Notes

Persulfate-Initiated Polystyrene: Aggregation of Potassium α,ω-Polystyrene Sulfate in Toluene

NIRA MISRA and BROJA M. MANDAL*

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700032, India. *Received May 19, 1982*

Recently Broze et al.[1,2] reported that viscosities of solutions of halato-telechelic polymers (HTP) in nonpolar solvents increase rapidly at concentration levels as low as 1–1.5 g·dL^{-1}, referred to as C_{gel}. This phenomenon referred to as gelation was attributed to the formation of ionic multiplets through the ion pair end groups.[3] Theoretical consideration allows an increasing multiplet size with increasing polymer concentration. The association into multiplets releases however a decreasing amount of energy as the multiplet size increases. Nevertheless a "didimensional growth" of the multiplets is conceivable as previously reported for soaps.[3] On the other hand, an osmometric study performed by us in an earlier work[4] on related polymers indicated that the degree of association (multiplet size) of such polymers remains essentially constant within the investigated concentration range of 0.5–1.5 g·dL^{-1}.

In this note we use viscometric results to emphasize that the aggregation of such polymers occurs at a concentration much below C_{gel} as evidenced by a large Huggins constant (k') value and osmometric results to emphasize that the degree of association of the polymers remains essentially constant in the concentration region where viscosity increases sharply with concentration. Solution behavior of polystyrene sulfate (PSS) (f = 1.8 ± 0.1) has been dealt with in this work.

Experimental Section

Polystyrene bearing SO_4K end groups was prepared by polymerizing styrene at 60 °C under a N_2 atmosphere for 4 h (80% yield) in a mixed solvent medium consisting of *tert*-butyl alcohol (TBA) and water, using $K_2S_2O_8$ as initiator. $KHCO_3$ (same weight as $K_2S_2O_8$) was also used in the medium to keep it mildly alkaline. This pH condition is reported to be the best for the incorporation of sulfate group.[6] McAskill and Sangster found that about 95% of the $SO_4^{-}\cdot$ adds to styrene in preference to reacting with TBA even when the molar concentration of the latter (0.1 M) was 125 times greater than that of the former (0.8 mM).[7] A typical recipe consisted of 20 mL of styrene + 650 mL of TBA + 1000 mL of water and 0.19% each of $K_2S_2O_8$ and $KHCO_3$ (based on total volume). The system was homogeneous to start with. The polymer obtained as an emulsion was isolated by using KCl to break the emulsion. Thus at all stages of the polymer preparation the polymer was in contact with potassium ion. This practice was followed in order to have polymers having end groups of a single kind (viz., SO_4K).

The whole polymer was fractionated from 1% benzene solution using methanol as the nonsolvent.[8] The sulflate group in the polymers was determined with the help of the dye extraction method of end group analysis.[9,10] $\bar{M}_n$ was determined with a Hewlett-Packard high-speed membrane osmometer (Model 501) and Schleicher and Schull 0-8 membranes. The intrinsic viscosity was determined with a Schurz–Immergut type variable-shear viscometer.[11] The viscosity results were duly corrected for kinetic energy loss and extrapolated to zero shear rates.

Viscosities of highly viscous solutions used in other than intrinsic viscosity studies were determined in an Ostwald viscometer of 1.5-mm capillary bore. Glycerine was used as the reference liquid.

Table I
Characterization Data and Degree of Association ($\bar{n}$) of Potassium Polystyrene Sulfate in Toluene at 30 °C

sample no.	sulfate functionality[a]	$\bar{M}_n \times 10^{-4}$ in toluene: original	$\bar{M}_n \times 10^{-4}$ in toluene: acetylated	$\bar{n}$	$\bar{M}_w/\bar{M}_n$ [b]
F_4	1.8	72.2	22.1	3.3	1.63
F_6	1.8	51.8	15.8	3.3	1.63
F_7	1.9	42.4	11.7	3.6	1.32
F_8	1.9	33.1	9.1	3.6	1.16
F_9	1.8	22.0	6.9	3.2	1.20
F_{10}	1.8	14.7	5.5	2.7	1.18
PSABN[c]	0	6.8	6.7	1	

[a] Number of SO_4K groups per polymer molecule.
[b] Determined by GPC of the acetylated samples in THF.
[c] Polystyrene prepared by using AIBN initiator.

Conversion of the Sulfate End Group to an Acetyl End Group

The following reaction scheme was followed[12,13]

$$\underset{\text{(PSS)}}{\sim OSO_3K} \xrightarrow[\text{THF + toluene}]{SOCl_2} \sim OSO_2Cl \xrightarrow[\text{THF}]{H_2O}$$

$$\sim OH \xrightarrow[\text{dioxane, 15 °C}]{CH_3COCl} \underset{\text{(PSAC)}}{\sim OCOCH_3}$$

The procedures followed for the first two steps were already reported in detail.[4] The polymers so treated did not respond to the dye test, indicating complete elimination of the sulfate groups. The procedure described by Doty et al. was followed for acetylation.[14,15]

Results and Discussion

Table I presents the characterization data for several fractions of PSS. The sulfate functionality of the fractions was measured to be 1.8 ± 0.1. The degree of association ($\bar{n}$) of the PSS fractions in toluene refers to the ratio of the $\bar{M}_n$ of the PSS fraction to that of its acetyl derivative (PSAC). Figure 1 shows the η_{sp}/C vs. C plot for a representative fraction (F_4) of PSS and its corresponding acetyl derivative (PSAC) in toluene. The plot for PSAC is linear even up to the highest concentration used, viz., 0.9 g·dL^{-1} (not shown in the figure). On the other hand, the plot for PSS remains linear (with much higher slope) only up to 0.2 g·dL^{-1} and then η_{sp}/C increases rapidly and the increase becomes near asymptotic around 0.8 g·dL^{-1}, which may be approximated to the C_{gel}. The value of k' determined from the initial linear portion of the curve shown as an inset of Figure 1 has an abnormally large value, viz., 4, for PSS compared to the rather normal value, viz., 0.4, determined for PSAC. Large k' values have been reported for many instances of polymer association.[4,5,16-18]

A large value of k' is indicative of the high degree of chain entanglement even in dilute solution. This is presumably attributable to the thermolabile nature of the bonds in the aggregates,[3] which allows exchange of ion pairs between aggregates. η_{sp}/C may be expressed as a power series in C[16].

$$\frac{\eta_{sp}}{C} = [\eta](1 + aC + bC^2 + cC^3 + ...) \qquad (1)$$

(where $a = k'[\eta]$ and k' = Huggins' constant). Since the

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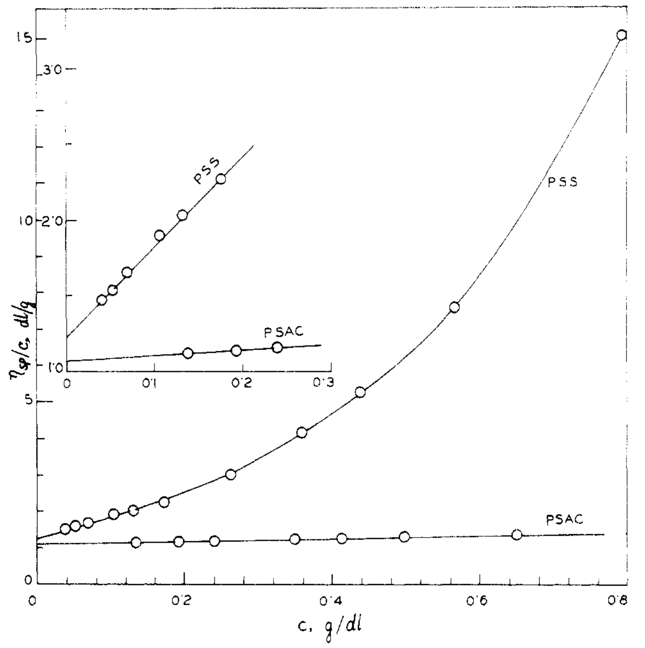

Figure 1. Plot of reduced viscosity vs. concentration for fraction F_4 of PSS as well as for the corresponding PSAC in toluene at 30 °C.

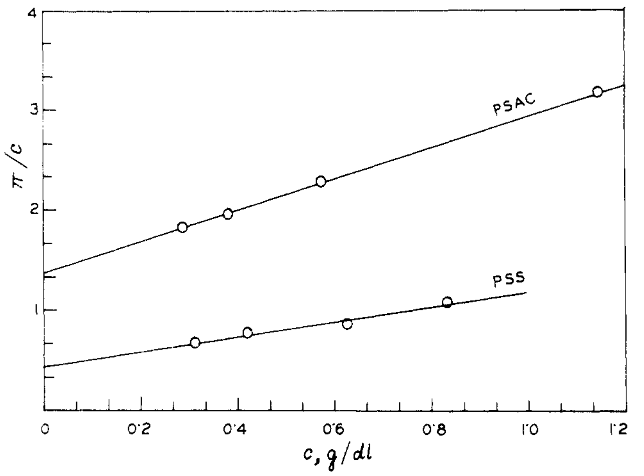

Figure 2. Osmotic pressure plots for fraction F_4 of PSS as well as for the corresponding PSAC. π in cm of toluene at 30 °C.

curvature in the η_{sp}/C vs. C plot appears at an unusually low concentration for PSS, it turns out that the coefficients for higher order concentration terms in eq 1 are dependent on k'. The high value of k' early brings about curvature in the plot of η_{sp}/C vs. C for PSS.

However, unlike k' the intrinsic viscosity is rather insensitive to polymer aggregation. For example, the $[\eta]$ of PSS (F_4), 1.23 dL/g, is only about 15% greater than that of PSAC, 1.06 dL/g. If the associates were linear, a degree of association of 3.3 (Table I) would have increased the $[\eta]$ about 2.3 fold. This follows from the relation between $[\eta]$ and $\bar{M}_n$.[19,20] This rather small effect of aggregation on $[\eta]$ has been reported by many workers.[4,5,16-18] However, little is known about the geometry of the aggregates. It is however questionable whether the $[\eta]$–M relation applicable for PS is valid also for PSS. On the other hand, a straightforward correlation of results obtained respectively by measurements on the solution in motion (viscometric method) and in rest (osmometric method) may not be justifiable for systems where interchange of molecules between aggregates occurs especially under the influence of shear. However, according to Otocka et al.[17] such a restriction does not seem to apply in the case of ion-pair aggregates.

Figure 2 shows that the π/C vs. C plot for PSS is linear in the concentration region where the η_{sp}/C vs. C plot shows sharp curvature (Figure 1). The fact that the osmotic pressure plot for the PSAC sample is also linear indicates that the contribution of the higher order concentration terms in the osmotic pressure equation in this concentration region is insignificant. Hence, the linear osmotic pressure plot for PSS indicates that the degree of association (multiplet size) remains essentially constant in the concentration region where viscosity shows a rapid increase. Thus, the sharp rise in viscosity as shown in Figure 1 should not necessarily be attributed to an increase in the degree of association of the polymers with concentration. It may perhaps be attributed to the increase with concentration of the degree of chain entanglement of the aggregated polymers, which was already high at much lower concentration levels as evidenced by the large value of k'.

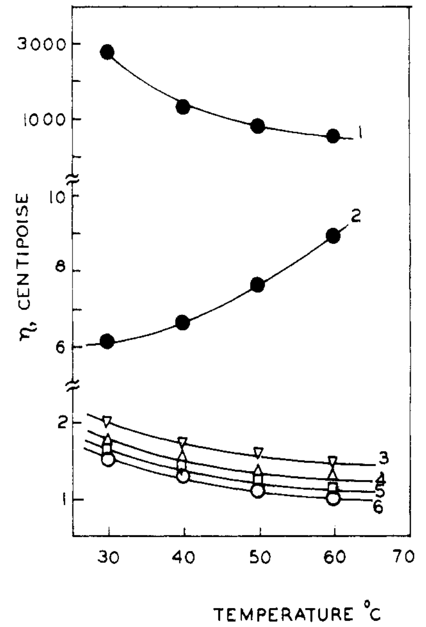

Figure 3. Viscosities of the solution of polystyrene sulfate (concentration 2.63%): curve 1, fraction 7 in toluene; curves 2–5 the same polymer fraction in toluene containing respectively 1%, 2.5%, 3.4%, and 4.3% ethyl alcohol; curve 6, acetyl derivative of PSS fraction 7 (F7AC) in toluene or in toluene + 2% ethanol.

It has been established in our earlier work that a small amount of alcohol breaks up the kind of polymer association in toluene discussed here.[4] Lundberg and Makowski[21] also demonstrated from solution viscosity measurements the ability of a small amount of alcohol to break up the association of metal sulfonate ionomers in xylene solutions of 2–3% ionomer concentration.

Figure 3 shows the viscosity and the effect of temperature on it for a 2.6% solution of PSS (fraction 7) in toluene and for its solutions containing increasingly greater amounts of ethyl alcohol. Our results generally agree with those of Lundberg et al.[21] for their slightly sulfonated polystyrene (0.32 mol % sulfonate). Our sample contained a lower percentage of sulfate groups (0.17 mol %) instead of sulfonate. Apart from this the major difference between their polymers and ours lies in the location of the salt groups. In their sample the groups were randomly distributed along the polymer chain while in our case these were present at the polymers ends.

As is expected, PSS exhibits a very high viscosity in toluene compared to that of PSAC. Addition of as little as 1% ethyl alcohol to the toluene solution of PSS sharply

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decreases the viscosity of the solution. Further increase of alcohol concentration brings about a much smaller change in viscosity until at around the 4.3% level the viscosity becomes close to that of PSAC in toluene. The latter does not exhibit any discernible change in viscosity when alcohol is added to its solution in toluene (curve 6, Figure 3). The effect of temperature on viscosity of PSS solutions at various alcohol levels is different. Thus at the 1% level viscosity increases with an increase in temperature while at the others (2.5–4.3%) it decreases with temperature. Similar observations from studies using the sulfonated ionomers have been interpreted on the basis of an exothermic solvation equilibrium involving alcohols and the salt groups.[21–23] At the 1% alcohol level solvation is incomplete and increasing the temperature desolvates some of the solvated species and increases the viscosity of the solution while at higher alcohol concentrations solvation is complete and sufficient excess alcohol is present so that increasing the temperature over a 30 °C span fails to desolvate the polymers and viscosity decreases with temperature as is usually expected for the variation of viscosity with temperature.

Finally, we would like to point out that previously persulfate initiated emulsion polystyrene was reported to have low sulfate functionality ($f \simeq 0.2$) as measured by the dye extraction method of analysis[9] According to the same analytical method the present polymers prepared in a different way analyzed to have a sulfate functionality of 1.8 ± 0.1. The reason for the difference in sulfate functionality between conventional emulsion polystyrene and polystyrene as prepared here is being looked into.

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Introduction of Nitrogen Functionality on Hydrogenated Butadiene/Styrene Copolymers

W. J. TREPKA

Research and Development Division, Phillips Petroleum Company, Bartlesville, Oklahoma 74004.

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Polymers containing functional groups are of interest because these groups can be sites for subsequent reactions, e.g., graft polymerization or for further modification. One method of preparing functional group containing polymers is by polymerization or copolymerization of functional monomers.[1,2] Another method is by chemical modification of a polymer. Platé, in a review,[3] discussed chemical modification of polymers and reactivity of functional groups on macromolecules, and more recently, 1982, Schulz, Turner, and Golub[4] extensively reviewed recent advances in the chemical modification of unsaturated polymers.

Butadiene homopolymer and butadiene/styrene copolymers contain olefin unsaturations that are active sites for chemical modification. Ethylene/propylene rubber (EP) contains no unsaturation and must be cured (cross-linked) by peroxides, but ethylene/propylene/diene rubber (EPDM) can be cured by sulfur because of unsaturation introduced by the diene termonomer.[5] Halasa[6,7] prepared anionic graft polymers by polylithiating polymer backbones with *n*-BuLi/*N,N,N′,N′*-tetramethylethylenediamine (TMEDA) complex. Complexation with TMEDA dramatically increased the reactivity of *n*-BuLi.[8] EPDM (ethylene/propylene/1,4-hexadiene terpolymer) was polylithiated and reacted subsequently with CO_2 to introduce carboxy functionality.[7] Waldbillig[9] prepared graft polymers of EPDM by the reaction of (dialkylamino)alkyl methacrylates with the polylithiated (*n*-BuLi/TMEDA) polymer.

Hydrogenated butadiene/styrene copolymer does not contain olefin unsaturation. The aromatic groups of the polystyrene must provide the active sites for functional modification. Cationic reactions such as chlorination and sulfonation are difficult to control and can result in gelled, highly cross-linked polymers. There are numerous examples of utilization of the aromatic activity of styrene for polylithiation. For example, divinylbenzene–styrene polymer was brominated smoothly in the presence of Tl(II) salt catalyst and the product easily lithiated by treatment with excess *n*-butyllithium.[10] The polymer also was directly lithiated with *n*-butyllithium and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) complex. The lithiated residues were converted subsequently to polymers containing $-CO_2H$, $-SH$, sulfide, $-B(OH)_2$, amide, silylchloride, phosphine, bromide, alcohol, and trityl groups, respec-

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