

Rigid Rod Water-Soluble Polymers

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SYNOPSIS

For many applications such as enhanced oil recovery, it is essential to have an extremely water soluble shear stable polymer that can impart high viscosity at very low concentration for economic reasons. It is known that rigid rod polymers can deliver high viscosity at low molecular weight compared with the traditionally used flexible chain polymers such as hydrolyzed polyacrylamides. Polymers with helical or double stranded conformations may be considered as truly rigid rod in solution. New sulfonated water soluble aromatic polyamides, polyureas, and polyimides were prepared via interfacial or solution polymerization of sulfonated aromatic diamines with aromatic dianhydrides, diacid chlorides, or phosgene. Some of these polymers had sufficiently high molecular weight (<200,000), extremely high intrinsic viscosity (~ 65 dL/g), and appeared to transform into a helical coil in salt solution. These polymers have been evaluated in applications such as thickening of aqueous solutions, flocculation and dispersion stabilization of particulate materials, and membrane separation utilizing cast films. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

There is a potentially large market for highly efficient water soluble polymers, particularly in enhanced oil recovery applications, drilling operations, oil well production, etc. Current water soluble polymers such as polyacrylamide, polyethyleneoxide, polysaccharides, etc., are all very high molecular weight flexible coil polymers. They suffer from loss of viscosity in solution due to shear, upon addition of ions, increasing temperature, or other environmental conditions. Clearly, therefore, there is a need for a new highly efficient water soluble polymer for enhanced oil recovery and for many other applications. To achieve this goal, one needs to develop a new concept from an understanding of the polymer structure-solution property relationship. In this article we present the development of a new concept of rigid rod water soluble polymers that should overcome the deficiencies of current polymers. We consider the origin of viscosifying efficiency of polymers in solution and expand on the different factors involved.

Viscosifying efficiency of a polymer is defined as the relative increase in the viscosity of a solvent per unit concentration of the polymer in solution at the temperature and shear rate of concern as shown in eq. (1):

$$\text{Efficiency} = \frac{\eta - \eta_s}{C} \quad (1)$$

where η = viscosity of the solution, η_s = viscosity of the solvent, and C is the concentration. In the absence of any intra- or intermolecular interaction (via secondary valence forces), this efficiency is a primary function of the hydrodynamic volume of the individual macromolecules in solution and the interpolymer entanglement.

Hydrodynamic size of a polymer is related to a measurable quantity named intrinsic viscosity, $[\eta]$, defined as

$$\begin{aligned} [\eta] &= \lim_{C \rightarrow 0} \left[\frac{\eta - \eta_s}{\eta_s C} \right] = \lim_{C \rightarrow 0} \left[\frac{\eta_{\text{rel}} - 1}{C} \right] \\ &= \lim_{C \rightarrow 0} \left[\frac{\eta_{\text{sp}}}{C} \right] = \lim_{C \rightarrow 0} [\eta_{\text{red}}] \quad (2) \end{aligned}$$

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where η_{sp} = specific viscosity and η_{red} = reduced viscosity, dL/g. In practice $[\eta]$ is obtained by extrapolating reduced viscosity values, obtained at $1.2 < \eta_{rel} < 1.5$, to zero concentration. Since shear rate during the viscosity measurement plays an important role, the intrinsic viscosity, particularly for high molecular weight samples should be measured at low shear rates. The higher the intrinsic viscosity of a polymer in a particular solvent system and at a temperature of concern the more efficient is the polymer.

The dependence of viscosity on molecular weight is a characteristic property of macromolecular solution and for the dependence of the intrinsic viscosity on molecular weight (M), one obtains¹:

$$[\eta] = KM^a \quad (3)$$

where K and a are constants whose values depend on the nature of the polymer, solvent, and temperature. This equation is considered as a general viscosity law of macromolecules and is sometimes called the "Mark-Houwink" or "Staudinger-Kuhn" equation. The value of K depends primarily on chain bond dimensions and on the freedom of rotation about them. The constant a depends on solvent, shape of macromolecule, volume demand of the chain (excluded volume effects), draining characteristics of the chain, etc. Solvent can also influence the value of K , especially when it alters the chain morphology.

In general, macromolecules in solution can be divided into three categories: 1) flexible coil, 2) rigid rod, and 3) rigid coil polymers. According to the theories of flexible linear polymers, the values of the exponent a in eq. (3) are limited to between 0.5 and 0.8.² For an ideal Gaussian coil in a θ (theta) solvent, in the absence of any external forces when the second virial coefficient is zero, i.e., the polymer-solvent interaction is nil, the value of the exponent is 0.5. For real flexible coils, which are subject to the chain expanding effect of a good solvent, thus causing expansion of the coil, the value of a gradually increases to a maximum value of 0.8.

Rigid rod polymers of length L and diameter d can be represented by a prolate ellipsoid (i.e., ellipse rotating about the major axis) of length l and diameter b by eq. (4) with l/b directly related to the molecular weight. According to the theory of Simha,³ for large values of l/b the intrinsic viscosity varies closely as $(l/b)^{1.8}$, i.e., as $M^{1.8}$. Thus, rod-shaped molecules should also obey the equation with the exponent at ~ 1.8 rather than 0.5–0.8.³ There are basically two different kinds of restricted axial rotation

leading to rigid rod conformation: helix formation and parallel bond formation.

$$\frac{l}{b} = \left(\frac{2}{3}\right)^{1/2} \frac{L}{d} \quad (4)$$

To complete the analysis of the dependence of $[\eta]$ on M , it is convenient to introduce a concept of a stiff chains, which may be considered as intermediate between completely rigid rod and flexible coils, for which the exponent a is 0.8–1.8. Although there are considerable examples of polymer systems in which $0.8 < a < 1.8$, some theories for such a rigid coil (also sometimes referred to as "worm-like") have been developed.⁴ It is believed that these molecules in solution have partial rod like character along the backbone giving rise to increased expansion of the chain (rod-like behavior), very large excluded volume effect or very large draining effects.

Thus, it is apparent from the previous discussion that a polymer of higher efficiency or intrinsic viscosity can be obtained for the same molecular weight if one can produce rigid rod polymers with a high Mark-Houwink coefficient. Figure 1 illustrates the intrinsic viscosity versus molecular weight relationship for three different polymers. Line A is for polyacrylamide in water (highly flexible coil), line B is expected for a polymer that is a helical rigid rod, and the line C is expected for a rigid rod polymer with low mass per unit contour length as in a parallel bond polymer. If one wants a polymer having intrinsic viscosity of 20 dL/g, one would need a polyacrylamide of 7 million in molecular weight. Whereas for a helical rigid rod polymer and a parallel bond rigid rod polymer, one would need much lower molecular weights of 200,000 and 15,000, respectively. Therefore, if one could make water-soluble polymers with rigid rod characteristics via introduction of water-solubilizing groups, such as sulfonates, sulfates, hydroxides, amides, amines, quaternary ammonium, ethers, etc., onto polymers that are expected to have rigid rod characteristics, one would obtain a new class of water soluble polymers with unique properties. Xanthan gum, a biosynthetic polymer, is a very unique polymer being sold currently. This polymer has been characterized as a helical polymer with high shear, salt, and temperature stable viscosity. However, its intrinsic viscosity decreases drastically on increasing salt concentration, suggesting some shrinkage of the polymer coil.

The advantages of a rigid rod polymer are as follows. As long as the rigidity is not solvent induced, the intrinsic viscosity and relative viscosity should

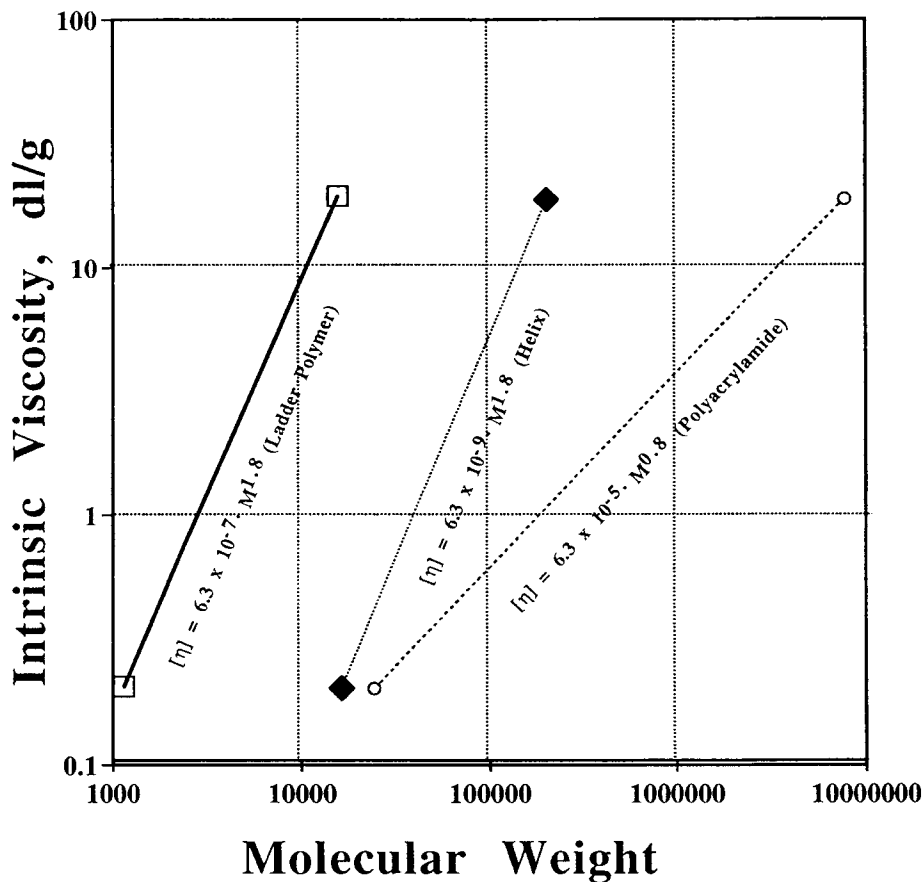


Figure 1 Intrinsic viscosity versus molecular weight relationship for polymers having different Mark-Houwink constants.

be independent of solvent, temperature, and other environmental conditions. Second, highly efficient viscosifying ability at much lower molecular weight. Third, since the molecular weights are going to be low, the polymer should be resistant to shear degradation. Fourth, since the approach is expected to be synthetic, the polymer is expected to be stable toward biological activity. Finally, rigid rod polymers exhibit different rheological behavior from flexible coil polymers, i.e., they are more pseudoplastic, which may be of use in many applications.

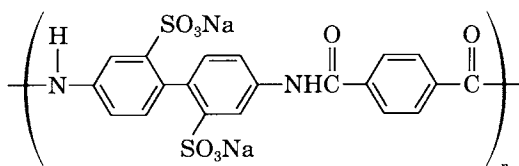
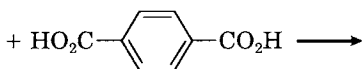
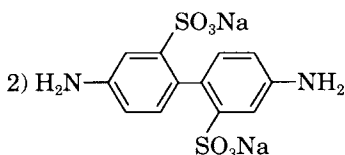
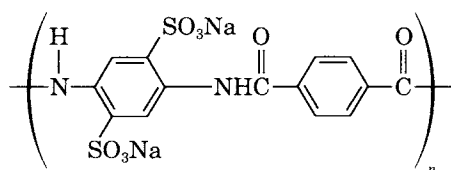
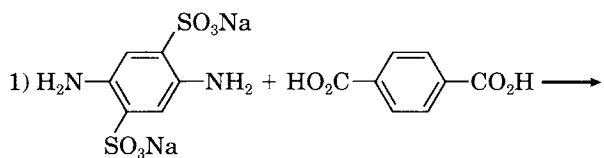
One disadvantage that can be expected of these polymers is their tendency to form liquid crystals leading to precipitation in extreme cases. This liquid crystalline state may also be very interesting and useful in some applications: We now consider briefly polymers with rigid backbones. One area of polymer chemistry getting considerable attention lately is thermally stable polymers.⁵⁻⁷ Many of these thermally stable polymers are presumed to be rod-like. Polymers with backbones comprised of cyclized

chains, inflexible bonds, and polymers containing bulky pendant groups may provide examples of such inflexible polymers. Many of these are novel plastic materials and are infusible and insoluble in most solvents. Some of these polymers are soluble and stable in strong acids (such as 98% sulfuric acid, methane sulfonic acid). They are presumably polyelectrolytes in the strong acids because of extensive protonation, and it is probably this protonation that renders them soluble. By the same token, many of these polymers may yield water solubility upon sulfonation of the appropriate groups. Synthesis of polymers of these types by using presulfonated monomer is also an alternative to obtaining water soluble rigid rod polymers.

Polyamides are an interesting class of polymers where depending on the molecular composition and the orientation of the successive monomer units, one can obtain the extremes of random orientation (flexible coil in the case of Nylon 6,6) to the perfect order (the rigid rod for helical polypeptide) with ar-

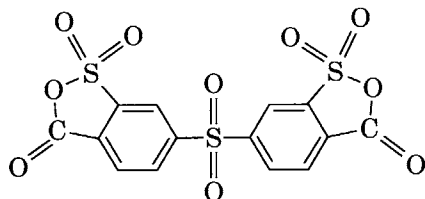
omatic polyamides being somewhat a stiff chain type.

If one synthesizes aromatic polyamides and renders them water soluble via sulfonation of the aromatic ring, one would obtain a stiff chain polymer. These polyamides may also transform into helices via hydrogen bonding between amide linkages as in polypeptides when the solvent becomes poorer, such as in brine. The examples of polyamide sulfonates are as follows:



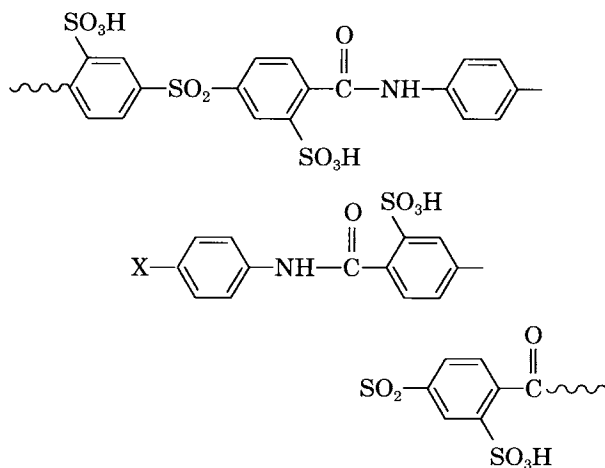
By a similar token polyureas ($-\text{Ar}-\text{CO}-\text{NH}-\text{CO}-\text{Ar}-$) and polyisocyanates ($-\text{NAr}-\text{CO}-$), where Ar stands for aromatic group, may also form helices considered to be rod-like.

Other than natural polymers, examples of synthetic water-soluble polymers that may have inflexibility of the backbone are very rare. Vollmert¹ made a new monomer from toluene and H_2SO_4 :



By reaction of this anhydride with aromatic di-

amines, such as benzidine, 4,4-diaminodiphenylsulfone, a strong polyelectrolyte, polyamide sulfonic acid with regular chain structure of $\text{MW} > 30,000$, could be prepared:



Neher⁸ made some polyureas via the reaction of phosgene with a variety of sulfonated aromatic diamines. These polymers were water soluble as ammonium salts had cation exchange properties and were highly colored. They were claimed to be useful against certain virus diseases in animals. Thoma et al.⁹ synthesized a group of alternating copolymers from similar sulfonated diamines and aromatic diisocyanates. Sodium salts of most of these polymers were water soluble. Although there are a number of examples of rigid rod polymers in the literature, these few mentioned above are the only water-soluble rigid polymers we could find.

EXPERIMENTAL

Interfacial Polymerization Procedure

The following procedure was typical for interfacial polycondensation reactions carried out to obtain polyamide systems. The equipment consisted of a 1-quart Waring Blender that had been modified with a nitrogen purge to the motor compartment to prevent possible ignition of flammable organic solvents. The jar was placed on the blender base, the opening was covered with aluminum foil, the cover was put in place, and a glass addition funnel was placed through the cover opening and the foil.

To the jar was added 200 cc of deionized water (DI) and 2.65 g (0.025 mol) of sodium carbonate. This was stirred slowly until the solid had dissolved. Then slowly with stirring, 2.1523 g (0.00625 mol) of

purified diaminobenzidine disulfonate or other sulfonated diamines (DABS) was added and this was rinsed in with 50 cc of water. This gave a clear solution of the DABS disodium salt.

A second solution was prepared by adding 2 g of polyethyleneglycol 200 diisostearate surfactant to 100 cc of purified chloroform. A third solution was prepared of 1.238 g (0.00625 mol) of purified terephthaloyl chloride (TPC) in 100 cc of purified chloroform.

The reaction sequence was carried out by turning the blender containing the DABS/Na₂CO₃ solution on high speed, adding the surfactant/CHCl₃ and allowing the emulsion to form by agitating for 30 s on high speed. The TPC/CHCl₃ solution was then added in one portion, and the blender was switched to low speed. The reaction mixture was blended for 15 min and then allowed to stand off the blender base unagitated for an additional 15 min.

The thickened mixture was transferred to a flask and diluted with 200 cc of water. The polymer was precipitated with 500 cc of acetone and filtered under suction using a polypropylene filter in a Buchner funnel. It was redissolved in 150 cc of water, again precipitated with 500 cc of acetone, and filtered. The procedure was followed twice more using 100 cc of water, 300 cc of acetone and 200 cc of water and 500 cc of acetone, respectively.

The repeated precipitations gave polymer free of carbonate and chloride salts. The wet polymer was dried at 40°C to give a 1.6 g white fibrous solid at 49.3% yield. This material had an intrinsic viscosity of 23.0 dL/g.

Aqueous Solution Polyurea Preparation

A typical phosgenation procedure to DABS polyamide would be carried out as follows and as outlined in Figure 2. To 41.33 g (0.12 moles) of purified DABS was added 500 cc of deionized water in a phosgenation reactor. The initial slurry had a pH of 2–3. To

this was added a total of 41.25 cc of 20% aqueous NaOH. During this time, the DABS went into solution as the disodium salt. The resulting pH was 7.0. The reactor temperature was maintained at 12–15°C as 10 g (0.1 mol) of gaseous phosgene was added over a 10-min period. The pH was maintained constant at pH 7 by addition of 20% NaOH controlled by the pH stat. At this point, additional water was added to reduce the solution viscosity and maintain adequate stirring. An additional 12 g (0.12 mol) of phosgene and 1700 cc of water were added in the next 29 min. At this time, the phosgene addition was stopped, the reactor pH raised to 10, and the mixture agitated to react any excess phosgene. A total of 100.25 cc of 20% NaOH were consumed during the reaction.

The reactor was rinsed with 150 cc of water and 500 cc of acetone. The mixture was filtered and precipitated with 2100 cc more acetone. The mixture was filtered and the wet polymer blended with one liter of CH₃OH and filtered. This process was repeated twice more. After drying, this gave 50 g of DABS polyurea disodium salt in essentially quantitative yield.

Interfacial Polyurea Polymerization

The reaction to prepare poly-4,4'-biphenylurea-2,2'-disulfonic acid disodium salt (DABS-U Na) was similar to polyamide preparation and was carried out by initially preparing an emulsion of 100 cc of deionized water, 40 cc of chloroform, and 0.8 g of polyethylene glycol 200 diisostearate in a Waring Blender jar. This was placed in a stirred reactor maintained at 50°C. A second solution of 10.332 g (0.03 mol) of DABS, 9.8 cc of 20% sodium hydroxide, and 97.7 cc of deionized water was prepared. A third solution of 23 g (0.23 mol) of phosgene in 179 g of chloroform was prepared.

The DABS and phosgene solutions were added simultaneously to the stirred reactor containing the

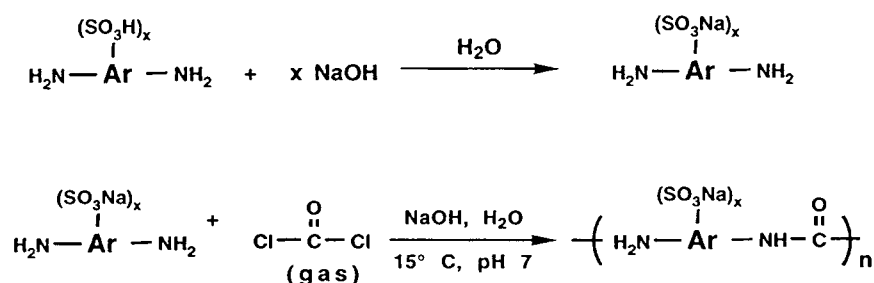


Figure 2 Synthetic route for the preparation of sulfonated aromatic polyureas.

emulsion over a period of 53 min. During this time, the temperature was maintained at 13–15°C with external cooling, pH at 7.0, by addition of 20% sodium hydroxide and stirring at 550 ppm.

After the addition of the DABS solution was complete, the solution viscosity increased. Phosgene addition was continued until a total of 4.066 g (0.041 moles) had been added. A total of 300 cc of deionized water was added to decrease the viscosity of the solution.

The pH was raised to 10 and the polymer was precipitated with 500 cc of acetone, filtered, and methanol washed. The polymer was redissolved in 200 cc of water and precipitated a second time with acetone. Filtration washing and drying gave 7.3 g (70.1% yield) of DABS-U Na. The viscosity of a 1 wt % solution of this polymer in deionized water was 4 mPa·s.

RESULTS AND DISCUSSION

The approach in this study had been to synthesize some model polymers based on available raw materials and of expected rigid rod behavior. Aromatic polyamides and polyureas were therefore synthesized from sulfonated diamines and aromatic acid chloride. Tables I and II show the structure of these polymers and their molecular weight as related to 1% solution viscosity at 25°C in DI water measured using Brookfield LVT viscometer and either a small sample adapter or a UL adapter. As it is seen, polyamides made from monosulfonated phenylene diamine and tere- or iso-phthaloyl chlorides were not soluble in water. Polymers made from disulfonated paraphenylene diamine and terephthaloyl chloride were only of oligomeric nature and formed extremely brittle films. No further evaluation of these polymers were done. Synthesis and application of these polymers are covered by a U.S. patent.¹⁰

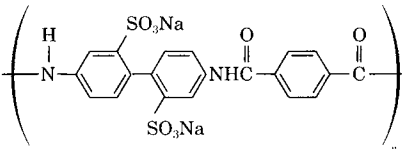
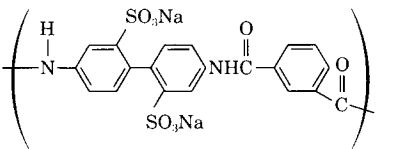
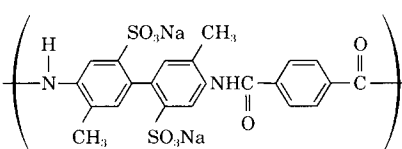
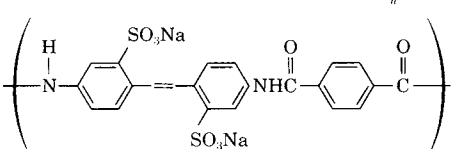
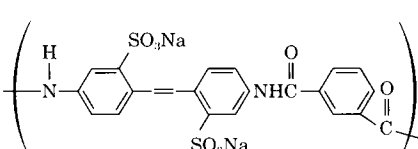
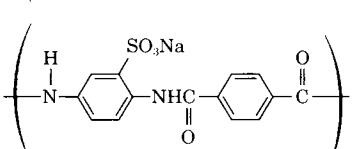
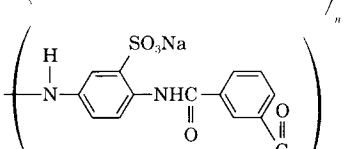
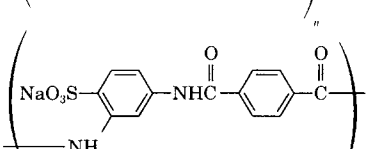
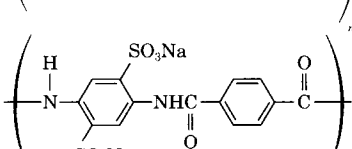
Polyamide made from diaminostilbene disulfonate and tere- or iso-phthaloyl chloride were of extremely high viscosity in DI water. Assuming that condensation polymers can hardly have molecular weight in excess of 200,000, these polymers in DI water can be presumed to be of rigid rod type. Unfortunately, these stilbene based polymers precipitated out of solution on addition of NaCl in excess of 0.2%. Detailed studies on these polymers were not therefore carried out. Polyamides made from DABS and isophthaloyl chloride also produced only low molecular weight polymer (1% solution viscosity in DI water of up to 27 mPa·s). On the other hand,

polyamides from DABS and terephthaloyl chloride could be produced with varying molecular weight up to 2500 mPa·s viscosity for 1% solution in DI water. This could be achieved by varying purity of the monomers, type of surfactant, type of organic phase, concentration of monomer in the reaction mixture, for example. Polyamides made from 4,4'-diamino-3,3'-dimethyl biphenyl-2,2'-disulfonic acid (DMBS) and terephthaloyl chloride were also produced with reasonably high molecular weight but not to the extent exhibited by DABS, presumably because of the steric hindrance of the methyl groups of DMBS. Here, we discuss detailed results on poly-4,4'-biphenyl-2,2'-disulfonic acid terephthalamide, disodium salt (PBDT), with only few comments on the other polyamides.

Intrinsic viscosity of these polyamide sulfonates were measured in a No. 100 Ubbelohde dilution capillary viscometer at 25°C. The concentration of the polymer solution is adjusted by trial and error to produce a viscosity of about 2.0 mPa·s. Exactly 7 mL of this solution is placed in the viscometer and the elapsed time (t_e) measured. The solution is then diluted by consecutively adding solvent and measuring elapsed time after each dilution. Reduced viscosity $[(t_e/t_s) - 1]/c$, where t_s = elapsed time for solvent, c = concentration of polymer in g/dL, is then plotted against concentration of polymer. For most polymers, this produces a linear plot with positive slope, and extrapolation of reduced viscosity to zero concentration produces the intercept called intrinsic viscosity. There is a deviation of this behavior for a flexible chain in deionized water, where at higher concentration reduced viscosity first decreases with decreasing concentration and then increases sharply on further dilution. This anomalous behavior is due to great expansion of the chain as the ionic strength falls due to the decrease in polyelectrolyte concentration. Expansion of the polymer is so great that at infinite dilution in DI water the polymer behaves as a rod shaped rather than a flexible coil polymer.¹¹ Upon addition of salt, there is a considerable decrease in reduced viscosity and intrinsic viscosity signifying decrease in polymer size due to shrinkage of the coil.

Figures 3–5 show the reduced viscosity versus concentration plots for PBDT of three different molecular weights measured both in DI water and in 3% NaCl solution. The low molecular weight polymer (Fig. 3) shows no effect of salinity on reduced viscosity. The higher molecular weight polymers, on the other hand (Figs. 4 and 5), exhibit quite unusual behavior. In DI water, the polymers

Table I Structural Variations in Sulfonated Aromatic Polyamides^a

Polymer Structure	Water Solubility	1% Solution Viscosity (mPa · s) ^b
	Yes	3–2500 (2) {MW = 70M–160M} [η] = 0.5–65 dL/g
	Yes	27 (8) {MW = 114M}
	Yes	245 (2)
	Yes	3400
	Yes	5500
	Colloidal	28 (8)
	Colloidal	4.3 (8)
	Colloidal ^c	3.3 (8)
	Yes	1.1 (8)

^a Polymers were prepared by interfacial polymerization in CHCl₃/H₂O using PEG 200 surfactant.

^b Numbers in parenthesis are the shear rates in s⁻¹ at which the determinations were carried out.

^c Aerosol TR 70 was used as the surfactant.

Table II Summary of Data for Sulfonated Aromatic Polyureas

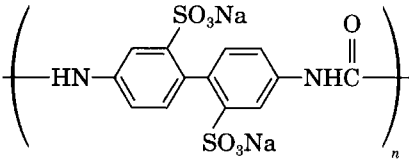
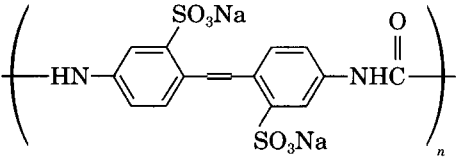
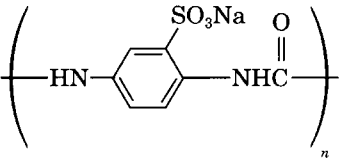
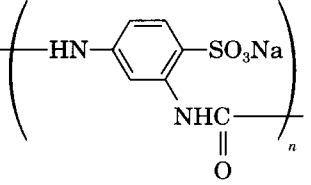
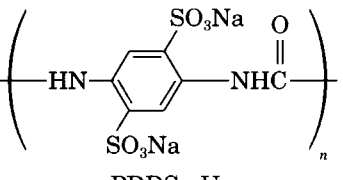
Polyurea Structure	Range of 1% Solution Viscosity (mPa·s)	Film Forming Ability	Solubility Behavior
 <p>DABS · U</p>	2.3–9.5 MW = 50M–100M	Strong clear films	Water soluble, cloudy in 3% NaCl
 <p>DASS · U</p>	1.8–2.5	Yellow brittle films	Water soluble, soluble to 10% NaCl
 <p>PDAS · U</p>	1.1–2.4	Films shatter during preparation	Water soluble, soluble to 2% NaCl
 <p>MDAS · U</p>	Low	Non-film forming	—
 <p>PDDS · U</p>	Low	Non-film forming	—

exhibit a polyelectrolyte effect, i.e., an upturn of the curve on dilution. Upon addition of 3% NaCl, the reduced viscosity increases significantly instead of showing a decrease as in the case of flexible polymers. Extrapolation of both these curves to zero polymer concentrations appears to exhibit the same intrinsic viscosity values. Since it has been postulated that at infinite dilution in DI water, polyelectrolytes assume rigid rod behavior and since the intrinsic viscosity in 3% NaCl is the same as in DI water, it is presumed that the PBDT may have a relatively flexible coil character in DI water but

transforms into a rigid rod polymer upon addition of salt. It is quite likely that the polymer transforms into helices in the presence of salt where repulsive interactions between neighboring sulfonate groups are reduced.

Figure 6 shows the reduced viscosity versus concentration relation for a sample of PBDT at different salt concentrations. The polyelectrolyte effect is seen at zero salt concentration. Upon addition of only 0.05% NaCl, the polyelectrolyte effect is eliminated. There is a decrease in reduced as well as intrinsic viscosity values up to a salt concentration of 0.1%,

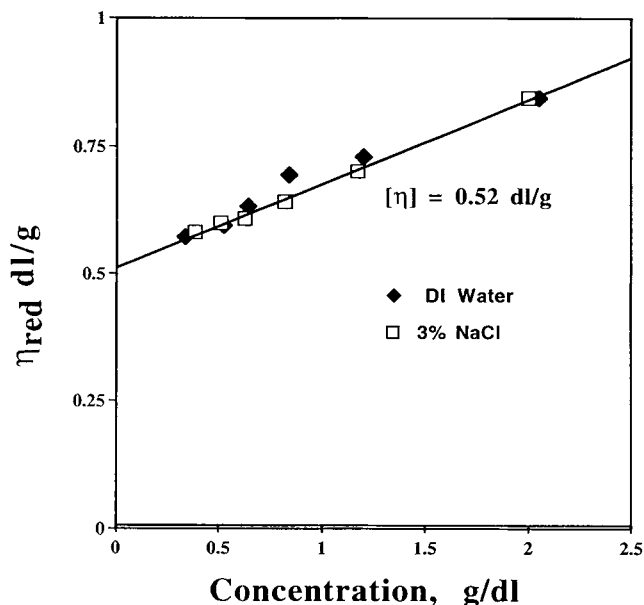


Figure 3 Reduced viscosity versus concentration curve for a sample of low molecular weight poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) at 25°C in DI water and 3% salt solution.

above which there is an increase in the both reduced and intrinsic viscosity values reaching a maximum at 2% NaCl. There is then a decrease again on further increase in salinity. Figure 7 shows this behavior

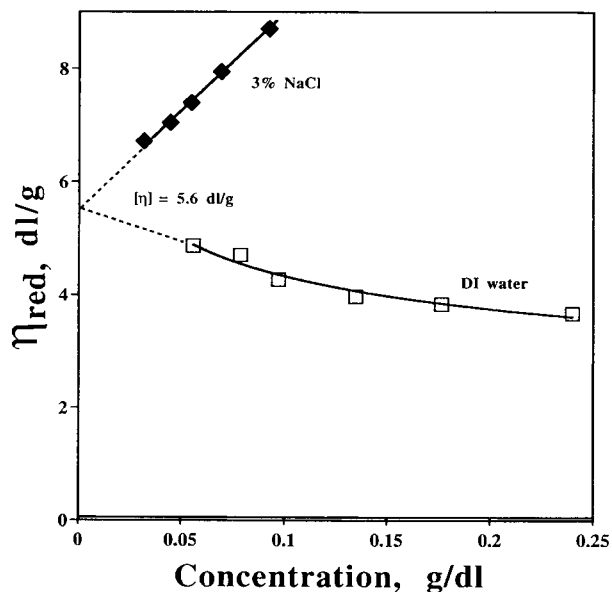


Figure 4 Reduced viscosity versus concentration curve for a sample of medium molecular weight poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) at 25°C in DI water and 3% salt solution.

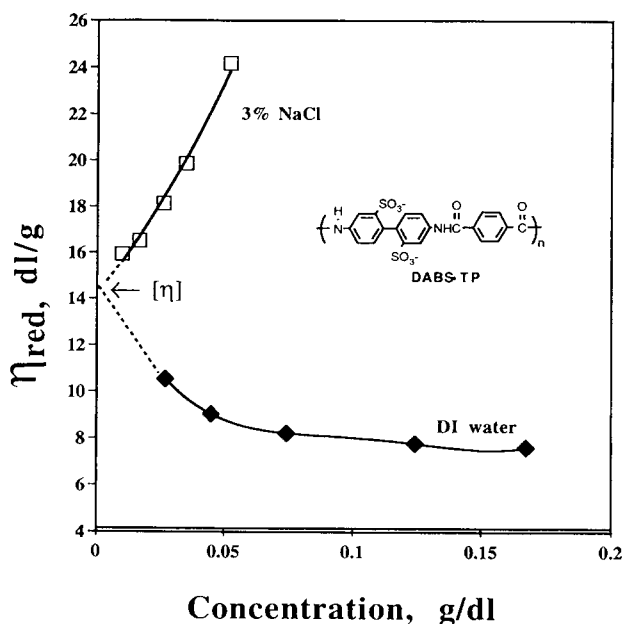


Figure 5 Reduced viscosity versus concentration curve for a sample of high molecular weight poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) at 25°C in DI water and 3% salt solution.

clearly when intrinsic viscosity is plotted against concentration of NaCl. Again it shows that in DI water the polymer assumes rigid rod characteristics

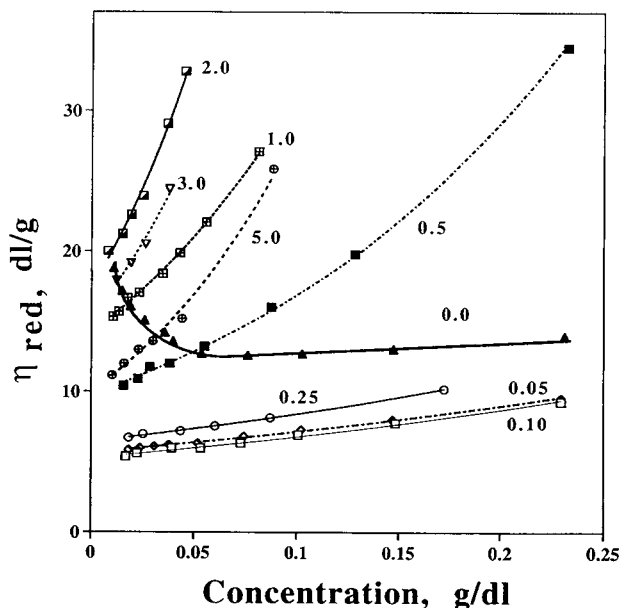


Figure 6 Reduced viscosity versus polymer concentration for a sample of poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) in different weight % sodium chloride solutions at 25°C.

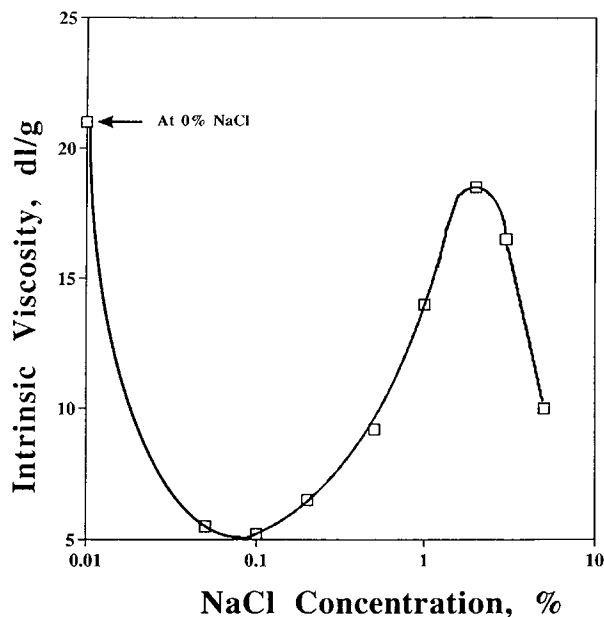


Figure 7 Intrinsic viscosity of poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) as a function of sodium chloride concentration in solution at 25°C.

due to expansion of the polymer. Upon addition of salt, there is an initial decrease in intrinsic viscosity apparently due to shrinkage of the coil. This is followed by a sharp increase in intrinsic viscosity, apparently due to transformation to a helical conformation, that comes to a maximum at 2% NaCl. Further increase in salt concentration leads to aggregation of the helices resulting in a decrease in intrinsic viscosity and eventual precipitation of polymer.

Since extrapolation of reduced viscosity to zero concentration is difficult in the presence of DI water, determination of intrinsic viscosity in DI water was always carried out using Fuoss equation as shown in Figure 8. Figure 9 shows the relationship between the 1% solution viscosity and the intrinsic viscosity for several PBDT samples in DI water.

Figure 10 shows the relationship between 0.25% solution viscosity and salt concentration for PBDT and poly-3,3'-dimethyl-4,4'-biphenyl-2,2'-disulfonic acid terephthalamide, disodium salt (PDMBDT). It is observed that the presence of the methyl groups make the polymer change to a helical conformation at a higher salt concentration and exhibit less drastic viscosity increase with salt concentration. On the other hand, PBDT exhibits a 100-fold viscosity increase at 2% NaCl concentration. Figure 11 compares the viscosity of a PBDT samples in 3% salt and DI water as a function of polymer concentration

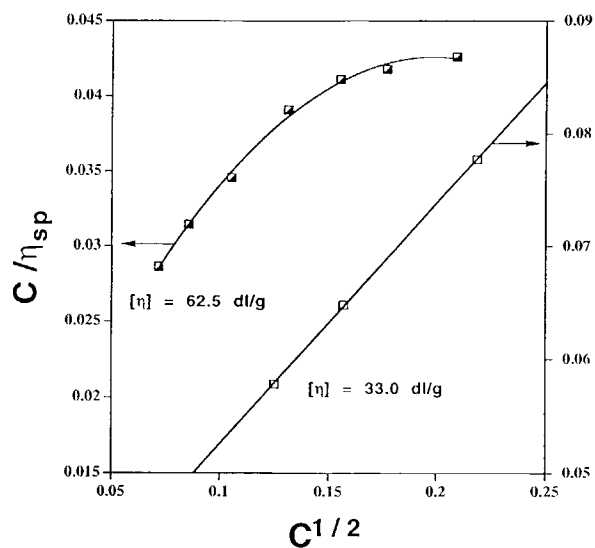


Figure 8 Plot of Fuoss eq.: $C/\eta_{sp} - 1/[\eta] + BC^{1/2}$ to obtain intrinsic viscosity, $[\eta]$, in DI water at 25°C.

showing a large increase in viscosity in the presence of salt.

Figure 12 shows the rheological behavior of the high molecular weight PBDT sample. Solutions in 3% NaCl not only show extreme efficiency but also exhibit a highly pseudoplastic and thixotropic nature that is characteristic of rigid rod polymers.¹² Solutions in DI water do not show such thixotropic behavior and exhibits less pseudoplasticity. Solutions

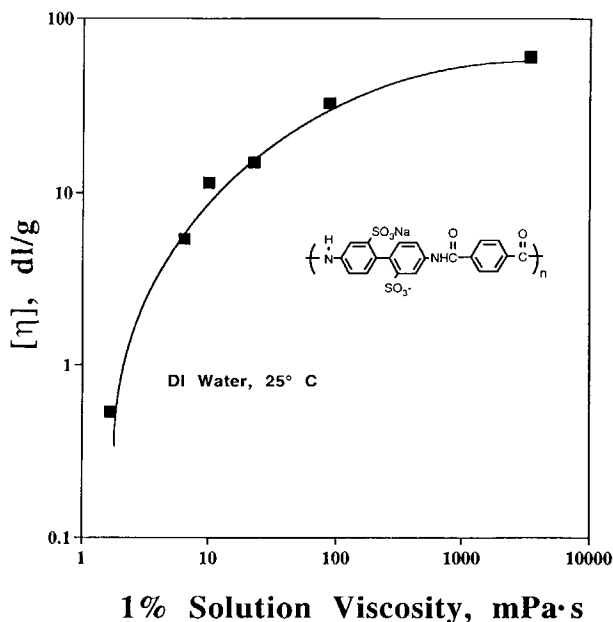


Figure 9 Intrinsic viscosity of polyaramide as a function of their 1% solution viscosity in DI water at 25°C.

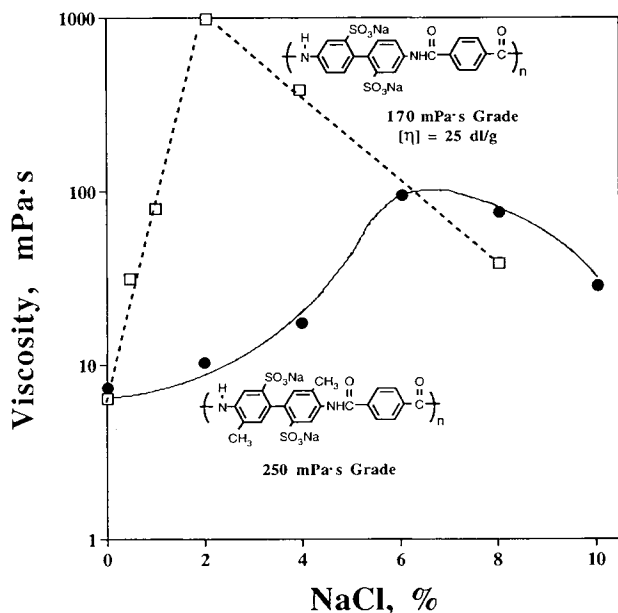


Figure 10 Viscosity of 0.25% solution of two different types of polyaramides in water as a function of sodium chloride concentration in solution at 25°C.

in 3% NaCl also exhibit yield stresses indicating the presence of aggregates or gel type structures in solution.

Figure 13 shows the viscosity enhancement of 0.25% PBBDT by different salts. KCl and NaCl ap-

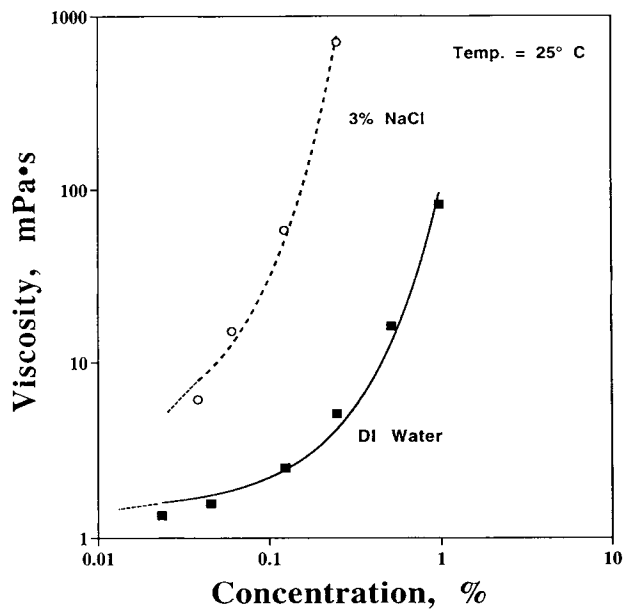


Figure 11 Viscosity of a poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) sample with intrinsic viscosity of 25 dL/g as a function of concentration at 25°C.

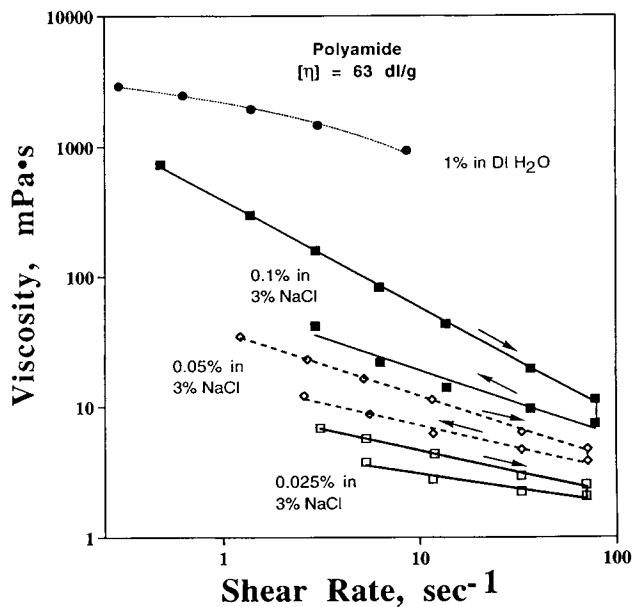


Figure 12 Viscosity versus shear rate curves for a poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) sample with intrinsic viscosity of 63 dL/g at different concentrations in 3% NaCl solution as compared with 1% solution in DI water at 25°C.

pear to exhibit similar viscosity enhancements, LiCl shows a somewhat lower viscosity enhancement. CaCl₂ also shows viscosity enhancement but at a much lower concentration. If the CaCl₂ concentra-

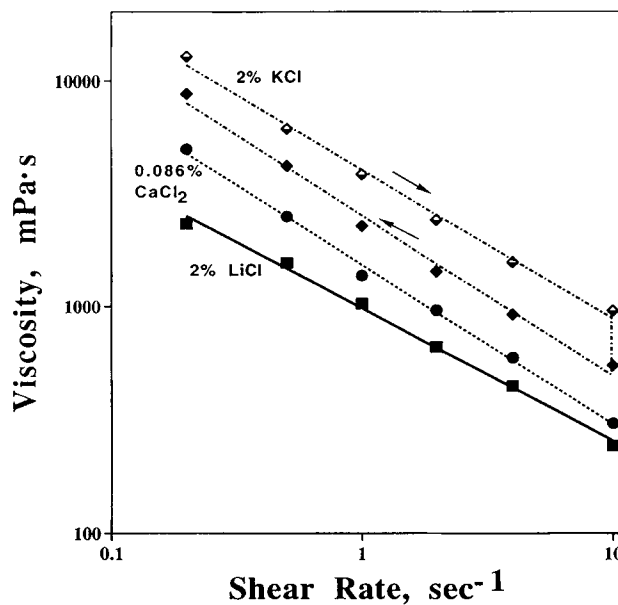


Figure 13 Viscosity versus shear rate curves for a poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) sample in different salt solutions at 25°C.

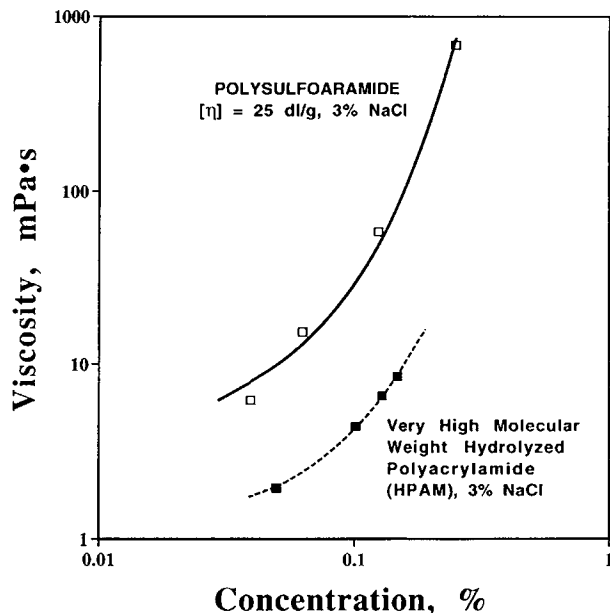


Figure 14 Comparison of viscosity versus concentration curves for a sample of poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) with intrinsic viscosity of 25 dL/g with a very high molecular weight hydrolyzed polyacrylamide sample.

tion exceeds 0.1%, there is a precipitation of the polymer taking place apparently due to binding of one calcium ion with two adjacent sulfonate groups of the polymer.

Figures 14 and 15 compare the rheological efficiency of PBDT with a high molecular weight hydrolyzed polyacrylamide sample (HPAM), xanthan gum, and a hydrophobe association polymer, exhibiting the superiority of PBDT over the other polymers. Figure 16 compares the rheological behavior of a 0.25% PBDT sample in 2% NaCl with a typical 6% bentonite mud used for oil well drilling. The presence of a yield value, extreme pseudoplasticity, i.e., high viscosity at low shear rate and low viscosity at high shear rate, makes PBDT a suitable candidate not only as a clear drilling fluid, but for other applications such as fracturing of oil well, water control of underground formations, etc.

Figure 17 shows that when a solution of high molecular weight HPAM is stirred in a Waring blender, there is a considerable degradation of the polymer as evidenced from a permanent viscosity loss. Compared with that a PBDT solution shows no viscosity loss. This stability toward shear could be due to the fact that PBDT polymers are of low molecular weight (<200,000) compared with the HPAM whose average molecular weight is around 10 million.

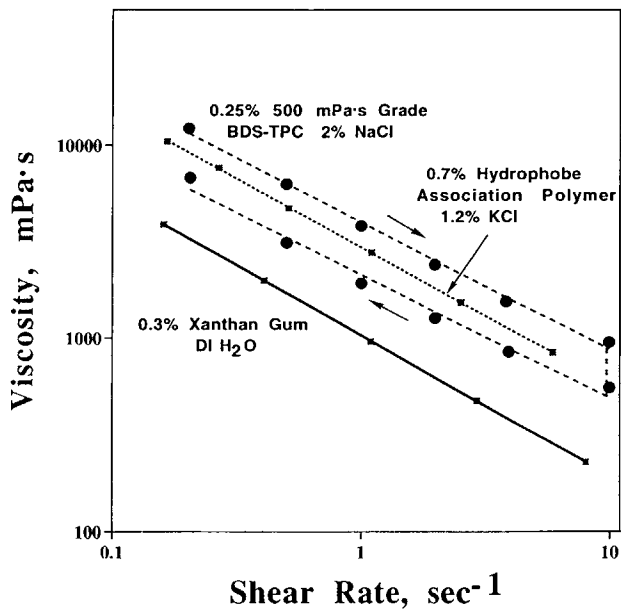


Figure 15 Comparison of poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) polymers with other polymer systems.

Another class of model water soluble polymers synthesized were aromatic polyureas. These were made by reacting an aromatic diamine sulfonate in water with phosgene under a constant pH 7. The various diamines used were as follows:

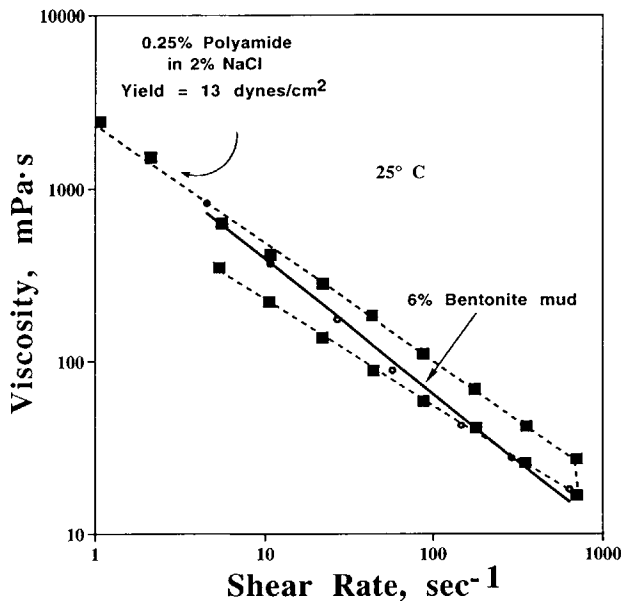
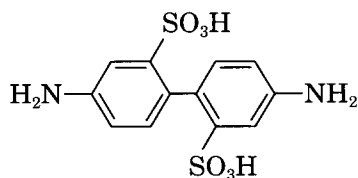
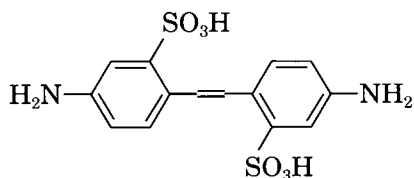


Figure 16 Comparison of a poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) polymer with 6% Bentonite mud used for drilling of oil wells.

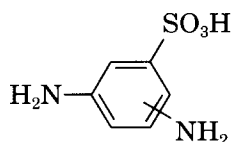
1) 4,4'-Diaminobiphenyl-2,2'-disulfonic acid



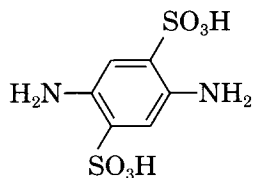
2) 4,4'-Diaminostilbene-2,2'-disulfonic acid



3) Para or metadiaminobenzene sulfonic acid



4) 2,5-Diaminobenzene-1,4-disulfonic acid



Except for No. 1, all the polyureas produced were of very low molecular weight as evidenced from their brittle yellow films and maximum viscosity of only 4.1 mPa·s for a 1% solution in DI water. Although clear films could be obtained with benzidine disulfonate polyurea, the maximum viscosity achieved was only about 9.5 mPa·s for a 1% solution, making none of the polyureas candidates for thickeners. However, the utility of these polyureas as well as the polyamides were investigated as candidates for water selective membranes, dispersants in coal water slurry, and as grinding aids.

When one plots log viscosity versus log concentration, one usually sees a curve with gradually increasing slope, as shown in Figures 11 and 14. Figures 11 and 14 cover up to a concentration of only 1%. To assess what might be happening at higher concentration, a low viscosity grade PBDT was chosen (otherwise the viscosity becomes too high to make proper measurements). Figure 18 shows a peculiar behavior of this polymer, i.e., the polymer shows an increase in viscosity first, it comes to a maximum, and is then followed by a decrease in vis-

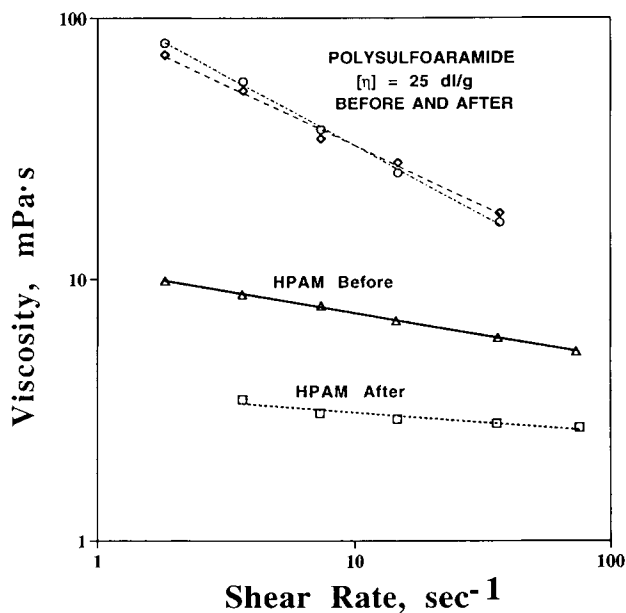


Figure 17 Comparison of the shear degradation of 0.1% polymer in 3% NaCl solution of a poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) sample with that of a high molecular weight hydrolyzed polyacrylamide sample when both were put into a Waring blender at 25°C and low speed for 5 min.

cosity on increasing concentration and finally exhibits a slow rise again. Above the maximum the solution gradually turns pearlescent. This phenomenon for other polymers has been attributed to the formation of polymeric liquid crystals formed at or above a critical polymer concentration. Presumably by analogy PBDT forms liquid crystals in aqueous solution. As shown in Figure 19, this phenomenon of liquid crystal formation could not be observed with polyamide made from benzidine disulfonic acid and isophthaloyl chloride or polyurea made from benzidine disulfonic acid.

Sulfonated polyamides and polyureas could be cast into clear strong films. Film casting is carried out from a viscous solution on glass, polished stainless steel, or corona treated mylar film depending on the chemical nature of the polymer. Polyamides adhere too strongly to glass or corona treated mylar; polished stainless steel or chrome plated steel is desirable for them. Polyureas, on the other hand, can be cast onto glass. All these films exhibit microcrystalline (i.e., crystal size less than 50 Å) behavior according to X-ray diffraction studies. Films of PBDT are somewhat hazy and opalescent and exhibit the sharpest X-ray diffraction peak. A benzidine disulfonic acid polyurea sample was converted

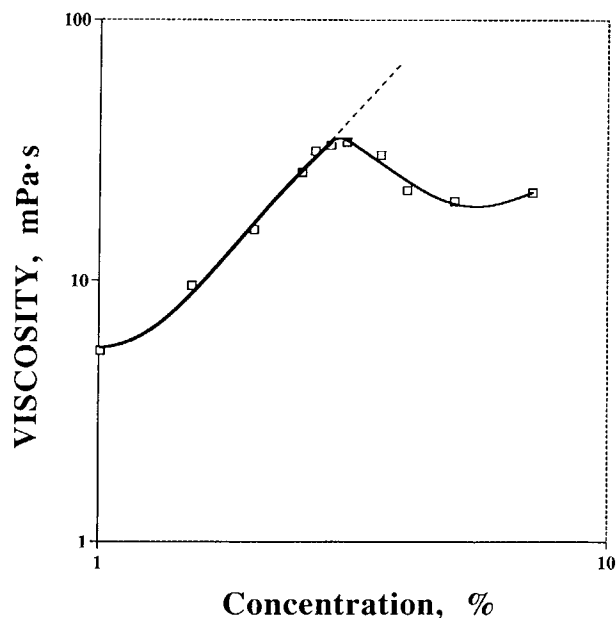


Figure 18 Viscosity of a poly(4,4'-biphenylene-2,2'-disodium sulfonate terephthalamide) sample as a function of concentration at 25°C.

to a mixed sodium and tributylamine salt by treating the solution of polyurea in water with H^+ form of ion exchange resin and then neutralizing with NaOH and tributylamine. Five percent solutions of these polymers were made in solvent based on composition. For example, 75 and 100% Na forms were soluble in water, 50 : 50 Na/NBu₃ is soluble in a mixture of 75% water and 25% acetonitrile, 25 : 75 Na : NBu₃ is soluble in a mixture of 67% water and 33% acetonitrile, and the 100% NBu₃ form is soluble in 67% water and 33% acetonitrile. Except for the 100% NBu₃ form, these polymers formed clear strong films. The 100% NBu₃ form precipitated out during drying of the cast film and was not obtained in a coherent form. All films studied were tested for pervaporation of ethanol-water mixtures, and permeability for water and oxygen.

In pervaporation, ethanol containing 10% water is placed on one side of a membrane while vacuum was drawn on the other side. The gases on the vacuum side were analyzed via mass spectrometry for ethanol and water. Table III shows the data for PBDT and BDS-polyurea and compares with CMC/SPA (a blend of carboxy methyl cellulose and sodium polyacrylate). These data show the overwhelming superiority of the polyurea sample in both selectivity and total permeation rate in concentrating ethanol.

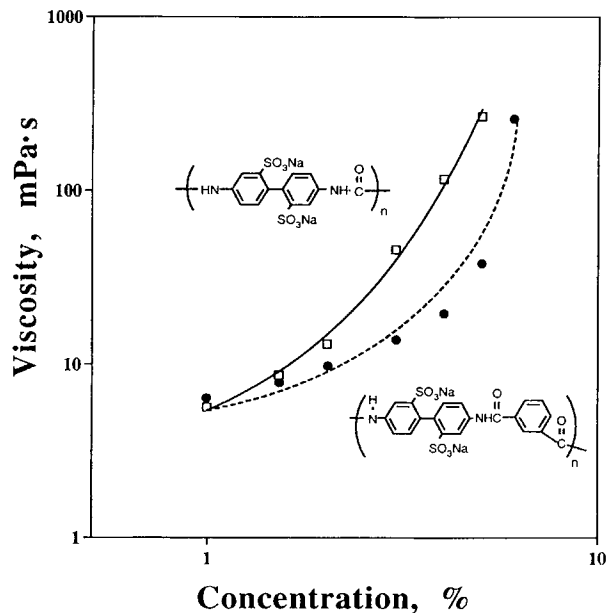


Figure 19 Viscosity versus concentration curves for a polyurea sample and a sample of polyamide made from isophthaloyl chloride and benzidine disulfonate.

Water vapor transmission rates and oxygen permeability were also determined for these films at 25°C and 60% relative humidity using Permatron W and Oxtran 10-50, respectively (both made by Modern Controls Inc., Minneapolis, MN). For comparison, several other films of both water soluble polymers and perfluorinated membranes of commercial interest were included. Table IV shows the data for all these polymer membranes. Polyurea and polyamide samples show extremely high water permeation and extremely low oxygen permeation to give a very high selectivity for separating moisture from oxygen. Data on Nafion also looks good. These data indicate the utility of these membranes for drying of compressed air, natural gas, carbon diox-

Table III Pervaporation Performance of Rigid Rod Polymers^a

Membrane	Water Selectivity ^b	Total Permeation Rate (G · mil/m ² · h)
CMC/SPA	196	14.75
PBDT	60.8	111
BDS Polyurea	1723	204

^a 90/10 EtOH/water feed.

^b $\alpha = \frac{(\text{wt fraction water/wt fraction EtOH}) \text{ in permeate}}{(\text{wt fraction water/wt fraction EtOH}) \text{ in feed}}$

Table IV Water and Oxygen Permeability of Different Membranes at 25°C and 60% Humidity

Polymer	$P_{H_2O} \cdot 10^{10}$ cc(STP) · cm (cm ² · s · cm · Hg)	$P_{O_2} \cdot 10^{10}$ cc(STP) · cm (cm ² · s · cm · Hg)	$a \times 10^{-6}$ P_{H_2O}/P_{O_2}
BDS-polyurea ^a	99,450	0.029	3.43
BDS-IPC polyamide ^b	122,550	0.038	3.23
BDS-TPC polyamide ^c	37,070	0.026	1.43
Nafion	239,320	19.7	0.012
Polyacrylamide	3538	0.0058	0.61
Methocel ^d E5 cellulose ether	3259	0.41	0.008
Polyvinylalcohol	860	0.0052	0.165

^a BDS, Benzidine disulfonate.

^b IPC, Isophthaloyl chloride.

^c TPC = Terephthaloyl chloride.

^d Trademark of The Dow Chemical Company.

ide. The membrane properties of these polymers are covered by a U.S. patent.¹³

For many applications, such as enhanced oil recovery, it is essential that the polymer solution viscosity be stable for extended periods of time. Unfortunately, we find that for all the polyamides and polyureas there is a considerable viscosity loss upon standing. Three different PBBDT samples exhibited viscosity loss upon standing at room temperature over a 6-month period at pH 6.5–7.0. The higher the viscosity grade, the more pronounced is the viscosity loss. Similar behavior was observed for the benzidine disulfonic acid based polyurea and polyamides for 1% solutions at pH 6.5 and 55°C. Here again, a considerable viscosity loss of the solution is observed as a function of time. At this point it is not clear whether these viscosity losses are due to hydrolysis of the amide or urea linkages or due to some conformational changes taking place in solution.

CONCLUSIONS

From an analysis of the Mark Houwink's constants found in literature for several polymers, it can be concluded that despite bulky side groups and cyclized units in the backbone, polymers tend to behave like flexible coil polymers in solution if the main chain contains any rotatable bond. The only truly rigid rod polymers appear to be those with helical conformations in solution as observed with many polyamides, polyamino acids, polyisocyanates. Polymers having double-stranded backbones such as ladder and spiro polymers are also expected to be rigid rod types.

Several water soluble polyamides and polyureas, made by reacting aromatic sulfonated diamines with tere- or iso-phthaloyl chloride and phosgene, respectively, have been characterized and evaluated for various applications. PBBDT made via interfacial polycondensation of benzidine disulfonic acid and terephthaloyl chloride could be produced with varying viscosity for a 1% solution in DI water up to 2500 mPa · s (intrinsic viscosity of 65 dL/g). Molecular weights of these polyamides are not expected to be more than 200,000. Viscosity measurements suggest that these polyamides appear to transform into helical coils in salt solution exhibiting extremely high thickening efficiency, are highly shear stable, and have high pseudoplasticity with yield. This makes these polymers potentially useful for applications such as oil well drilling and fracturing. In 2% KCl, these polymers exhibit thickening efficiency greater than that found with high molecular weight hydrolyzed polyacrylamide or xanthan gum. However, these polyamides precipitate out of solution when monovalent salt concentrations exceed about 6% or when divalent salt concentrations exceed about 0.1%. These polyamides also appear to form liquid crystals in DI water at concentrations exceeding 3%, which is also characteristic of rigid rod polymers.

Polyamides made with terephthaloyl chloride and diaminostilbene disulfonic acid or diamino dimethyl biphenyl disulfonic acid also could be produced with reasonably high viscosity grades and exhibit similar rigid rod characteristics. Other polyamides or polyureas could not be produced with sufficiently high molecular weights to be useful as thickeners. However, many of these were found to be good disper-

sants for solid suspensions, particularly in systems containing low divalent ion concentrations. Many of these polymers formed strong clear films with extremely high permeability and selectivity for water vapor, making them potentially useful as pervaporation and dehydration membranes.

All these polymers unfortunately exhibit viscosity loss in solution as a function of time that make them unsuitable for many applications, but they may be suitable for applications such as fracturing of oil wells where postapplication breakdown of the polymer is desirable.

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