

Narrow Molecular Weight Distribution Poly(styrenesulfonic Acid). Part I. Preparation, Solution Properties, and Phase Separation

WILLIAM R. CARROLL* and HENRYK EISENBERG, *Polymer
Department, The Weizmann Institute of Science, Rehovoth, Israel*

Synopsis

A method is described for the conversion of polystyrene to poly(styrenesulfonic acid) without change in the molecular weight distribution; the reaction is performed at room temperature in 100% H₂SO₄ and uses Ag⁺ catalyst. The resulting polyelectrolyte has solubility and other characteristics significantly different from those of previously investigated poly(vinylsulfonic acid). This permits a study of the influence of the aromatic group on the local and long range interactions in solution. The barium salt of poly(styrenesulfonic acid) is unusual in showing both upper and lower consolute temperatures in solution.

INTRODUCTION

Recent studies¹ on solution properties of salts (X-PVS) of poly(vinylsulfonic acid) (PVSA) have disclosed interesting phenomena in relation to phase separation behavior in the presence of simple added salts (XY). The phase separation phenomena are highly specific with respect to both the monovalent counterions and coions studied, and it was possible to show that excluded volume theory, applicable to nonionic, two-component polymer solutions, may be extended to multicomponent polyelectrolyte solutions as well. The possibility of varying both the type of simple salts, XY, as well as their concentration, permits the study of such systems at and around the Flory² Θ temperature under a wide variety of conditions.

We are now extending these studies to salts (X-PSS) of poly(styrenesulfonic acid) (PSSA) with monovalent counterions, as well as with some divalent counterions. This extension is undertaken for a number of reasons. The basic difference between PVSA and PSSA is the presence of the aromatic phenyl ring in the repeating unit of the latter compound. The sulfonic acid group is thus situated in a different medium and it is of interest to investigate to what extent the aromatic group affects solubility properties, configurational parameters, and molecular interactions. Furthermore, the ultraviolet absorption characteristics provide a means for

* Visiting Scientist, 1962-63; permanent address: National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, U. S. Public Health Service, Department of Health, Education, and Welfare, Bethesda, Maryland.

convenient concentration determination in general and also for special applications, as in ultracentrifugation, where the behavior in very low concentration ranges is important; also, perturbations in the optical properties give a means of detecting local interactions as a function of solvent composition and temperature. The latter can be studied in both atactic and stereoregular samples. Finally, since polystyrene (PS) is now available over a wide range of molecular weights in very narrow molecular weight distributions,³ it becomes attractive to try to prepare the corresponding PSSA and to study the detailed variations in many properties as a function of well-defined chain length.

The problem of preparing the completely sulfonated derivative without altering the molecular weight distribution of the parent polystyrene is a difficult one. It is of obvious importance that the sulfonation reaction should produce neither chain degradation nor crosslinking, and yet should give practically complete *para* substitution. Whereas in ordinary chemical reactions partial yields are acceptable, since the main product may be separated from undesirable secondary products by standard procedures, in the present instance, side reactions amounting to no more than 0.1%, or even less, of the main reaction may completely vitiate the final result. It is sufficient to consider that formation of one intermolecular sulfone crosslink (a well-known side reaction in the sulfonation of aromatic rings) per macromolecular chain would lead to a doubling of the molecular weight of the sulfonated material. Thus, a side reaction entirely undetectable under normal conditions may lead to completely useless products in this case. We have tested a number of sulfonation reactions previously described and found that they do not satisfy the stringent requirements of our work. However, a modification of the method used by Kato et al.⁴ is quite simple and gives satisfactory results.

This report describes the new procedure and the isolation of the sulfonated polystyrene and also summarizes some of the unique properties of the polyelectrolyte in comparison with poly(vinyl sulfonate). Studies on a series of narrow molecular weight distribution samples of PSSA are continuing.

EXPERIMENTAL

The sulfonation reaction is heterogeneous and requires careful attention to several details, specified below, to avoid secondary reactions. Basically, finely divided polystyrene powder is mixed rapidly at room temperature into 100% sulfuric acid containing a fairly high concentration of silver ion as catalyst. As sulfonation proceeds, the PS becomes soluble, and the reaction is complete in 5–15 min. Separation of the polyelectrolyte is then accomplished by dilution, dialysis, concentration by ultrafiltration, and either lyophilization from water, or neutralization and precipitation from 2.5M KCl at low temperature.

Preparation of 100% Sulfuric Acid

Pure, 100% sulfuric acid was prepared by mixing analytical grade, concentrated (96%) H_2SO_4 and pure, slightly fuming oleum to give a substance melting at 10.3°C .⁵ To prepare the oleum in pure form (analytical grade oleum was not readily available), an isothermal distillation was arranged between 96% H_2SO_4 and commercial fuming H_2SO_4 (65% oleum). The simple apparatus for this distillation consisted of a clean desiccator (freed of all traces of grease) containing half-full beakers of 96% H_2SO_4 and oleum. After about 24 hr. in the covered desiccator, the sulfuric acid beaker had been enriched with SO_3 to the point where it was now fuming but was uncontaminated with the impurities in commercial oleum. This enriched acid was then used for the preparation of 100% sulfuric acid by mixing with 96% acid to give the required material with a freezing point of 10.3°C .

Preparation of Finely Divided PS Powder

The conditions for the production of finely divided powder depend to some extent upon the molecular weight of the polymer sample. For sample S-111 ($\bar{M}_w = 239,000$), 1 g. was dissolved in 100 ml. methyl ethyl ketone (MEK), methanol added slowly with rapid stirring to the first sign of turbidity (13.0 ml.), then the turbid mixture added in a thin stream to 200 ml. methanol with rapid stirring. After the fine precipitate settled, the supernatant was decanted, the powder washed three times with methanol and dried in air. For sample TAPS 24 ($\bar{M}_w = 6,700,000$) 1 g. was dissolved in 130 ml. MEK with warming; about 16.5 ml. methanol was added slowly with stirring to first turbidity, then excess methanol (about 100 ml.) added rapidly with vigorous stirring to prevent the coalescing of the precipitated particles. The precipitate was allowed to settle, the supernatant decanted, and the powder washed and dried as before. Samples of intermediate molecular weight were prepared by either the first or the second method, choosing the one giving the better result.

Sulfonation of PS Samples

For sample S-111, 400 mg. Ag_2SO_4 was dissolved in 40 ml. 100% H_2SO_4 in a glass-stoppered Erlenmeyer flask containing a Teflon-covered magnetic stirring bar. The polymer powder (200 mg.)* was added rapidly with vigorous stirring. The reaction was nearly completed within 5 min. and allowed to proceed for another 10 min., yielding a clear, somewhat viscous, faintly straw-colored solution. The temperature during this process did not rise appreciably above room temperature. The reaction mixture was filtered with slight pressure through a coarse fritted glass filter into 200 ml. well-stirred, ice-cooled water. The highly acid aqueous solution was dialyzed extensively against distilled water, 0.1N HNO_3 , and again water,

* The amount of polymer reactant may be conveniently increased for samples of lower molecular weight but should be decreased for higher molecular weight samples because of the high viscosity ultimately developed in the reaction mixture.

until neither Ag^+ (by Cl^- test) nor SO_3^- (by Ba^{++} test) could be detected in the diffusate, and the pH of the diffusate was neutral. To avoid formation of colloidal silver the sulfonation reaction was carried out in dim light and the prolonged dialysis in total darkness. The dialyzed material was concentrated on an LKB concentrator and the filtrate tested for Ag^+ and inorganic sulfate; no precipitates could be detected. A fraction of the concentrated solution in the acid form (PSSA) was stored in the refrigerator for further experiments. The bulk of the solution was carefully neutralized with KOH (as the polymer is more stable in the salt form), filtered through a Millipore filter (0.45μ), and lyophilized to yield a white, fluffy powder.

Characterization

Light-scattering measurements were performed on solutions of polymer in 2.5*M* KCl in the Sofica apparatus at various temperatures after careful filtration of each solution through a Millipore filter (0.45 or 0.22μ). For the higher molecular weight samples, it was usually necessary to carry out a preliminary filtration through a 1.2μ filter to avoid clogging the smaller filter.

Refractive index increments were measured in the Hilger-Rayleigh interference refractometer.

Viscosity determinations were made in size 50 Ubbelohde viscometers at various temperatures in water baths resulted to $\pm 0.02^\circ\text{C}$.

Dry weights were measured in closed weighing bottles after exhaustive drying in an Abderhalden apparatus fitted with a liquid air trap. Under high vacuum, constant weights were reached after a few hours with the sample at room temperature, and increasing the sample temperature to 80°C . (refluxing benzene) had no appreciable effect.

Ultraviolet absorption spectra and extinction coefficients were measured in Beckman DU and Unicam spectrophotometers on samples carefully calibrated by dry weight determination.

Phase separation temperatures were determined by observing the temperatures at which turbidity appeared or disappeared in solutions containing the polymer and various concentrations of KCl or barium acetate. The rate of temperature change of the water bath was less than $1^\circ\text{C}/\text{hr}$. for the KCl solutions and about $1^\circ\text{C}/\text{min}$. for the barium acetate solutions.

Sedimentation determinations were made in the Spinco model E ultracentrifuge by standard procedures.

Density increments of the polymer were determined at 25.0°C . from the densities of solutions measured in a capillary-neck pycnometer of about 7.5 ml. capacity.

RESULTS AND DISCUSSION

Sulfonation of PS

The sulfonation of PS proceeds in concentrated (96%) H_2SO_4 at high temperature and in the absence of catalyst to yield somewhat degraded

but also crosslinked and colored products. Crosslinking is presumably due to sulfone formation resulting from attack of sulfonated groups on unreacted phenyl rings. Better results have been obtained by sulfonation with SO_3 complexes in organic solvents.^{6,7} The use of Ag_2SO_4 as a catalyst to accelerate the reaction in H_2SO_4 and prevent formation of side products has also been suggested.⁸ Using granular PS, catalyst concentrations of the order of 1.3×10^{-2} equiv./monomole of PS, 96% sulfuric acid, and a temperature of 100°C ., Kato et al.⁴ obtained soluble products of reasonable viscosity. We find that by use of 100% H_2SO_4 , the reaction proceeds much more rapidly, even below room temperature. We increase the catalyst concentration markedly (to about 1 equiv. Ag/monomole PS) in order to decrease the likelihood of a sulfonated phenyl group encountering an unreacted, uncomplexed ring, which may lead to undesirable sulfone formation.

The sulfonation of PS to PSSA in 100% H_2SO_4 is a heterogeneous reaction; the PS is initially insoluble in H_2SO_4 but as the reaction proceeds the reacted PSSA goes into solution to yield a highly viscous, clear solution. If no catalyst is used, the reaction proceeds rather slowly to yield an inhomogeneous, elastic gel. In the presence of Ag_2SO_4 the reaction is much faster and is essentially limited by the size of the PS particles. If coarse, granular material is used, the particles are quickly coated with a gelatinous material, many coalesce, and an intractable mass is formed. The crucial step in the procedure is thus the use of a very fine PS powder, dispersing it quickly in the catalyst-containing 100% H_2SO_4 . Titration results show that close to 100% sulfonation is complete within 5–15 min., and that reaction for as long as 24 hours produces no further change. This indicates that mono substitution in the *para* position occurs exclusively. With no special precautions, yields average 90% of the expected product, small losses occurring during the several transfers and filtrations.

One precaution is necessary when the silver catalyst is used: colloidal silver is produced when the polymer solution is exposed to light during dialysis, and this may be removed only by high-speed centrifugation. It is more convenient to protect the solution from light until the silver ion has been removed completely. The incorporation of one or two dialyses against 0.1N HNO_3 in the isolation procedure is designed to facilitate this complete removal of silver ion.

Stability

Early in our work we were dismayed to find that dried samples of the acid form of the polyelectrolyte (PSSA) that had been stored for several weeks had intrinsic viscosities as much as 80% lower than freshly prepared samples. Stored, lyophilized samples gradually turned yellow or even orange, and had a water content when in equilibrium with room air of as much as 42%. In addition, the absorption spectrum began to lose detail, although the extinction coefficient at 261.5μ remained roughly constant. None of these difficulties was encountered when neutralized samples

(K-PSS) were stored in the dry state, so our standard procedure now includes the titration to neutrality with KOH before lyophilization. The completely dried potassium salt regains less than 20% moisture when exposed to room air.

Analysis and Titration

In preparation for elemental analysis, a neutralized polymer sample was equilibrated to constant weight at 22°C. and 50% R.H. Under these conditions the sample contained 12.4% water as found by dry-weight determination, and gave the following analysis.

ANAL. Calculated for $C_8H_7O_3SK$: C, 43.2%; H, 3.17%; S, 14.4%; K, 17.6%. Found (corrected for H_2O): C, 43.5%; H, 3.14%; S, 14.5%; K, 17.55%.

This analysis, together with the routine titrations which always showed one acid group per monomeric residue within experimental error, demonstrate the fact that the sulfonation reaction produces a completely monosubstituted derivative.

Molecular Weight

Since a primary concern in evaluating the success of the sulfonation reaction is that there should be no degradation or crosslinking as evidenced by changes in chain length, light-scattering measurements were made to determine the molecular weight of the sulfonated product. The weight-average degree of polymerization of K-PSS, derived from PS sample S-111, was found to be 2240. This is in good agreement with the value of 2140 for the parent polymer determined by us by light scattering in cyclohexane and toluene, and the value of 2300 as reported by Rudd⁹ without

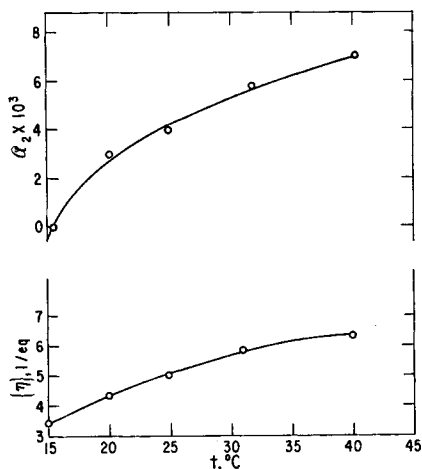
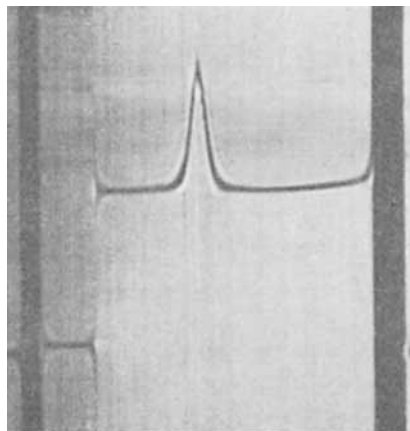
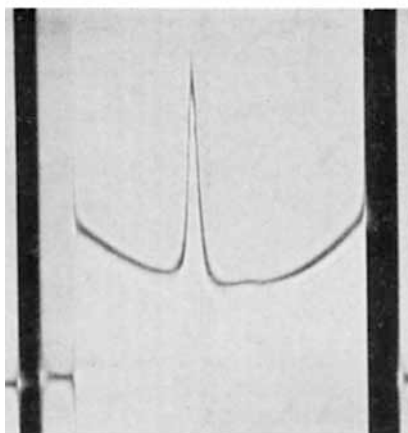


Fig. 1. Second virial coefficient α_2 and intrinsic viscosity $[\eta]$ as functions of temperature. S-111 K-PSS in 2.5M KCl.

specification of the method used. Our measurements on the polyelectrolyte sample were performed at various temperatures in 2.5*M* KCl. The variation of the second virial coefficient, α_2 (determined from light scattering), and the intrinsic viscosity, $[\eta]$ as a function of temperature are shown in



(a)



(b)

Fig. 2. Sedimentation patterns of (a) 0.35% S-111 polystyrene in cyclohexane at 35°C. (photographed 50 min. after reaching speed of 56,100 rpm, phase plate angle = 60°, $S_{35^\circ} = 6.14 \times 10^{-13}$); (b) 0.48% K-PSS from S-111 polystyrene in 2.5*M* KCl at 21.0°C. (photographed 40 min., after reaching speed of 56,100 rpm, phase plate angle = 55°, $S_{21^\circ, 2.5M \text{ KCl}} = 9.53 \times 10^{-13}$).

Figure 1. The concentration, C_u , used in the evaluation of α_2 and $[\eta]$ is expressed in monomoles per liter. It is seen that both α_2 and $[\eta]$ increase as the temperature is increased above the Θ temperature. The refractive index increment, $(\partial n / \partial C_u)_\mu$, appropriate to an analysis of light-scattering data in multicomponent systems,¹⁰ was found to be 34.7×10^{-3}

in 2.5*M* KCl at 25°C. and 546 $m\mu$; the subscript μ specifies constancy of the chemical potentials of the solvent and the salt.

A further confirmation of the lack of secondary reaction in the sulfonation procedure is given by the sedimentation pattern of the sulfonated material. Figure 2 shows the patterns of the K-PSS and the starting S-111 polystyrene. A very small amount of a more rapidly sedimenting component is apparent in the polyelectrolyte sample and it is uncertain whether this is the result of a small amount of crosslinking during the sulfonation reaction or indicates a heterogeneity in the starting material.

The density increment, $(\partial\rho/\partial C_u)_\mu$, required in the evaluation of sedimentation data is 64.2 g./monomole in 2.5*M* KCl.

Phase Separation in KCl

The solubility of K-PSS is considerably greater than that of the potassium salt of poly(vinylsulfonic acid). In 2.5*M* KCl the critical temperature for S-111 K-PSS is 12.6°C., whereas the KCl concentration required to yield the same critical temperature for K-PVS is less than 0.5*M*.¹ Thus, in spite of the hydrophobic phenyl rings in poly(styrene sulfonate), higher concentrations of KCl are required to salt it out.

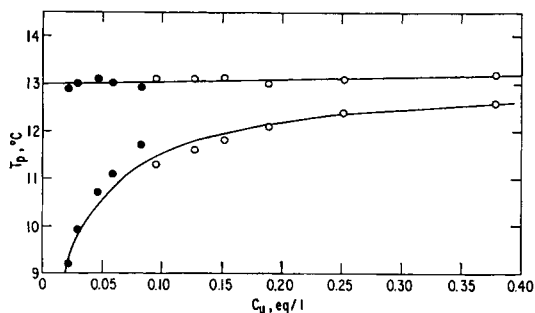


Fig. 3. Precipitation temperatures (lower curve) and dissolution temperatures (upper curve) obtained for S-111 K-PSS in 2.5*M* KCl as a function of polymer concentration: (●), and (○) two separate determinations.

The precipitation temperatures T_p in 2.5*M* KCl as a function of concentration of K-PSS are shown in Figure 3. Quite unlike the corresponding behavior of K-PVS, the precipitation is not strictly reversible, and temperatures higher by 1–4°C. are required to obtain clear solutions from the well-stirred, precipitated two-phase systems. The critical temperature (12.6°C.) for this sample, obtained from the appearance of turbidity upon gradual lowering of the temperature of clear solutions, leads to the correct value for the Θ temperature ($15.3 \pm 0.3^\circ\text{C}.$) when combined with preliminary data on other molecular weight samples. The lack of complete reversibility in the precipitation behavior may be attributed to preferred conformations caused by interactions of the aromatic rings in the precipitated phase.

Ultraviolet Spectra

Further evidence that interactions of the phenyl groups vary as a function of solvent and may play a role in stabilizing particular coil configurations is given in Figure 4, where it is seen that the extinction coefficient at the absorption maximum of $261.5 \text{ m}\mu$ varies as a function of the KCl concentration. Figure 5 shows the ultraviolet absorption spectra of K-PSS in water solution and in $2.5M$ KCl, the specific extinction coefficient at the $261.5 \text{ m}\mu$ maximum being 1750 in water when the concentration is expressed as grams per milliliter of the potassium salt of the polymer. The corresponding monomolar extinction coefficient is 389.

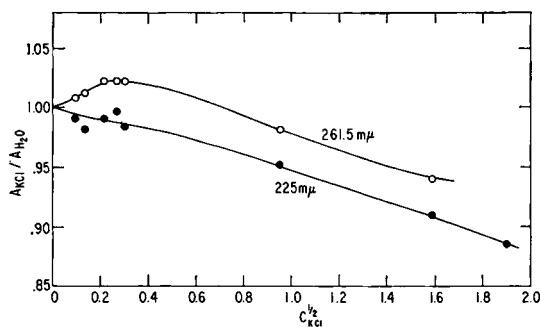


Fig. 4. Relative absorbance of K-PSS at 261.5 and $225 \text{ m}\mu$ in water and salt solutions as a function of KCl concentration.

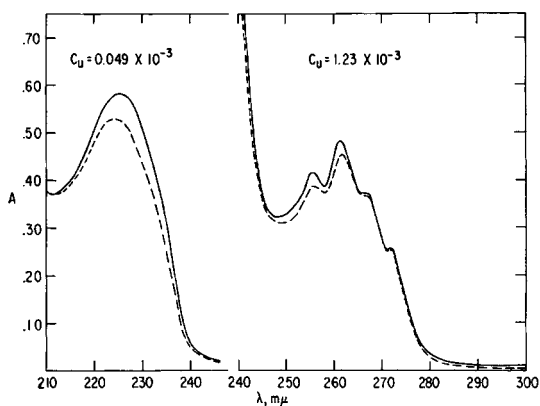


Fig. 5. Absorbance of K-PSS in the ultraviolet spectrum: (—) polymer in water; (---) polymer in $2.52M$ KCl.

High- and Low-Temperature Phase Separations of the Ba Salt of PSSA

An unusual phase separation takes place with solutions of PSSA in the presence of barium. At room temperature a water solution, 0.025 equiv./l.

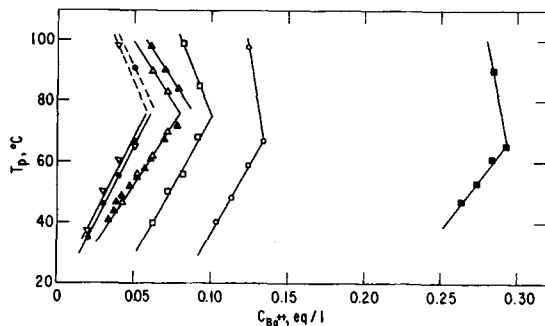


Fig. 6. Phase separation temperatures as functions of barium ion concentration for various concentrations of PSSA: (∇) 0.0053 equiv./l.; (\bullet) 0.0105 equiv./l.; (Δ) 0.021 equiv./l.; (\blacktriangle) 0.026 equiv./l.; (\square) 0.0526 equiv./l.; (\circ) 0.105 equiv./l.; (\blacksquare) 0.263 equiv./l. Barium acetate used as titrant; sample TAPS 19 (degree of polymerization = 4370).

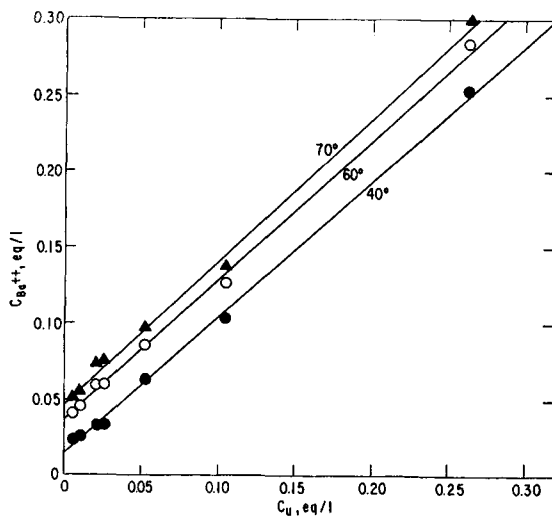


Fig. 7. Composition curves for incipient precipitation in system PSSA-Ba at constant temperatures.

in PSSA and 0.030M in barium acetate, shows a heavy, white precipitate. This precipitate dissolves as the temperature is raised to 61°C. giving a perfectly clear solution. If the temperature is then raised to 98°C., a turbidity appears, and after 1-2 min. the solution separates into two clear phases. Lowering the temperature reverses this phase separation, and in the temperature range 98-61°C. the solution is clear and homogeneous. Below 61°C. the original white precipitate forms again. The whole process is reversible. With lower concentrations of barium, only the low-temperature second phase is observed, but with higher concentrations of barium, more of the high-temperature second phase appears, and at a lower tem-

perature. This general behavior is illustrated in Figure 6 for a wide range of polymer concentrations.

The lower-temperature precipitation follows the general characteristics of a similar transition described by Michaeli¹¹ for poly(methacrylic acid) in the presence of various divalent cations. However, in the case of PSSA we have not been able to produce either of the phase separations with Ca, Mg, or Sr.

For the lower branches of the precipitation temperature curves shown in Figure 6, it is seen that with increasing polymer concentration, increasing amounts of barium ions are required to produce the phase separation. At constant temperature, plots (Fig. 7) of polymer against barium acetate concentration (horizontal sections through Fig. 6) yield parallel straight lines. At 60°C. we have

$$(C_{\text{Ba}^{++}})_p = 0.92 C_u + 0.04$$

where $(C_{\text{Ba}^{++}})_p$ is the concentration in equivalents per liter required to produce phase separation. A similar description was used by Michaeli for the case of poly(methacrylic acid). In his interpretation the intercept represents the concentration of free ions in solution and the slope the number of Ba^{++} equivalents bound per monomer unit. The slopes of the lines are independent of temperature, meaning that the amount of Ba^{++} bound (and required to produce precipitation) is independent of temperature and is close to one equivalent per monomer unit. The amount of free Ba^{++} in solution increases with temperature in the lower precipitation branch. This is reversed as we pass to the upper precipitation branch; the upper and lower branches of the precipitation curves in Figure 6 appear to be symmetrical around the region of complete insolubility, indicating that the amount of free barium again decreases once the high-temperature range is reached. It is clear that at this stage it is impossible to give more than a preliminary description of the phenomena of the phase transitions in the presence of barium, and that for a complete interpretation much more detailed work is required.

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Résumé

Une méthode est décrite pour la conversion du polystyrène en acide polystyrène sulfonique sans changer la distribution des poids moléculaires; la réaction est effectuée à température de chambre dans l'acide sulfurique à 100% et on utilise un catalyseur à base d'ion argent. Le polyélectrolyte résultant a une solubilité et d'autres caractéristiques différent significativement de celles jusqu'ici décrites pour l'acide polyvinylsulfonique. Ceci permet une étude de l'influence du groupe aromatique sur les interactions locales et à grandes distances. Le sel de barium de l'acide polystyrène-sulfonique se comporte inhabituellement en ce sens qu'il présente en solution des températures de miscibilité inférieure et supérieure.

Zusammenfassung

Eine Methode zur Umwandlung von Polystyrol in Polystyrolsulfonsäure ohne Änderung der Molekulargewichtsverteilung wird beschrieben; die Reaktion wird bei Raumtemperatur in 100% H_2SO_4 und mit Ag^+ als Katalysator ausgeführt. Der gebildete Polyelektrolyt besitzt eine Löslichkeit und andere Eigenschaften, welche sich wesentlich von denjenigen der früher untersuchten Polyvinylsulfonsäure unterscheiden. Damit wird eine Untersuchung des Einflusses der aromatischen Gruppe auf die lokalen und weitreichenden Wechselwirkungen in Lösung ermöglicht. Das Bariumsalz der Polystyrolsulfonsäure ist insofern ungewöhnlich, als es sowohl eine untere als auch eine obere Entmischungstemperatur zeigt.

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