that

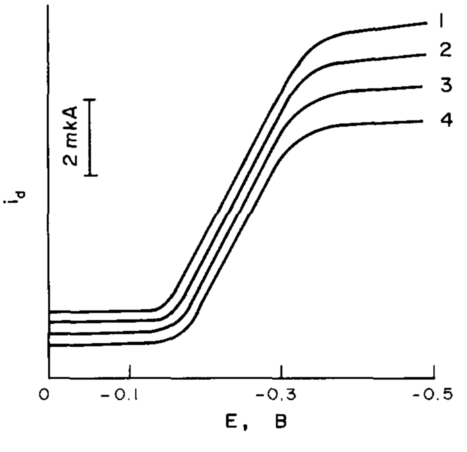

Fig. 1. Current–voltage curves of pseudonitrosite of Sr–SSA in the presence of an acetate buffer solution obtained during polymerization. $t$, min = 0(1), 10(2), 25(3), 60(4); $[M]_0 = 0.3$ mol/l; $[I]_0 = 1.4 \times 10^{-3}$ mol/l, 70°.

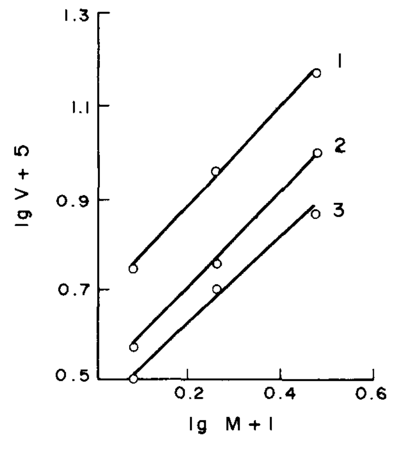

Fig. 3. Dependence of initial rate of polymerization of Ca–SSA (1), Sr–SSA (2), and Ba–SSA (3) in water at 70° on monomer concentration. $[I]_0 = 1.4 \times 10^{-3}$ mol/l.

Table 1. Polymerization parameters of Ca-, Sr- and Ba-salts of SSA in water and water-salt mixtures ($[I] = 1.4 \times 10^{-3}$ mol/l, 70°)

| Monomer | $[M]_0$, (mol/l) | Salt additions, (mol/l) | $V_0 \times 10^4$, (mol/l·sec) | The order with respect to monomer | $k_p/k_t^{1/2}$, (l/mol·sec)$^{1/2}$ | $\bar{M}_v \times 10^{-4}$ |
|---|---|---|---|---|---|---|
| | 0.12 | — | 0.22 | | | 2.72 |
| | 0.18 | — | 0.48 | 0.96 | 0.43 | 2.80 |
| | 0.30 | — | 0.75 | | | 5.20 |
| Ca-SSA | 0.30 | [NaCl] = 1.0 | 2.20 | — | — | — |
| | 0.30 | $[CaCl_2] = 0.5$ | 2.16 | | — | |
| | 0.12 | — | 0.37 | | | 7.90 |
| | 0.18 | — | 0.70 | 1.02 | 0.87 | 9.67 |
| | 0.30 | — | 1.00 | | | 19.40 |
| Sr-SSA | 0.30 | [NaCl] = 1.0 | 2.10 | — | — | — |
| | 0.30 | $[CaCl_2] = 0.5$ | 2.13 | — | — | — |
| | 0.12 | — | 0.54 | | | 11.30 |
| | 0.18 | — | 0.91 | 1.06 | 1.18 | 15.23 |
| | 0.30 | — | 1.38 | | | 29.10 |
| Ba-SSA | 0.30 | [NaCl] = 1.0 | 2.16 | — | | — |
| | 0.30 | $[BaCl_2] = 0.5$ | 2.13 | — | — | — |

there is no transfer to monomer. We did not examine the possibility of transfer to polymer; however, the molecular weight distribution for sodium polystyrenesulphonate (according to the kinetic data of polymer decomposition in water solutions in the presence of $K_2S_2O_8$) differs from the distribution of Flory. On this basis, some possibility of transfer to polymer for the radical polymerizations of Ca-, Sr- and Ba-SSA can be admitted. The values of $k_p/k_t^{1/2}$ are presented in Table 1. Table 1 shows that increase of $V_0$ in the order of increasing cation radius was caused by increasing $k_p/k_t^{1/2}$. The observed changes of $k_p/k_t^{1/2}$ may be connected with the change of the nature of the cation. The influence of the nature of the cation on the polymerization of ionogenic monomers may be explained in terms of ionic equilibria. The following scheme represents the existence of different ionic forms for ionogenic monomer and macroradical with ionogenic groups of acidic character

$$\underset{\mathrm{I}}{AX} \rightleftarrows \underset{\mathrm{II}}{A^-X^+} \rightleftarrows \underset{\mathrm{III}}{A^-\|X^+} \rightleftarrows \underset{\mathrm{IV}}{A^- + X^+} \qquad (1)$$

where $A^-$ is monomer or polymer anion; $X^+$ is cation; **I**, **II**, **III**, **IV** are the non-ionized form of monomer, the contact ion-pair, the solvent-separated ion-pair and free ions respectively. Due to possibility of co-existence of different forms **I–IV** [shown in scheme (1)], the mechanism of radical polymerization of ionogenic monomers is more complicated than that for classical systems. The simplified scheme of elementary reactions for the radical polymerization of ionogenic monomer is represented below:

$$I \xrightarrow{k_d} 2\dot{R}$$

$$\dot{R} + A_b \xrightarrow{k_i^{(b)}} R\dot{A}_b$$

$$\sim\dot{A}_q + A_b \xrightarrow{k_p^{(q),(b)}} \sim A_q\dot{A}_b \qquad (2)$$

$$\sim\dot{A}_q + \dot{A}_b\sim - \left[\begin{array}{l} \xrightarrow{k_{t,1}^{(q),(b)}} \sim A_qA_b\sim \\ \\ \xrightarrow{k_{t,2}^{(q),(b)}} \sim A_q(+H) + \sim A_b(-H) \end{array}\right.$$

$$\sim\dot{A}_q + R'Y \xrightarrow{k_{tr}^{(q)}} \sim A_qY + \dot{R}'$$

where $A_b$ and $A_q$ are different ionic forms of monomer and macroradical respectively ($b$ = **I, II, III, IV** and $q$ = **I, II, III, IV**). According to the difference of reactivity of forms **I–IV** for monomer and macroradical with the usual factors determining the reactivity of ionogenic monomers in polymerization, there is a considerable influence due to intramolecular and intermolecular electrostatic interactions in the system and the conformation of growing macroradicals. The existence of the different values $k_i^{(q)}$, $k_p^{(q),(b)}$, $k_{t,1}^{(q),(b)}$, $k_{t,2}^{(q),(b)}$ and $k_{tr}^{(q)}$ in scheme (2) is the reason for "peculiar" character of the polymerization of ionogenic monomers and it leads to change of kinetic parameters of the polymerization [5, 22].

Besides solvating and dissociating possibility of the medium, pH, ionic strength, nature of ions $A^-$ and temperature, the nature of cation $X^+$ may influence equilibrium (1) so changing the proportions of the various ion forms in the system. This influences the reactivity of the ionogenic monomer in the polymerization. The peculiarities of polymerization and copolymerization of ionogenic monomers [5, 22, 23] are shown not only when all four forms (**I–IV**) of ionic equilibria (1) exist; only two forms (e.g. **III** and **IV**) with different reactivities are enough. It is necessary to note that the authors did not try to establish the peculiarities of polymerization; the influence of the nature of cation on the overall rate of the process was mainly taken into account. It is known [3] that the extent of ion binding to polystyrenesulphonates increases with increasing cation radius. The viscosity data (Fig. 5) indirectly confirm this point. Figure 5 (curves 1, 2) shows that $\eta_{sp}/c$ decreases in the order Ca-PSSA > Sr-PSSA > Ba-PSSA (for fixed concentration of polymers). This effect was caused by decrease of the effective size of the macromolecules, as $(\eta_{sp}/c) \sim (R^2)^{1/2}$ [24], with increase of binding of cations to macroions in order of increasing cation radius $Ca^{2+} < Sr^{2+} < Ba^{2+}$. The increase of cation radius must lead to decrease of electrostatic repulsion between monomers and growing macroradicals. The factors mentioned above must increase $k_p$ and $k_t$. The increase of $k_p/k_t^{1/2}$ in the order $Ca^{2+} < Sr^{2+} < Ba^{2+}$

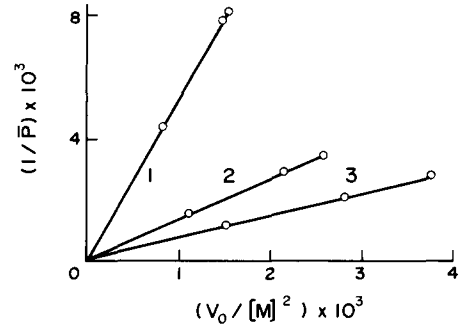

Fig. 4. Dependence of $1/\bar{P}$ on $V_0/[M]^2$ for the polymerization of Ca–SSA (1), Sr–SSA (2) and Ba–SSA (3) in water at 70°. $[I]_0 = 1.4 \times 10^{-3}$ mol/l.

was mainly caused by increase of $k_p$, as confirmed by increase of $\bar{M}_v$ (Table 1).

Table 1 shows that, with increasing monomer concentration and with addition of salts (KCl, $CaCl_2$, $SrCl_2$ and $BaCl_2$), $V_0$ increases for Ca-SSA, Sr-SSA and Ba-SSA. It is the result of increase of effective ionic strength of the solution ($\mu$). It is explained by the relationship of $\mu$ with the rate constant for a reaction between two ions in solution according to the Debye–Hückel theory of dilute electrolyte solutions

$$\log k = \log k_0 + z_A z_B \mu^{1/2} + (b_A + b_B - b_{AB\neq})\mu, \quad (3)$$

where $k_0 = k$ at $\mu \to 0$; $z_A$, $z_B$ are the charges of $A$ and $B$ ions; $b_A$, $b_B$ and $b_{AB\neq}$ are constants of $A$ and $B$ ions respectively and active complex $AB$. If the charges of $A$ and $B$ ions are of the same sign, then with increasing $\mu$ the value of $k$ increases. The increase of $\mu$ leads to decrease of electrostatic interactions between monomers and growing macroradicals. The factors mentioned above must mainly increase $k_p$ and this effect leads to increase of $V_0$.

Figure 6 shows that the influence of cation radius on the relative rates of polymerization of Ca-, Sr- and Ba-SSA is more significant for smaller values of $\mu$ (curve 1), but the increase of $\mu$ with increasing concentration of monomers leads to decrease of the effect of cation radius on $V_0$ (curves 1–3). For large values of $\mu$ (due to addition of neutral salts), $V_0$ does not depend on cation radius (Table 1). This is the result of decrease of electrostatic interactions in the polymerization system and stabilization of the reactivity of ionogenic monomer. For large values of $\mu$, stabilization of sizes of macromolecules [the viscosity data indirectly confirm this result (Fig. 5 curve 3)] due to levelling of suitability of monomer units to growing macroradicals also should lead to equality of the values of $V_0$ for Ca-, Sr- and Ba-SSA.

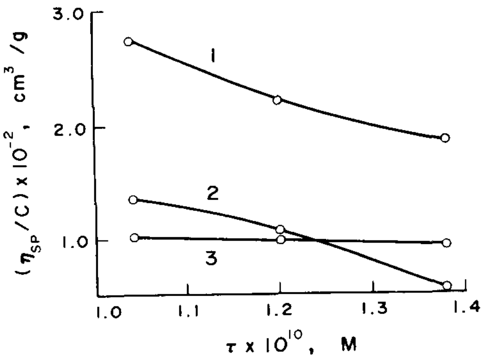

Fig. 5. Dependence of $\eta_{sp}/C$ on cation radius (r) for Ca-, Sr- and Ba-salts of PSSA with $\bar{P} = 5400$ (1, 3) and 720 (2). 1, 2—in water; 3—in 0.5 mol/l KCl; $C \times 10^2$, g/cm³ = 0.025 (1, 3) and 0.1 (2).

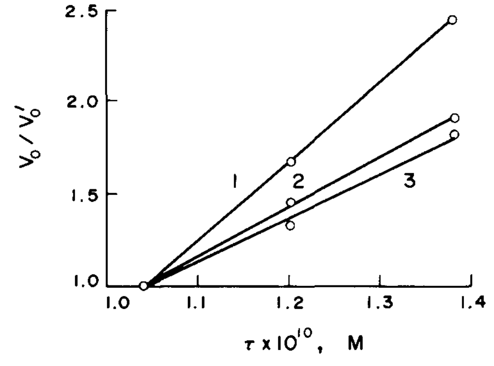

Fig. 6. Dependence of relative rate of polymerization of Ca-, Sr- and Ba-salts of SSA on cation radius. $[M]_0$, mol/l = 0.12(1); 0.18(2); 0.3(3). $[I]_0 = 1.4 \times 10^{-3}$ mol/l, 70°. $V'_0 \times 10^4$ (for Ca-SSA) = 0.22(1); 0.48(2); 0.75(3) mol/l·sec.

Similar increase of $V_0$ with increasing cation radius for small $\mu$ has been observed for the polymerization of styrenesulphonates with monovalent counterions. Under identical conditions and for fixed concentration of monomers, $V_0$ (for K-SSA) > $V_0$ (for Na-SSA) [5]; the result can be explained by more significant binding of $K^+$ ions to macroions as compared with that of $Na^+$ ions [3]. This confirms the common character of the influence of cation radius on the reactivity of styrenesulphonates with monovalent and divalent counterions in radical polymerization in aqueous solutions for small values of $\mu$.

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