Macromolecules **1980,** *13,* 1013–1016

Gel Permeation Chromatographic Characterization of Sulfonated Polystyrenes

Wolfgang Siebourg,[†] Robert D. Lundberg,[‡] and Robert W. Lenz[*,§]

Materials Research Laboratory, Chemical Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received December 31, 1979*

ABSTRACT: Sulfonated polystyrenes containing approximately 2–5 mol % sulfonate groups in the form of either the sodium or tri-*n*-butylammonium salts were chromatographed by gel permeation chromatography (GPC) on polystyrene columns. The most effective solvent systems for this purpose were found to be two- or three-component mixtures of polar solvents and inorganic salts. For the ammonium salts, a THF–$LiNO_3$ solution was found to be effective, while for the sodium salts, a THF–DMF–$LiNO_3$ mixture was required. In poor solvents, multiple-peak GPC distributions were obtained which were believed to be caused, in part at least, by adsorption of the sulfonated polystyrene on the gel phase.

Nonpolar polymers containing small amounts of polar units, particularly ionic units, are known to have unusual solution properties. Recent investigations on partially sulfonated polystyrene and ethylene–propylene terpolymer have shown that, even at sodium sulfonate levels as low as 0.6 mol % of the backbone units, the solubility of the polymer is greatly reduced in nonpolar solvents, and a two-component solvent system containing a polar solvating agent must be used to completely dissolve the polymer.[1]

For polar polymers containing ionic substituents, such as sulfonate groups, it has been found that the addition of salts, such as lithium bromide, to polar solvents considerably increases the solubility of the polymer.[2] The presence of the salts can also greatly change the solution behavior of the polymers, but often in an unpredictable manner. For example, polyacrylonitrile containing 0.2 mol % sulfonate units (prepared by copolymerization with a sulfonate-containing monomer) showed very different solution properties in dimethylformamide (DMF) as compared to solutions in the same solvent containing 0.1 M lithium bromide, depending on whether the solution properties were determined by solution viscosity or by gel permeation chromatography (GPC). That is, the addition of LiBr to DMF caused only a very small decrease in the intrinsic viscosity of the polymer but a very large decrease in its elution volume in the GPC chromatogram.

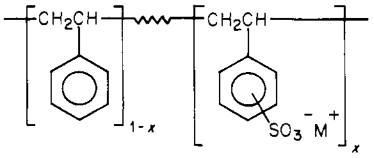
Two different proposals have been made to explain the apparently very much higher effective volume of the polymer in DMF.[2,3] One suggestion was that, in DMF, supermolecular associations or aggregates are formed which are destroyed by addition of LiBr.[3] The other suggestion was that intramolecular electrostatic repulsions of the ionic groups along the polymer chain caused expansion of the random coil and an increase in the effective volume.[2] The electrolyte LiBr is believed to screen these groups, thereby permitting the molecular configuration to contract, reducing the hydrodynamic volume.

Two other effects have been proposed to account for the unusually large elution volumes of some polymers observed in some GPC analyses in which a nonpolar polystyrene gel stationary phase was used either with nonpolar polymers in polar solvents or with polar polymers in solvents of varying polarity or solute interaction behavior. One suggestion is that polar groups in the polymer can associate extensively with polar solvent molecules, causing a considerable increase in the hydrodynamic volume.[4] For copolymers of acrylonitrile and polar monomers, such as ethyl vinyl ether, this apparent association resulted in an extensive broadening of the observed molecular weight distribution to the point that two GPC peaks were observed for the polymer dissolved in DMF. Addition of LiBr, in this case, greatly reduced the polymer–solvent interaction and gave a single-peak distribution curve at a higher elution volume.[4]

Another explanation for the observed change in effective volume with changing solvent polarity for a given polymer–stationary phase combination was based on specific adsorption effects on the latter.[5,6] That is, nonpolar polymers, such as polystyrene, in polar solvents, such as DMF, can preferentially adsorb on the polystyrene gel and exhibit a delayed elution. Polar polymers, such as poly(vinylpyridine), could show the same behavior in solvents of low polarity. Hence, in the GPC chromatograms deviations from the expected molecular weight–hydrodynamic volume behavior could occur because of differences in the solubility parameters of the polymer undergoing elution, the solvent, and the gel-phase polymer.[5]

In several cases, this type of mismatch has resulted not only in a greatly incorrect indication of the average molecular weight value but also in giving GPC distribution curves with two or more peaks for monomodal polymers,[2,3,7] as mentioned above. However, it is known that the properties of a single solvent can be essentially duplicated by a mixture of two or more solvents of different polarities,[8] so it should be possible for a polymer that contains both nonpolar and polar properties to find a good solvent system which would not cause adverse adsorption or solvation effects. If so, the polymer should be capable of being chromatographed by a size-exclusion mechanism only.

Such adverse effects were observed in the present investigations on the GPC analysis of sulfonated polystyrenes with compositions ranging from approximately 2 to 5 mol % sulfonate units in the form of either their sodium salts or their tri-*n*-butylammonium salts, structure 1, where $x = 0.02–0.05$ and M = Na or $(CH_3CH_2CH_2CH_2)_3NH$ for NaPSS or APSS, respectively.



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Results and Discussion

A number of different solvent systems were evaluated for the GPC analysis of the sulfonated polystyrenes before

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[†] Permanent address: Bayer-AG, Plastics and Coatings Division, 5090 Leverkusen, West Germany.

[‡] Permanent address: Exxon Research and Engineering Co., Corporate Research Laboratories, Linden, NJ 07036.

[§] Presently Senior Humboldt Awardee, Institut für Makromolekulare Chemie, Universität Freiburg, West Germany.

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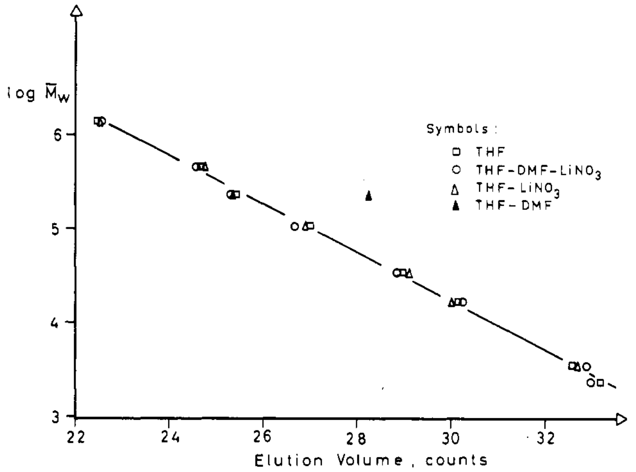

Figure 1.

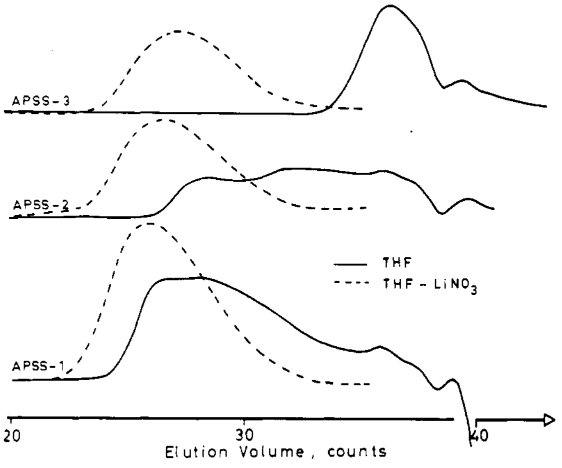

Figure 2.

it was found that good, reproducible chromatograms could be obtained for both types of salts with either a two- or three-component system consisting of THF, DMF, and $LiNO_3$. The tri-*n*-butylammonium salts, APSS, could be chromatographed in a THF–$LiNO_3$ solution with reliable results, but the sodium salts, NaPSS, could only be chromatographed in the ternary solvent system.

Polystyrene Standards. In order to use the ternary system for estimating absolute molecular weights based on normal polystyrene standards, it had to be determined first that the nonpolar polystyrene standards could be chromatographed in this solvent to give a simple relationship between molecular weight and elution volume that could be applied to the determination of molecular weights of the sulfonated polystyrenes. The results for this evaluation for four different solvent systems on the polystyrene standard samples are shown in Figure 1.

It is seen in Figure 1 that identical elution volumes were obtained on the standard polymers dissolved in any of three different solvent systems: in THF alone, in a solution of $LiNO_3$ in THF (2 g/L), and in a three-component solution of $LiNO_3$, THF, and DMF (2 g/L of salt in a 10:1 THF–DMF mixture). The one exception observed was for a standard polystyrene sample dissolved in a 10:1 THF–DMF mixture. In that case, the polymer eluted 5 counts later than in the other solvents, most likely because of adsorption on the gel phase due to the disparity in solubility properties between the nonpolar polystyrene and the highly polar solvent. Apparently the addition of $LiNO_3$ in this solvent mixture served to "salt in" the polymer in some manner directly opposite to that observed in the case of addition of LiBr to a DMF solution of polyacrylonitrile. In the latter case the polar polymer was eluted much later for the DMF–LiBr solution than for a solution in DMF alone, presumably because of a "salting-out" effect which reduced the polymer–solvent interaction.[2]

Ammonium Salt Polymers. The tri-*n*-butylammonium salts of the sulfonated polymers, APSS, were soluble in THF to concentrations of at least 50 g/L. However, when these solutions were chromatographed, very broad, multiple-peak distribution curves were obtained as shown in Figure 2 (solid lines). In contrast, when a THF–$LiNO_3$ solvent system was used, single-peak distributions of the expected shape were obtained by GPC analysis, as shown in Figure 2 (dashed lines). The latter also had lower elution volumes, indicating that in THF either (1) the polymers had a much smaller hydrodynamic volume because of intramolecular association or (2) the polymers were adsorbed on the column because of poor solute–solvent interactions, resulting in a delayed elution; a combination of both effects is also possible.

For the former explanation to apply, the addition of $LiNO_3$ would have to shield the intramolecular ionic associations and permit coil expansion. For the latter explanation to apply, the addition of $LiNO_3$ would have to increase the solute–solvent interaction in order to reduce or eliminate the solute–gel interaction and permit the polymer to elute according to its hydrodynamic volume. The adsorption explanation seems to be favored by the observation of multiple peaks in the THF chromatogram.[4]

An attempt was made to distinguish between these two possible explanations in the following manner. A solution of the APSS polymer in THF at a tenfold higher concentration than normal was injected onto the column; the chromatogram obtained is shown in Figure 3 (upper curve). The only peak to appear within a reasonable elution volume came at about 38 counts, which is the point at which low molecular weight impurities in the polymer normally appear in this system. No polymer peak appeared up to 45 counts, at which point a THF–$LiNO_3$ solution was injected onto the column. Shortly after that point a very broad peak was observed with a maximum at about 50 counts. It is not known whether this peak represents an impurity introduced into the column in the first large injection or possibly a fraction of the polymer which was not as strongly absorbed as the main component. Unfortunately, since a refractive index detector was used on the instrument, it was not possible to identify this fraction. However, between counts 78 and 83 a very large peak appeared (shortly before the peak characteristic of the pure THF–$LiNO_3$ solvent as shown in the lower curve) which clearly represented most, if not all, of the large amount of polymer injected on the column.

These results appear to be best accounted for by the adsorption explanation. That is, injection of the good solvent, THF–$LiNO_3$, almost immediately redissolved and eluted the impurity and then chromatographed the adsorbed polymer so that it eluted at close to the expected elution volume.

The apparent molecular weights, as indicated by the chromatograms relative to known polystyrene standards, of the APSS polymers in THF–$LiNO_3$ solution are listed in Table I. Included in this table are the data for the original polystyrene sample (PS) used for the sulfonation reaction. It can be seen that there was an apparent continuous decrease in molecular weight with increasing degree of sulfonation, suggesting that some polymer degradation occurred during the sulfonation reaction. As would be expected if such a random degradation process occurred, there was also an apparent narrowing of the molecular

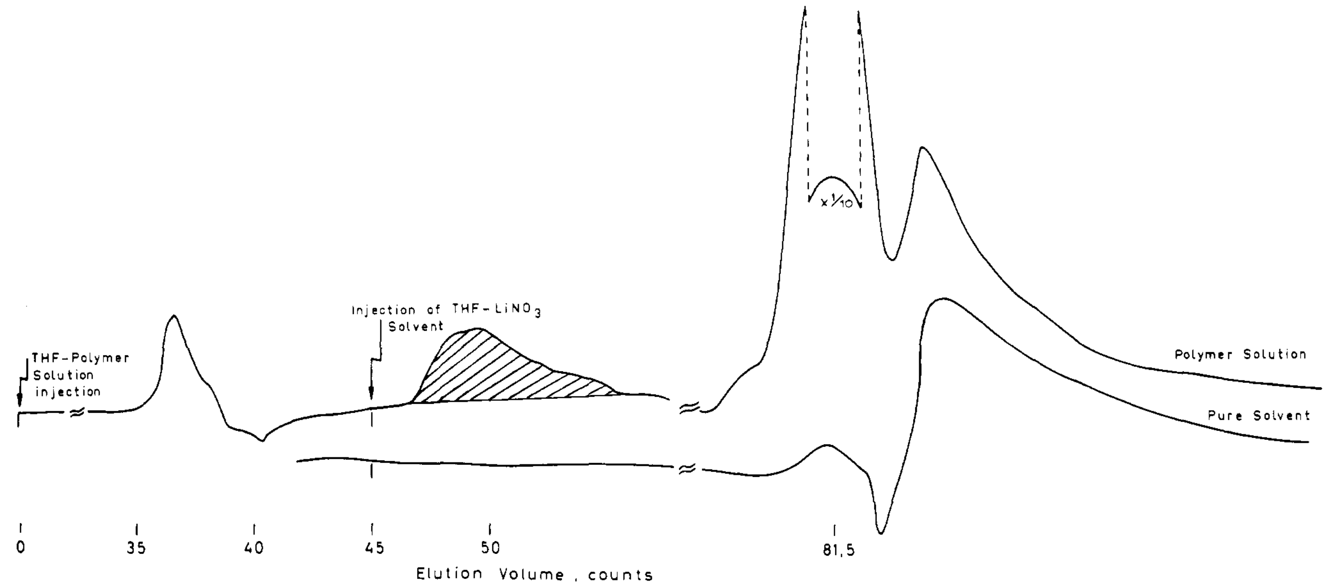

Figure 3.

Table I
Molecular Weights of Ammonium Salt Polymers Chromatographed in THF-LiNO$_3$ Solution and in THF-DMF-LiNO$_3$ Solution

polym	deg of sulfonation, mol %	THF-LiNO$_3$ $10^{-3}\bar{M}_w$	THF-LiNO$_3$ $10^{-3}\bar{M}_n$	THF-LiNO$_3$ $\bar{M}_w/\bar{M}_n$	THF-DMF-LiNO$_3$ $10^{-3}\bar{M}_w$	THF-DMF-LiNO$_3$ $10^{-3}\bar{M}_n$	THF-DMF-LiNO$_3$ $\bar{M}_w/\bar{M}_n$
PS[a]	0	267	76	3.5			
PS	0	261	77	3.4	271	79	3.4
APSS-1	2.2	229	67	3.4	173	32	5.4
APSS-2	3.9	180	58	3.1	182	49	3.7
APSS-3	5.3	131	44	2.9	178	39	4.5

[a] Unreacted polystyrene in THF in the absence of LiNO$_3$.

weight distribution toward the most probable distribution, in which the $\bar{M}_w/\bar{M}_n$ ratio would be 2.

These results have shown that two types of sulfonated polymers can be characterized by GPC provided that the solvent systems are carefully selected. Inappropriate choice of the solvent can lead to pronounced column adsorption effects; the data shown in this study are consistent with this hypothesis. It should be cautioned, however, that the hydrodynamic volumes of these polymers may also be sensitive to solvent choice and consequently may have some influence on the molecular weight parameters obtained.

Sodium Salt Polymers. The sodium salts of the sulfonated polystyrenes, NaPSS, were very poorly soluble in the THF-LiNO$_3$ solvent and could not be chromatographed with this system. However, a ternary solvent system consisting of a 10:1 THF-DMF mixture containing 2 g/L of LiNO$_3$ was very effective for this purpose, with the results shown in Figure 4 and Table II.

The sodium salt polymers had observed molecular weights very similar to those of the ammonium salts at comparable degrees of sulfonation, indicating that the elution behavior of the two types of polymers in their specific solvents were essentially the same.

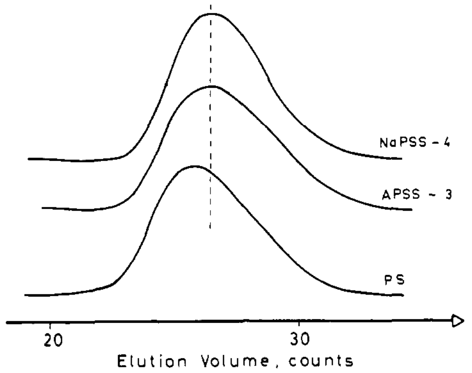

Figure 4.

Table II
Molecular Weights of Sodium Salt Polymers Chromatographed in THF-DMF-LiNO$_3$ Solution

polym	deg of sulfonation, mol %	$10^{-3}\bar{M}_w$	$10^{-3}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
PS	0	271	79	3.4
NaPSS-1	1.17	234	68	3.4
NaPSS-2	2.56	206	54	3.8
NaPSS-3	4.19	199	58	3.4
NaPSS-4	6.05	172	56	3.1

It is interesting to note in this regard that when the THF-DMF-LiNO$_3$ solvent system was used for the ammonium salt polymers, considerably different molecular weight and distribution results were obtained compared to results obtained for the same samples dissolved in THF-LiNO$_3$, as shown in Table I. For the former, there was very little variation in $\bar{M}_w$ with degree of sulfonation and much broader distributions were obtained. This result could again be indicative of the occurrence of adsorption effects in the THF-DMF-LiNO$_3$ system with the APSS samples, which suggests that it is a much poorer solvent for the ammonium salt polymer than for the sodium salt polymer and also that the THF-LiNO$_3$ system is a better solvent for the former. Obviously there are significant differences in the specific cation solvation properties of the two solvent systems, and this analytical technique is very sensitive to small changes in solute–solvent interactions.

Experimental Section

Polymers. Various salts of partially sulfonated polystyrene were prepared at the Exxon Research and Engineering Co. For the preparation, polystyrene was reacted with acetyl sulfate as the sulfonating agent in acetic anhydride.[1,9] After neutralization of the products with either aqueous sodium hydroxide or tri-*n*-butylamine solutions, sodium poly(styrenesulfonate) (NaPSS) or the tri-*n*-butylammonium poly(styrenesulfonate) (APSS) was obtained. The degree of sulfonation of the investigated samples was between 1 and 7 mol %, as indicated in Table I.

GPC Characterization. GPC measurements were made on a Waters 201 instrument having a high-pressure solvent delivery system and a refractive index detector. A set of five μ-Styragel columns (10^6, 10^5, 10^4, 10^3, 500) purchased from Waters Associates was used, and the instrument was operated at ambient temperature. Four solvent systems were used in these studies at polymer concentrations of 0.1% w/v: (1) tetrahydrofuran (THF); (2) tetrahydrofuran + 2 g/L $LiNO_3$ (THF/$LiNO_3$); (3) 10:1 tetrahydrofuran/dimethyl formamide (THF/DMF); (4) 10:1 tetrahydrofuran/dimethyl formamide + 2 g/L $LiNO_3$ (THF/DMF/$LiNO_3$). The flow rate was kept at 1.45 mL/min, and calibrations were made with commercially available, narrow-distribution polystyrene standards purchased from Waters Associates. Generally 0.1 mL of the polymer solution was used for the analysis. The molecular weight averages in the Table I are average values of two or three measurements, and their reproducibility was within 5%.

Acknowledgment. We thank the Exxon Research and Engineering Co. for support of this work and acknowledge the use of the facilities of the NSF-sponsored Materials Research Laboratory. We are particularly grateful to the late Dr. Henry Makowski of Exxon for supplying the polymer samples.

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Notes

Poly(2,6-dimethyl-1,4-phenylene oxide)–Polystyrene Interpenetrating Polymer Networks

H. L. FRISCH

Department of Chemistry, State University of New York at Albany, Albany, New York 12222

D. KLEMPNER,* H. K. YOON, and K. C. FRISCH

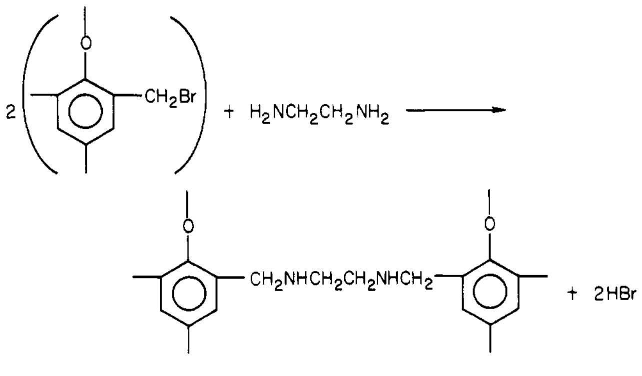
Polymer Institute, University of Detroit,
Detroit, Michigan 48221.

Received October 9, 1979

Interpenetrating polymer networks (IPN's) are a novel polyblend composed of two or more permanently entangled (catenated) chemically dissimilar, cross-linked polymers. True IPN's should be essentially free of covalent bonds between the different cross-linked, component networks (i.e., grafting) and be homogeneous blends. Most of the IPN's reported to date have involved heterogeneous systems,[1-9] usually with one rubbery phase and one glassy phase. This combination of rubbery and glassy polymers often results in a synergistic effect in properties,[3,6,7] particularly mechanical properties. Either high-impact plastics or reinforced rubbers result, depending on the morphology (i.e., phase continuity). The only instances in which apparently homogenous morphology has resulted are with IPN's in which grafting between the component polymer networks was a distinct possibility.[10-13] In this note we described IPN's which we believe approximate true IPN's with a single-phase morphology and no grafting between the distinct polymer networks. This was achieved by forming IPN's from polymers with known complete compatability by well-controlled cross-linking reactions.

Thus, IPN's, pseudo-IPN's (PDIPN's—only one polymer cross-linked), and linear blends of polystyrene (PS) incorporating poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (whose compatability has been reviewed elsewhere[14]) were prepared, using for the IPN's and PDIPN's the simultaneous interpenetrating network (SIN) technique. The polystyrene was cross-linked by incorporating divinylbenzene. Several methods have been reported for synthesizing cross-linked PPO: for example, materials such as polysulfonazides and (hydroxymethyl)diphenyl oxide[15,16] have been used. However, these methods were found to be difficult to employ for simultaneous IPN's in which these two polymer networks are formed in situ at about the same time. In this study the PPO was first brominated and subsequently cross-linked with diethylamine (Scheme I).

Scheme I



Solubility studies and elemental analyses were performed to confirm that cross-linking did indeed occur. The cured polymers did not dissolve in either tetrahydrofuran or trichloroethane (both good solvents for PPO); however, swelling did occur to about twice the initial dimensions.