Some Properties of Aqueous Solutions of Poly[(maleic acid)-alt-(p-sulfostyrene, styrene)]

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SYNOPSIS

By sulfonation of poly[(maleic anhydride)-alt-styrene] in mild conditions (SO₃/triethyl-phosphate, 298 K) a series of poly[(maleic acid)-alt-(p-sulfostyrene, styrene)] have been prepared having the same average chain length but various content of p-sulfostyrene units (from 18 to 83 mol %). A behavior of diluted aqueous solutions of two polyelectrolyte series (polyacids and Na-salts) has been compared, using viscosimetric, conductometric, and potentiometric measurements, and taking into consideration the degree of sulfonation and the kind of counterions (H^+, Na^+). Although the values of intrinsic viscosities [η] and equivalent conductivities λ of two copolymer series belong to two different ranges, in polyacid series they increase with increasing the degree of sulfonation, while in Na-salt series they decrease. According to the potentiometric titration and reduced viscosity data, the intensity of conformational chain transitions of sulfonated polycids also decreases with increasing the degree of sulfonation. The noticed effects are related to structural characteristics of functional copolymers, gradual increase of a charge density along the chains, lower mobility of the Na-salts, and to a diminished hydrophobicity of styrene units due to sulfonation. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Homopolymers and copolymers of maleic acid and their modified products are used as auxiliary agents[1] (scale inhibitors, dispersing agents, emulsifiers, coatings, adhesives, sizing agents, etc.). In hydrolyzed form they are polyelectrolytes[2], and their solution properties are governed mainly by electrostatic interactions between the "fixed" charges of polyions and "mobile" charges of counterions. Structural characteristic of maleic acid polymers[2] (such as two carboxylic groups bonded on two neighboring carbon atoms of the backbone, possibilities of ditactic configurations, influence of the character of alternative units, etc.), enables a variation of charge density along the chain, strong nearest-neighbor interactions, formation of hydrogen bonds, hydrophobic effect of alternative units, etc..

As all these effects influence the conformation of polyions and the balance of hydrophobic–hydrophilic interactions within the chains, they, in fact, influence the behavior and properties of polymer solutions.

The investigation of mentioned phenomena in aqueous solutions of homopolymer and alternating copolymers of maleic acid has been the subject of many papers and still remains a topic of considerable interest. Alternating copolymer of maleic acid and styrene is a real example of such behavior. Since the preliminary report by Ferry et al.,[3] more extensive work has been done, for example, by Kuppers,[4] Bojko et al.,[5,6] Strauss et al.,[7,8] Sugai et al.,[9–11] and Yamashita.[12] According to their results, the alternated MA/St copolymer always exhibits a two-step dissociation and anomalies in the range of dissociation of primary carboxyl group, both in potentiometric titration curve and in viscosities. Such behaviors are referred to the conformational chain transition from a compact globule to an extended coil and ascribed to the change in balance between

the hydrophylic (MA) and hydrophobic (St) interactions within a copolymer chain.

Although sulfonated MA/St copolymers are used as auxiliary agents,[13-16] there is no data in the literature about their solution properties. The purpose of this paper is to compare some solution properties for a series of partially sulfonated alternating MA/St copolymers having the same average chain length but different content of p-sulfostyrene units.

EXPERIMENTAL

Preparation of Copolymer

Poly[(maleic anhydride)-alt-styrene],MAn/St, was prepared by the heterogeneous free radical copolymerization from an equimolar mixture of monomers in toluene. Details about syntheses and modification of copolymer (polyacids, Na-salts), as well as their characteristics, are described elsewhere.[17,18] The intrinsic viscosities of MAn/St and MA/St determined in (DMF+0.05 mol/dm^3 LiBr) at 298 K are 0.626 and 0.608 dL/g, respectively.[19]

Sulfonation of poly[(maleic anhydride)-alt-styrene]

A range of poly[(maleic acid)-alt-(p-sulfostyrene, styrene)] was prepared using the modified R. C. Turner's procedure[20] and various ratios of MAn/St : SO$_3$ (Table I).

To a homogeneous suspension of MAn/St (30.3 g, 0.15 mol) and triethylphosphate (TEP, 2.73 g, 0.015 mol) in 1,2-dichlorethane (DCE, 300 g), stirred in a slow steam of dry nitrogen, a solution of freshly distilled sulfur trioxide (SO$_3$, 12 g, 0.015 mol) was slowly added for about 15 min. The mixture was stirred at room temperature for the additional 3 h, after which a solid was collected by filtration. The sulfonated copolymer was washed with fresh DCE, then with several portions of diethyl ether, and dried under vacuum at 313 K. The yield of sulfonated polyacid (H-44) was 41.7 g, sulfur content (ASTM 1551) 5.6 mass %, corresponding to 52.4 mass % or 44.8 mol % degree of sulfonation, intrinsic viscosity in (DMF+0.05 mol/dm^3 LiBr) at 298 K 0.640 dL/g.[19] The equivalent weight of polyacid was calculated from the sulfur content, assuming the alternating structure of copolymer precursor. The corresponding full sodium salt (Na-44) was prepared by neutralization of polyacid with diluted aqueous solution of sodium hydroxide.[18]

Measurements

Viscosity measurements were made at 298 K using a Cannon-Ubbelohde dilution-type viscometer, having the flow time of 300.5 s for water at 298 K.

Potentiometric titrations were performed at 298 K, under dry nitrogen flow, using Radiometer pHM 64 pH meter, equipped with a combined electrode. Dilute aqueous solution of polyacid 50 mL, c_p = 3.18

Table I Data for Sulfonation of Poly[maleic anhydride)-alt-styrene] in 1,2-Dichloroethane at 298 K to Poly[(maleic acid)-alt-(p-sulfostyrene,styrene)]

| Sulfonated Polyacid | Feed Ratio, mol | | | Sulfur Content, Mass % | Degree of Sulfonation, x, | | M^a of CRU |
	MAn/St	SO$_3$	TEP		Mass %	mol %	
H-0	—	—	—	—	—	—	220
H-18	1	0.50	0.10	2.5	23.4	18.3	238
H-30	1	0.75	0.10	4.0	37.5	30.8	250
H-44	1	1.00	0.10	5.6	52.4	44.8	262
H-68	1	1.50	0.15	8.0	75.0	68.7	280
H-83	1	2.00	0.20	9.3	87.0	83.1	289

^{a} Average molecular mass of constitutional repeating unit.
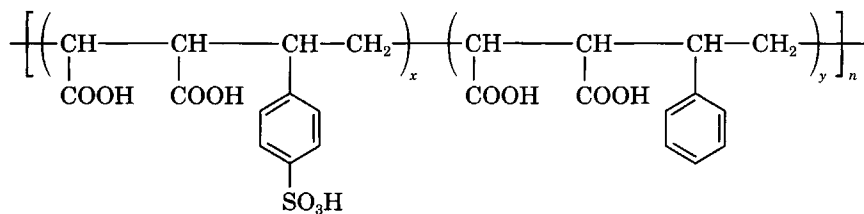
10^{-3} mol/dm^3 was titrated with 0.1 mol/dm^3 aqueous solution of NaOH. Degree of neutralization of copolymer α was calculated as $\alpha = [\text{NaOH}]/[c_p]$ for each addition of titrant. Electrical conductivity of diluted aqueous solutions of polyacids and Na-salts (in concentrations c_p from 3×10^{-4} to 90×10^{-4} mol/dm^3) was determined at 298 K with WTW Digitalmeter Digi 610. All solutions were prepared with water having 1.80 μS conductance. The equivalent conductivity λ was calculated using relation $\lambda = 1000 \, \kappa/c_p$, where κ is specific conductivity and c_p is concentration of copolymer in equiv/dm^3.

RESULTS AND DISSCUSION

According to previous works,[21-24] sulfonation of polymers in mild conditions (SO$_3$/TEP, 298 K) should produce neither degradation nor crosslinking of polymer. Using such conditions for sulfonation of alternating MAn/St, a range of sufonated MA/St has been prepared assuming approximately the same average chain length, but different content of sulfonated styrene units (Table I).

Sulfonated MA/St copolymers contain two chemically different functional groups: —COOH and —SO$_3$H. Carboxyl groups (two per each constitutional repeating unit) are bonded on two neighboring carbon atoms of the copolymer backbone, weakly dissociated in aqueous solution, unequal in strength but characterized by strong interactions. Sulfo groups (the content varies from 0.18 to 0.83 mol fraction per constitutional repeating unit) are located several bonds away from the copolymer backbone, and they are competely dissociated in aqueous solution. As both groups differ in hydration, they are surrounded by a different structure of water molecules. Using viscosity and conductivity measurements as well as potentiometric titrations of diluted aqueous solutions of individual copolymers (concentration c_p less than 1 g/dm^3) their behavior has been compared with regard to the degree of sulfonation and the kind of counterion (H$^+$, Na$^+$).

Viscosity Measurements

In the polyacid series, the intrinsic viscosity increases with the increase of the content of p-sulfostyrene units in copolymer (from 1.1 to 33.3 dL/g). Similar behavior of polyacid series has been noticed in N,N-dimethyl-formamide (DMF) solutions.[19] The lowest [η] values (for H-0 and H-18, determined by extrapolation of η_i/c_p to infinite dilution, Fig. 1), are a consequence of undissociated carboxyl groups,

compact conformation of macromolecules, and a still low concentration of sulfo groups (H-18).

By increasing the content of easily dissociated sulfo groups along the chain, the intramolecular repulsion forces expand polyanion so that [η] values increase ([Fig. 1(a), (b), Table II], [η] determined using the Fuoss equation,[25] $c_p/\eta i = 1/[\eta] + B/[\eta] \, c_p^{1/2}$). Highly sulfonated copolymers show better solubility, and their solutions are more stable in the presence of low molecular salts (NaCl). For in-
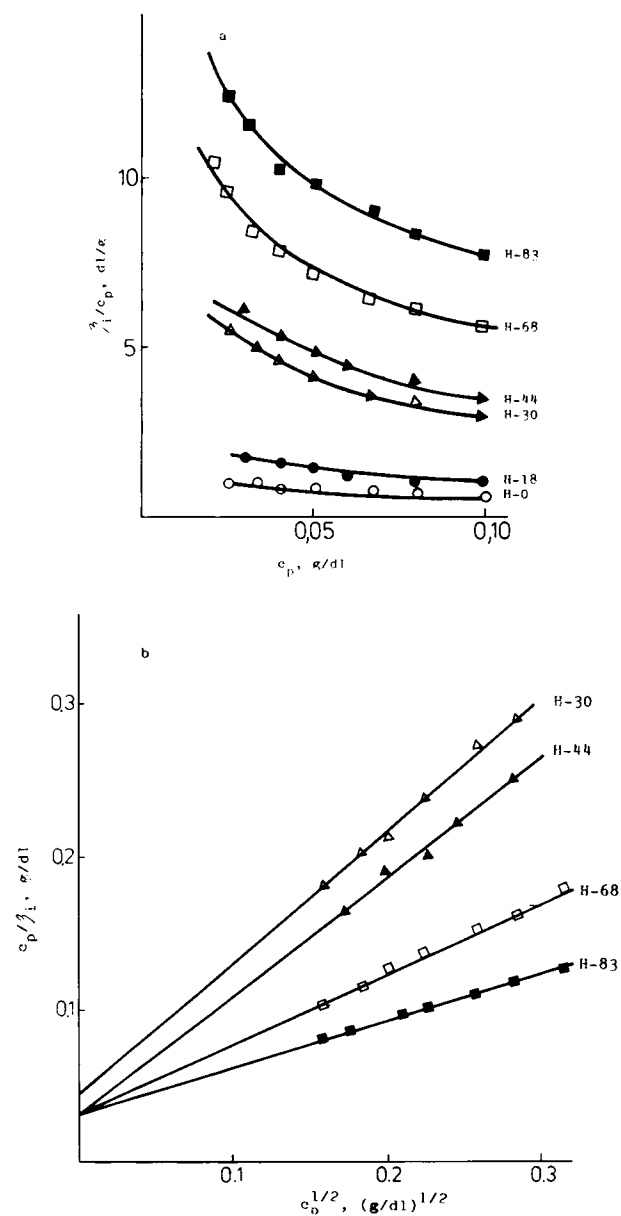

Figure 1 (a) Reduced viscosity η_i/c_p vs. concentration c_p; (b) Fuoss plots for aqueous solutions of partially sulfonated MA/St polyacids. Degrees of sulfonation are marked on curves.

Table II Intrinsic Viscosities [η] and Fuoss Empirical Constants B for Poly[(maleic acid)-alt-(p-sulfostyrene, styrene)] in Polyacid and Na-Salt Forms, H₂O, 289 K

Copolymer Polyacid	[η], dL/g	B	Copolymer Na-Salt	[η], dL/g	B
H-0	1.1[a]	—	Na-0	71.4	17.1
H-18	2.2[a]	—	Na-18	58.8	23.7
H-30	21.7	18.6	Na-30	45.5	31.1
H-44	31.3	24.4	Na-44	37.0	11.5
H-68	33.3	14.0	Na-68	31.3	10.2
H-83	33.3	10.3	Na-83	31.3	6.1

[a] Determined by extrapolation of η_i/c_p to c_p = 0. All others from Fuoss equation $c_p/\eta_i = 1/[\eta] + B/[\eta] \, c_p^{1/2}$.

stance, polyacids H-0, H-18, and H-30 are not soluble in 0.02 mol/dm³ NaCl, while polyacid H-68 is soluble in 0.5 mol/dm³ NaCl, having the intrinsic viscosity 0.435 dL/g. It is interesting that the solubility of polyacids in DMF decreases with the increase of sulfonation degree.[19] All copolymers in form of Na-salts show a typical polyelectrolytic behavior, e.g., the increase of reduced viscosity, η_i/c with dilution, the decrease of [η] with increasing the ionic strength c_s of solutions and showing the linear relationship between [η] and $c_s^{-1/2}$ (Fig. 2).

Intrinsic viscosities for Na-salts have been determined using the Fuoss equation[25] (Table II). Contrary to the behavior of polyacids, [η] of Na-salts decreases with increasing the degree of sulfonation (from 71.4 to 31.3 dL/g). The nonsulfonated copolymer, Na-0, has the highest [η], while Na-68 and Na-83 copolymers have the lowest [η] values,

which are very close to those of the corresponding polyacids H-68 and H-83 (Table II). It might be that in both copolymer forms the increased local concentration of conterions[26,27] blocks the carboxylate anions, so that only dissociated sulfo groups contribute to repulsions. The lower contribution in case of Na-salt ([η] is 31.3 dL/g) compared to that of polyacid ([η] is 33.3 dL/g) is possibly due to the stronger bonding of Na⁺ than H⁺.

The Fuoss plot intercepts and slopes [Fig. 1(b)], as well as the values of the Fuoss empirical constant B (Table II), suggest a kind of interaction (solute-solvent) that depends on the ratio of —SO₃H/—COOH groups in a single copolymer. It seems as though the influence of sulfo group dominates in copolymers with the degree of sulfonation above 50 mass %.

Figure 3 shows the change of reduced viscosity η_i/c_p of polyacids (H-0, H-44, and H-83) with increasing the degree of neutralization α and with increasing the ionic strength c_s of their aqueous solutions (c_s is 0, 0.02 mol/dm³ NaCl and 0.2 mol/dm³ NaCl). For each copolymer, reduced viscosity η_i/c_p increases with α, attains the maximum ($\eta_i/c_p)_{max}$ and, in turn, it decreases, possibly because a higher amount of counterions (attracted by a strong electrostatic potential in copolymer domain) reduces electrostatic repulsions. Such dependence is com-
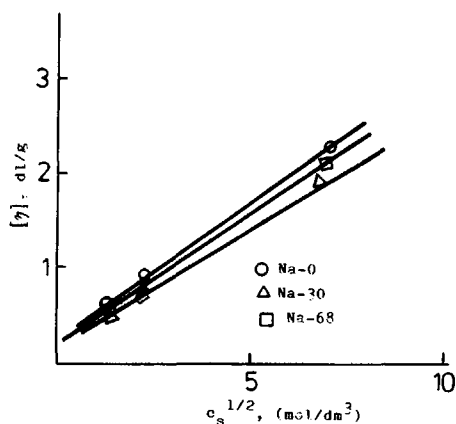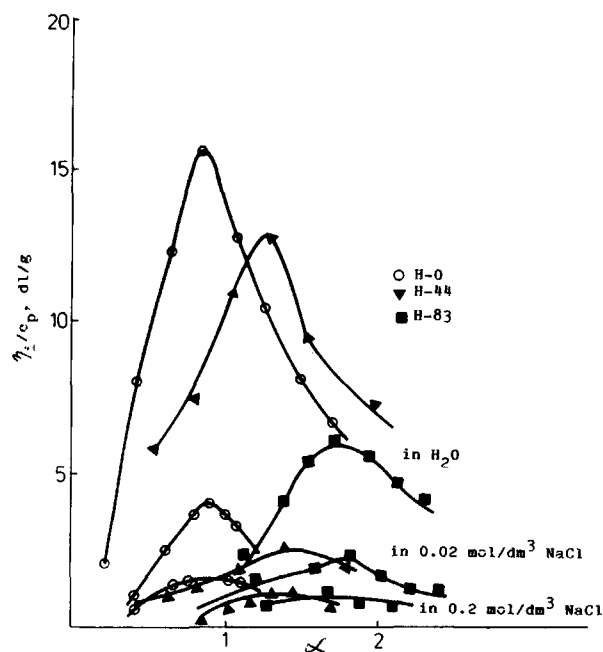

Figure 2 Intrinsic viscosity [η] vs. concentration of NaCl c_s for aqueous solutions of Na-salts of partially sulfonated MA/St copolymers, at 298 K. Degrees of sulfonation are marked on curves.

Figure 3 Reduced viscosity η_i/c_p vs. degree of neutralization α for aqueous solutions of partially sulfonated MA/St polyacids (degrees of sulfonation are marked on curves) containing 0, 0.02, and 0.20 mol/dm³ NaCl.

mon to maleic acid homopolymer[28] and some alternated copolymers (styrene, ethyl vinyl ether, isobutylene).[7,10,29] The $(\eta_i/c_p)_{max}$ values decrease with the increase of sulfonation degree (in salt-free solutions) and also with the increase of ionic strength of solutions (in 0.02 mol/dm^3 NaCl and 0.2 mol/dm^3 NaCl solutions).

Potentiometric Titrations

Potentiometric titration of polyelectrolyte solution is closely related to the electrostatic interaction between a dissociating proton and an ionized group on the polymer chain. Figure 4 presents potentiometric titration curves of three polyacids, having different degrees of sulfonation (H-0, H-44, and H-83) in salt-free aqueous solutions ($c_p = 3.13 \times 10^{-3}$ mol/dm^3) as the plot of pH vs. degree of neutrlization of copolymer α. The starting part of curves for polyacids with a higher content of p-sulfostyrene units (H-44 and H-83) begins at lower pH values belonging to the dissociation of sulfo group, continuing with a two-step dissociating part of carboxylic groups of
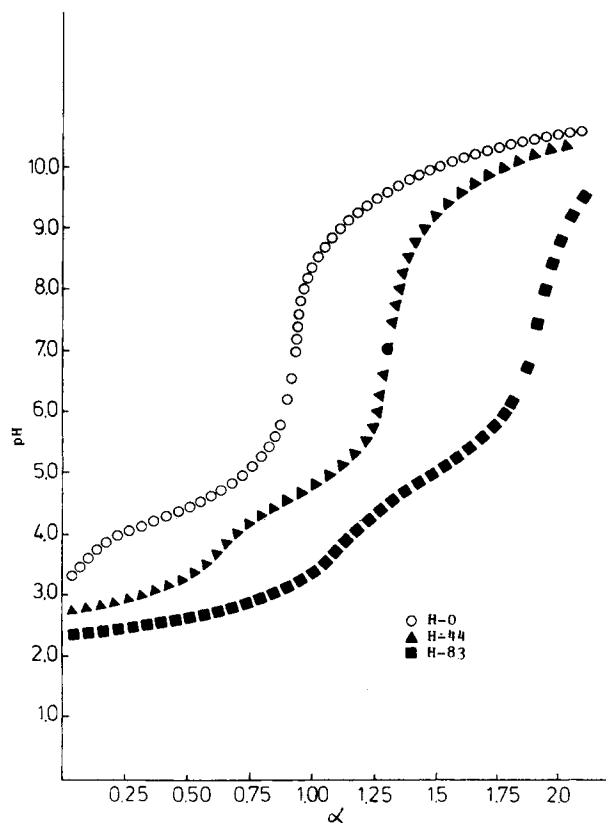
Figure 5   Equivalent conductivity λ vs. concentration $c_p^{1/2}$ for aqueous solutions of partially sulfonated MA/St copolymers in polyacid (H-) and sodium salt (Na-) forms. Degrees of sulfonation are marked on curves.

maleic acid units. The curves show anomalous shapes in the pH range of dissociation of primary carboxyl groups, which become less evident and shifted to higher α values as the degree of sulfonation increases (also with the increase of ionic strength of solutions). Such behavior is probably connected with a higher concentration of counterions and with a reduced hydrophobicity of sulfonated styrene units. For better understanding of the mentioned behaviors, a more detail analysis of potentiometric curves of partially sulfonated MA/St copolymers is required.

Conductivity Measurements

Electrical conductivity of aqueous solutions of polyelectrolytes is a measure of ionization. The number of ions contributes to the conductivity, depending on dimensions and charge densities of polyions. Figure 5 shows the dependence of an equivalent conductivity λ on the copolymer concentration c_p for diluted aqueous solutions of partially sulfonated copolymers in polyacid and Na-salt forms. For both copolymer series λ decreases with increasing c_p. The

Figure 4   Potentiometric titrations (pH vs. degree of neutralization α), of aqueous solutions of MA/St polyacids (degrees of sulfonation marked on curve) $c_p = 3.2 \times 10^{-3}$ mol/dm^3, titrant 0.10 mol/dm^3 NaOH.
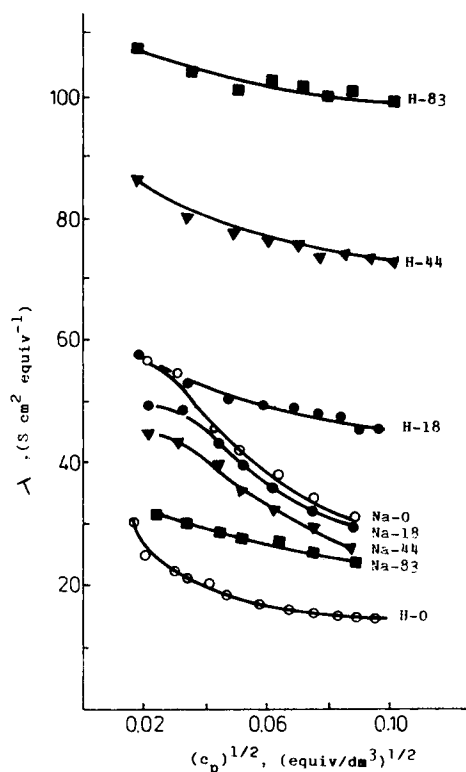
influence of c_p is lower in copolymers with the highest degree of sulfonation (H-83, Na-83).

Completely dissociated sulfo groups in polyacid series mainly contribute to the significant increase of λ (from 18 to 108 S cm^2 equiv^{-1}) with increasing the copolymer degree of sulfonation. The range of λ values for Na-salt series is lower (Fig. 5, from 23 to 58 S cm^2 equiv^{-1}) and decreases with the increase sulfonation degree. First, it is a concequence of larger dimensions of Na-salt macromolecules (Na-0, Na-18, Na-30, Na-44). Second, according to the counterion condensation theory,[26,27] full sodium salt copolymers with larger charge densities induce the increased counterion binding, resulting in a drop of the charge carrier number and, thus, contribute to a gradual diminishing of conductivity.

CONCLUSIONS

A substitution of sulfo group in the p-phenyl position of alternating MA/St copolymer does not change the structure and average chain length of the main chain, but the type and character of functionality producing a marked modification in physical properties. Diluted aqueous solutions of both series of copolymers (polyacids, Na-salts) show typical polyelectrolyte characteristics with some peculiar effects connected with structural characteristics of alternating MA/ST copolymer and the presence of easily dissociated sulfo groups. While the increase of sulfonation degree in polyacid series causes the increase of intrinsic viscosity, $[\eta]$, and equivalent conductivity, λ, in a series of Na-salts, these values (although different) decrease, due to a higher local condensation of counterion (Na$^+$) and larger dimensions of macromolecules. A gradual increase of the content of p-sulfostyrene units changes the hydrophobic- hydrophylic balance within chains and reduces the intensity of pH induced conformational chain transitions. Sulfonated copolymers show better solubility and stability of aqueous solutions in the presence of low molecular weight salts.

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