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Gelation of Sulfonated Rigid Polymers

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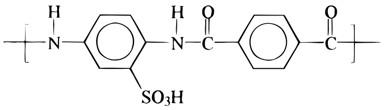
Thermoreversible gelation of polymers has been a subject of widespread research activities. The majority of the studies were concerned with flexible polymer chains that were crystallizable or contained stereoregular sequences.[1] But semiflexible and rigid polymers had also been extensively studied; among the well-known examples were poly(γ-benzyl-α-L-glutamate),[2,3] poly(alkyl isocyanates),[4] and polysaccharides.[5] In this paper, we would like to report preliminary results on the gelation of three sulfonated rigid polymers, two of which were aromatic polyamides,[5] and the third, a substituted poly(*p*-phenylene).

The first polymer, sulfonated poly(*p*-phenylene terephthalamide) (PPTS, **1**), was synthesized by the reaction of terephthaloyl chloride with 2,5-diaminobenzenesulfonic acid, as described by Vandenberg.[6] The sample used for the study had an intrinsic viscosity of 0.48 dL/g in sulfuric acid (98%) at 25 °C and a weight average molecular weight of about 6000 determined by light scattering at 25 °C in dimethylacetamide, DMAc, in which the polymer was soluble without the addition of LiCl. Dilute aqueous solutions (<2%) were prepared by heating to about 80 °C, at which temperature the polymer dissolved completely, followed by cooling to room temperature. The solutions were clear and fluid initially, but turned into gels after standing at room temperature for 1−2 days. The minimum concentration for gelation was about 0.6% by weight. Birefringence was observed when the polymer concentration was above a certain critical value, C_x, about 0.8% in water. Optical micrographs revealed nematic structures (Figure 1a). The gelation concentration was about 4% in DMAc, but C_x was much higher, about 13%. Nematic liquid crystalline structure was also observed (Figure 1b).



(I) Sulfonated Poly(*p*-phenylene terephthalamide), PPTS

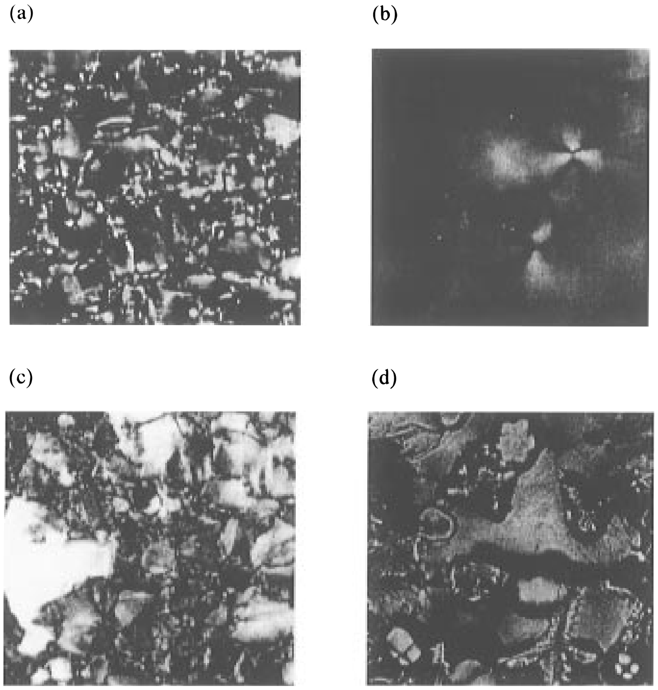


Figure 1. Photomicrographs of polymer gels (a) PPTS in water, 1%; (b) PPTS in DMAc, 15%; (c) PSST-Li in water, 1.63%; (d) PSBP−Na in water, 1.28%.

Birefringence disappeared upon heating. The temperature of the transition from the birefringent to the isotropic state was determined by sealing the edges of the cover slide with a suitable adhesive in order to minimize solvent evaporation and observing changes in birefringence as the sample was heated at 2−3 °C/min. The transition temperature was reproducible to about 3−4 °C. (The gel "melting" point determined by this procedure was about 6 °C higher than the value obtained by the inverted tube method.) The results for H_2O, DMAc, and their mixtures are shown in Figure 2. There was a systematic shift from high to low transition temperatures as the concentrations of DMAc in the mixed solvents increased. In all cases, the gelation process was reversible, i.e., gel formation upon storage at room temperature and gel melting at high temperatures. The process could be repeated many times.

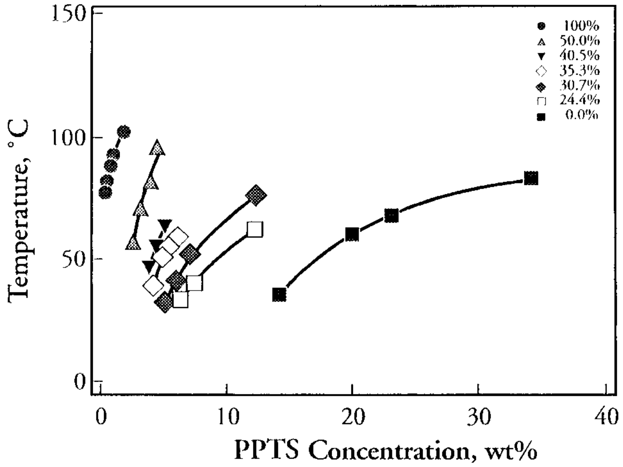


Figure 2. Birefringent to isotropic transitions of PPTS gels in water, DMAc, and their mixtures (legend indicates percent H_2O).

The lithium and sodium salts of PPTS, prepared by the neutralization of the sulfonic acid group with Li and Na carbonates, respectively, were more soluble in water than their parent polymer. They also formed birefringent hydrogels which were thermoreversible. The transition temperature of PPTS−Li and −Na are shown in Figure 3.

The second aromatic polyamide (**II**) investigated contained a stilbene moiety which should impart more rigidity to the chain. It was synthesized by the reaction of terephthaloyl chloride with 4,4′-diaminostilbene-2,2′-disulfonic acid. The intrinsic viscosity of the polymer in sulfuric acid (98%) was 0.63 dL/g at 25 °C. The two sulfonic acid groups in the repeating unit rendered the polymer slightly soluble in water. The critical concentration for the gelation of the aqueous solution was

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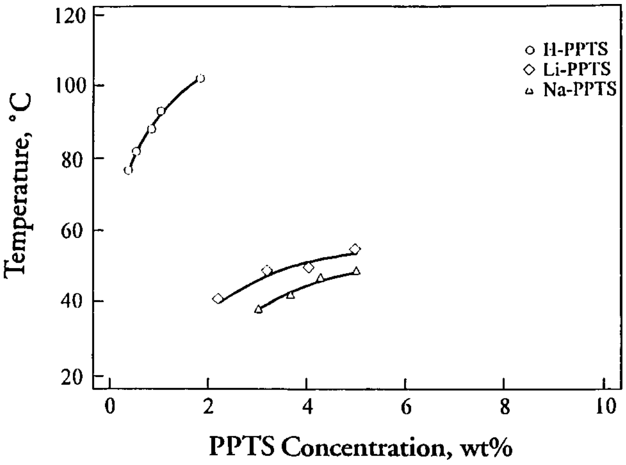
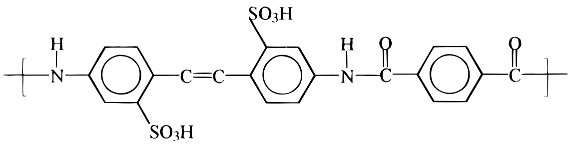


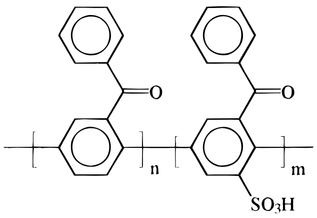
Figure 3. Birefringent to isotropic transitions of hydrogels of PPTS slats.

about 0.99%, and that of the Li salt, about 1.63%. Again the gels were birefringent and exhibited nematic liquid crystalline structures (Figure 1c).



(II) Poly(4,4'-stilbene terephthalamide 2,2'-disulfonic acid), PSST

The third polymer was obtained by the direct sulfonation of poly(benzoyl-1,4-phenylene) using fuming sulfuric acid. Poly(benzoyl-1,4-phenylene) was synthesized by Ni(0)-catalyzed coupling reaction of 2,5-dichlorobenzophenone, as described by Wang and Quirk,[7] and its molecular weight was determined by size exclusion chromatography to be 20 000 g/mol polystyrene equivalent, using tetrahydrofuran at 25 °C. The critical concentrations for the gelation of aqueous solutions were about 0.68% for the acid and about 1.28% for the Li salt. A representative photomicrograph of the Na salt (Figure 1d) shows a smectic structure.



(III) Partially sulfonated poly(benzoyl-1,4-phenylene, PSBP, n/m ≅ 1/1

Hydrogel formation and the attendant development of liquid crystalline structures of our polymers at concentrations much lower than those reported for other water soluble polymers such as hydroxypropyl cellulose[8] seem to merit further study.

References and Notes

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