

Association Phenomena between Copolymers of *p*-Styrenesulfonate (Cs^+)/3-Methacryloxypropyltrimethoxysilane and Hydroxypropylcellulose in Aqueous Solution and Solvent-Cast Films

GERALD SCHULTZ

Phys-Chem Scientific Corp. 36 West 20th Street, New York, New York 10011

SYNOPSIS

Association between copolymers of *p*-styrenesulfonate (Cs^+)/3-methacryloxypropyltrimethoxysilane [copolySS(Cs^+)/MAPTMS], and hydroxypropylcellulose (HPC) are shown to exist in dilute aqueous solution. Gels form at concentrations as low as 0.05 g/dL. The tendency to form gels is a function of mol % MAPTMS in the copolymer and molecular weight of HPC. Gels can be dispersed by the addition of dimethylformamide (DMF), a known disruptor of hydrogen bonding. Homopolymers of SS(Cs^+) and MAPTMS were also prepared. PolyMAPTMS shows anomalous behavior with regards to association with HPC in that gels form to a lesser degree than the trend exhibited by the copolymers. This is rationalized on the basis of the lack of chain expansion due to the absence of salt groups and their intrapolymer repulsions. In addition to the hydrodynamic data, the phase relationship of blends of HPC with either copolySS(Cs^+)/MAPTMS, polySS(Cs^+), or polyMAPTMS cast from aqueous solution strongly suggests specific interactions between polymers.

INTRODUCTION

Certain polymers interact strongly in solution via hydrogen bonding and in so doing form insoluble complexes.¹ This can occur even in strongly hydrogen-bonding solvents such as water where the energy of affinity between polymer chains is greater than between polymer and solvent.²

Of particular interest is that in systems where considerable negative enthalpies are involved the above behavior might foreshadow miscibility in polymer blends since it has been shown that specific exothermic interactions between mutually hydrogen-bonding polymers in the blend are a key factor in polymer miscibility.³⁻⁶ Of course, the role of solvent and overall energy of the system must be considered to determine the exact nature of miscibility where either gels or precipitates form in solution. Nevertheless, the literature discloses systems where

polymer association in solution leads to miscible blends where a single and often elevated glass transition is observed.⁷⁻⁹

In one of these systems,⁷ polyacrylic acid forms hydrogen-bonded precipitates from aqueous solution with HPC, which is known to form anisotropic solutions at about 30% in water.¹⁰ In another system,¹¹ laminarin, a linear polysaccharide, and polysilicic acid have been shown to associate presumably via hydrogen-bond formation. In dilute solution, HPC is modeled as having a disjointed rod structure, suggesting some chain rigidity.¹² The combination of chain rigidity and polymer association through hydrogen bonding provides interesting conditions for study.

The present article presents the hydrodynamic and phase behavior of a series of copolymers of *p*-styrenesulfonate/3-methacryloxypropyltrimethoxysilane [SS(Cs^+)/MAPTMS], homopolymers based on their comonomers, and hydroxypropylcellulose (HPC). This system shows a positive correlation between the tendency to form gels and miscibility

in solvent-casted blends. The data are explained on the basis of hydrogen bonding between the silanol groups in the copolymer and oxygen atoms in HPC. In addition, the degree of chain expansion in the copolymer is found to influence the hydrodynamic behavior of solutions of the above polymer system.

EXPERIMENTAL

Chemicals and Reagents

HPC-G, -M, and -H corresponding to molecular weights 370,000, 850,000, and 1,150,000, respectively, were supplied by the Aqualon Co. No attempt was

made to further purify or characterize these materials.

Solutions were made to 0.1 and 2.0 g/dL with deionized water for the various studies contained within this paper. In the case of the 2.0 g/dL solutions, several days were required to bring about complete solvation, particularly in the case of HPC-H grade. When the solutions were not in use, they were stored in the refrigerator to deter proliferation of biological organisms.

Polymer Synthesis

Copolymers of SS(Cs⁺)/MAPTMS were synthesized after a modified method of Ketterer and co-

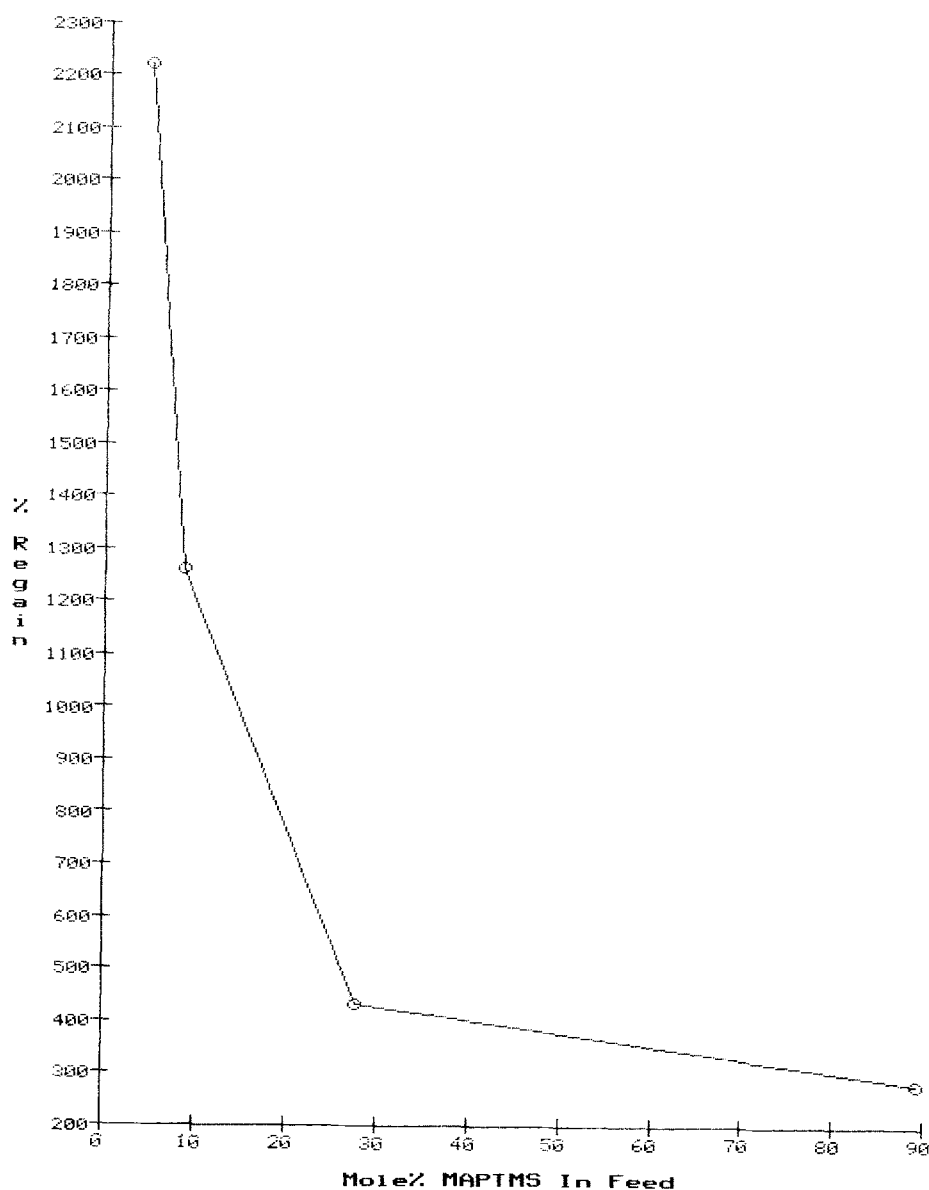


Figure 1 Regain vs. mol % MAPTMS in feed.

workers¹³ from aqueous solutions of *p*-styrenesulfonate (Na^+) supplied by Fluka and MAPTMS supplied by Petrarch. The MAPTMS was distilled under vacuum prior to use, taken from the center cut of the distillate which came over at 50–70°C depending on the pressure (about 1 mmHg). The $\text{SS}(\text{Na}^+)$ was used without prior recrystallization.

Various polymers were synthesized with initial mol % of MAPTMS in the feed of 100, 89.3, 27.3, 8.8, and 0%. Only the copolymer derived from 27.3 mol % Si in feed was subjected to elemental analysis. The mean value of mol % Si was determined to be 30.7%.

The comonomers were combined in aqueous solution and the pH was adjusted to 3 with HAc and HCl to increase the solubility of the MAPTMS and deter premature silanol condensation. Preboiled deionized water was used and polymerization was run under a nitrogen blanket. Homopolymers of MAPTMS and $\text{SS}(\text{Na}^+)$ as well as copolymers 27.3 and 89.3 mol % were synthesized at 35°C overnight

by free-radical initiation using 0.0136% sodium pyrosulfite (Fluka) and 0.0234% sodium persulfate (Fluka). Copolymer 8.8 mol %, also run at 35°C, was synthesized with 0.0069% sodium pyrosulfite and 0.0118% sodium persulfate. Under the conditions of synthesis, it is not known if polymerization went to completion.

Polymers varied from viscous solutions to hard gels depending on the mol % of MAPTMS in the feed. PolyMAPTMS and the 89.3 and 27.3 mol % polymers yielded aqueous gels. Poly $\text{SS}(\text{Na}^+)$ and the polymer made from 8.8 mol % in the feed yielded soluble materials.

Polymers were exchanged into the Cs^+ state by addition of 1*N* CsOH. In the case of the polymers that formed aqueous gels, dissolution of the gel occurred in 1–2 h at room temperature.

The above-treated polymers were then dialyzed against deionized water for 2–3 days until the pH within the bag was 5–6. Polymer solutions were filtered and their pH was adjusted to 7.0 with dilute

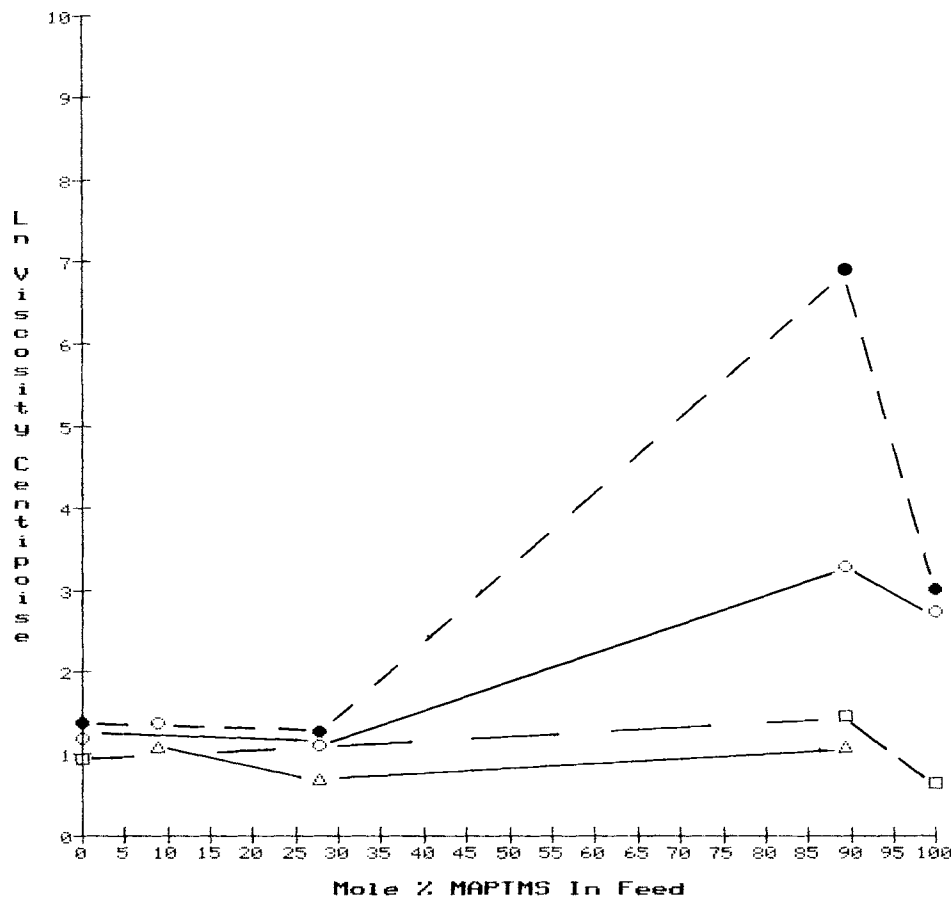


Figure 2 Ln viscosity vs. mol % MAPTMS in feed. Viscosity of 0.05 g/dL of SS/MAPTMS and 0.05 g/dL of HPC of varying molecular weights: (□) 0.05 g/dL HPC-G (370,000 MW); (○) 0.05 g/dL HPC-M (850,000 MW); (●) 0.05 g/dL HPC-H (1,150,000 MW); (△) no HPC.

CsOH. The pH of polyMAPTMS was adjusted to 9.3, since below this level, the solution tended to gel.

Under the conditions of synthesis, the MAPTMS comonomer would be expected to hydrolyze, liberating three silanol groups per mol of MAPTMS¹⁴ at pH 7. Evidence of this is that when solutions of copolymers are evaporated to dryness materials that are insoluble in water are formed. These materials, however, are swollen, indicating a network structure due to the formation of siloxane bonds between chains.

The 27.3% and 8.8% copolymers were concentrated under vacuum at 60°C to about 3 g/dL. The 89.3% copolymer as well as the 100% MAPTMS homopolymer were not concentrated due to their tendency to gel out at higher concentrations. Their concentrations were 1 g/dL or less.

All polymer solutions were stored in the refrigerator when not in use. Except in the case of polyMAPTMS at 1 g/dL, they showed no gelation after several months to more than 1 year of storage.

Viscosity Measurements

A Brookfield viscometer model LVT with a UL adapter was used with a temperature-controlled water bath set to $25.0 \pm 0.5^\circ\text{C}$. This viscometer is of the revolving cylinder type.

Solutions of polymer, 0.1 g/dL, were combined with 0.1 g/dL solutions of HPC of equal volumes. Solution viscosity was measured at a shear rate that would allow on-scale readings. Typically, this was at 7.34 and 14.68 s^{-1} . In the case of extensive gelation, a shear rate of 0.36 s^{-1} was used.

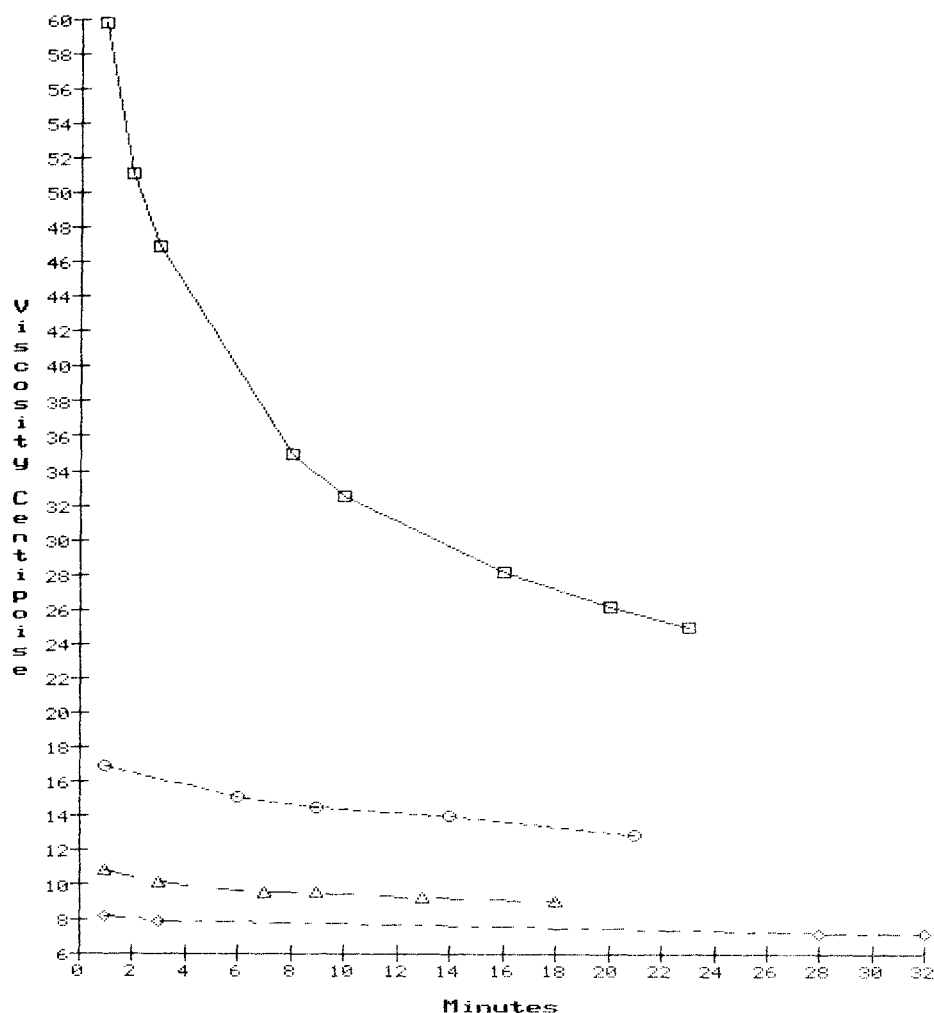


Figure 3 Viscosity vs. time. Viscosity of 0.05 g/dL of polymer made from 89.3 mol % MAPTMS in feed and 0.05 g/dL HPC-M at 25°C, 7.34 s^{-1} : (—□—) 0% DMF; (---○---) 1.2% DMF; (---△---) 2.4% DMF; (---◇---) 3.6% DMF.

Elemental Analysis

United States Testing Company of Hoboken, NJ, performed elemental analysis by wet techniques on Si and S to determine the comonomer ratio in the copolymer made from 27.3 mol % feed. Their mean value was 30.7%, with a standard deviation of -4 and $+7\%$ based on five separate polymer syntheses.

Water-Regain Study

Solutions of copolymers were evaporated to dryness to a constant weight at 100°C at 1 atm. They were immersed in deionized water for 1 day, after which the water was decanted and the swollen gel particles reweighed. The percentage of water uptake was calculated.

Film Coating

A 2 g/dL (1 g/dL in the case of polyMAPTMS) solution of polymer was combined with an equal volume of 2 g/dL of HPC solution of various molecular weights. After mixing, the solutions were poured onto clear glass microscope slides and evaporated to equilibrium dryness at room conditions.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between mol % of MAPTMS in the feed and the % regain of water in various oven-dried copolymers of SS(Cs^+)/MAPTMS that have been immersed in water for 1 day. It clearly shows that higher mol % of MAPTMS

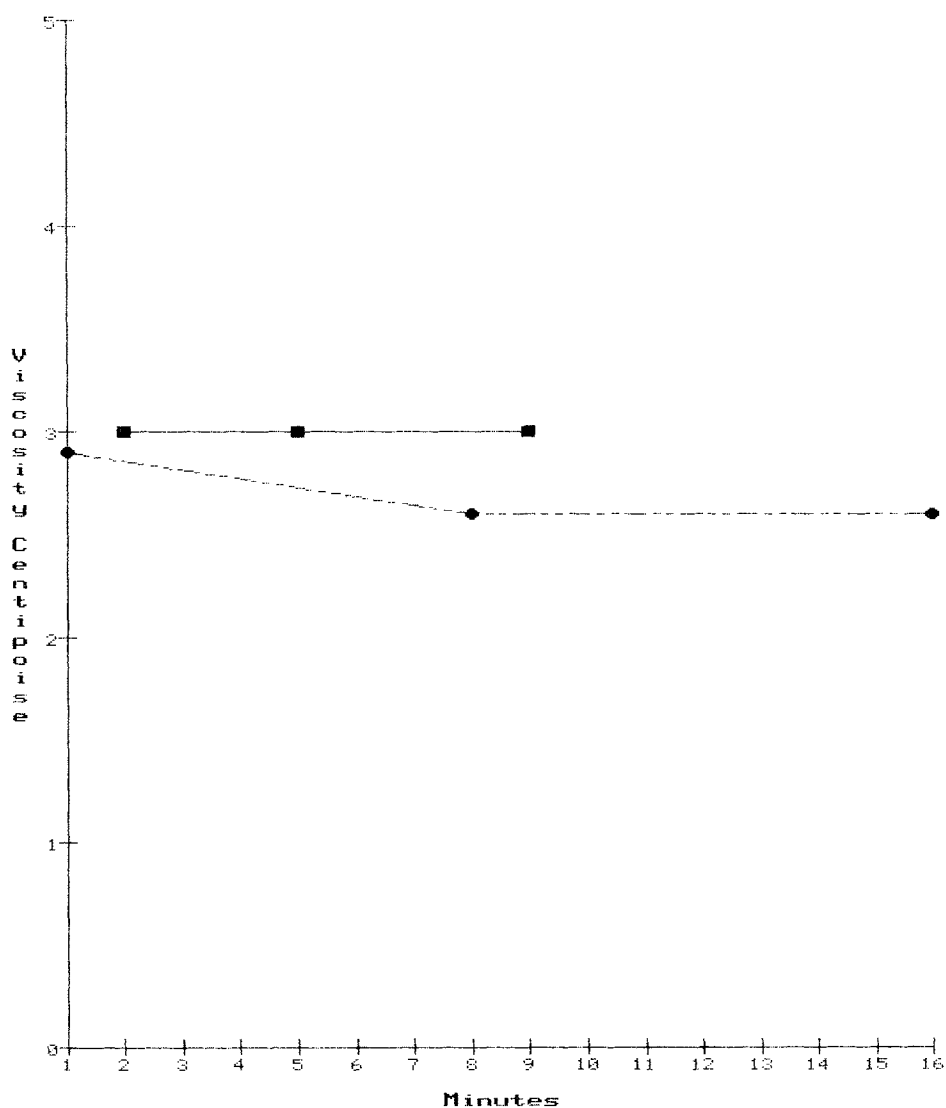


Figure 4 Viscosity vs. time. (—◆—) 0.05 g/dL HPC-M (850,000 MW); (—■—) 0.05 g/dL polymer with 89.3 mol % MAPTMS in feed.

in the feed results in lower regain. This is due to higher cross-linked density by the formation of siloxane bonds between polymer side chains.

Elemental analysis was done on the copolymer made from 27.3 mol % MAPTMS in the feed. It appears that for this copolymer the mol ratio in the feed closely resembles the mol ratio in the copolymer, which has an average value of 30.6 mol %. Therefore, although no quantitative relationship can be drawn *a priori* for the other copolymers, the mol % MAPTMS in the feed reflects the relative amount of MAPTMS in the copolymer.

Figure 2 shows the relationship between mol % MAPTMS in the copolymer feed ratio and viscosity for equivolume amounts of 0.1 g/dL solutions of the copolymers combined with 0.1 g/dL solutions of HPC of varying molecular weights. Obvious gelation occurs between the copolymer with 89.3% MAPTMS in the feed and HPC-M (MW 850,000) and HPC-H (MW 1,150,000). One notes the dramatic increase in viscosity over pure copolymer or pure HPC solutions. It is interesting that the 89.3% copolymer forms more extensive gels with HPC than does the homopolymer of MAPTMS with HPC. More will be said about this later on in the discussion.

For copolymers with 27.3 and 8.8% MAPTMS in the feed, no gelation is evident with high molecular weight HPC even at 1.0 g/dL copolymer and 1.0 g/dL HPC. It is proposed that this is due to the lower amount of silanol groups present in these copolymers of MAPTMS and, therefore, the lower degree of association with HPC.

Figure 3 shows the rheological behavior of a 0.05 g/dL solution of the 89.3 mol % copolymer and 0.05 g/dL solution of HPC-M as a function of time under low shear conditions (7.34 s^{-1}). The asymptotic falloff of viscosity with time, a characteristic of thixotropic behavior, is an indicator of disruption of interpolymer attractions.²

A dramatic reversal of gelation is evident with the addition of low concentrations of DMF, a known disruptor of hydrogen bonding. As the concentration of DMF is increased, the time dependence of the viscosity diminishes as does the viscosity at zero time. Figure 4 shows that in pure solutions of either the 89.3% copolymer or HPC-H there is no such time-dependent behavior at least in the range of concentrations and shears tried.

Table I presents the apparent phase relationship of solvent-cast films and the solutions of copolymers of SS(Cs⁺)/MAPTMS, polyMAPTMS, and polySS(Cs⁺) these films were cast from and of various molecular weights of HPC. Films that appear clearer to visible light are considered to have more single-phase character than do others that appear cloudy. However, caution must be exercised since optical clarity is not an indicator of polymer miscibility on the small-scale molecular level.⁶

One notes that as MAPTMS increases in the feed solvent-cast films exhibit more single-phase nature. Solutions of these compositions show a strong tendency to gel, which increases with increasing molecular weight of HPC, as shown in Figure 2. For the 27.3 mol % copolymer, even at 1.0 g/dL copol-

Table I Apparent Phase Behavior

Mol % MAPTMS in Feed	HPC (Mol wt.)	Appearance of Film ^a	Appearance of Solution
100	1,150,000 (H)	Clear	Gel
100	850,000 (M)	Clear	Gel
100	370,000 (G)	Clear	Solution
89.3	1,150,000 (H)	Clear	Gel
89.3	850,000 (M)	Clear	Gel
89.3	370,000 (G)	Clear	Weak gel
27.8	1,150,000 (H)	Slightly cloudy	Solution
27.8	850,000 (M)	Slightly cloudy	Solution
27.8	370,000 (G)	Slightly cloudy	Solution
8.8	1,150,000 (H)	Decidedly cloudy	Solution
8.8	850,000 (M)	Decidedly cloudy	Solution
8.8	370,000 (G)	Decidedly cloudy	Solution
0.0	1,150,000 (H)	Cloudy	Solution
0.0	850,000 (M)	Cloudy	Solution
0.0	370,000 (G)	Cloudy	Solution

^a Films are cast from 1 g/dL/1 g/dL solutions of SS/MAPTMS:HPC.

ymer to 1.0 g/dL HPC-H, no gelation occurs. Evidently, there is not enough silanol present to cause gelation, even though the concentration of copolymer is 20 times greater than the 89.3 mol % copolymer.

At 100% MAPTMS, one notes an apparent anomaly in that gels are weaker for the same molecular weight of HPC. By Table I, at a molecular weight of 370,000 of HPC, there is no gelation with the homopolymer of MAPTMS, whereas the 89.3 mol % copolymer displays evidence of gelation. As MAPTMS decreases in the feed, solvent-cast films display decidedly more double-phase character while solutions show no gelation.

Mention should be made here about the nature of the intermolecular attractions in the blend. Upon removal of solvent in blends of the above polymers cast from solution, one would expect condensation

of the silanol groups to form siloxane linkages. This would lead to polymer entanglements. Therefore, the relative importance of entanglements and the proposed hydrogen bonding in the above system is yet to be elucidated. However, there probably is a fair amount of free silanol groups in the blend since MAPTMS has three free silanols per mol of comonomer, some of which would not be expected to form siloxane bonds and therefore be available to hydrogen bond.

As a separate line of study, tetraethoxysilane was hydrolyzed under reflux in 70/30 methanol/water (v/v) at neutral pH to form $\text{Si}(\text{OH})_4$. One would expect $\text{Si}(\text{OH})_4$ to condense in time to form oligomers. However, under the conditions of this study, no visible turbidity or precipitate was evident. Therefore, any condensed product if it formed at all was still soluble. When the above solution was com-

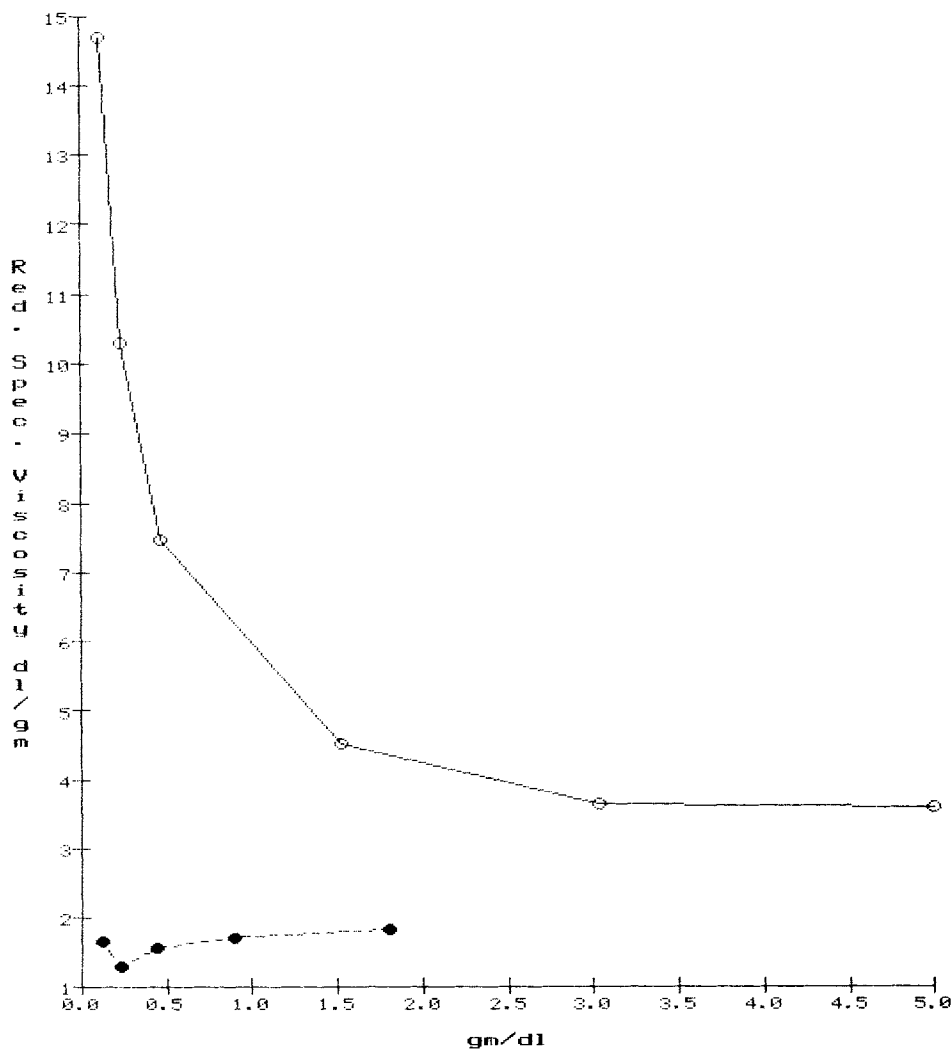


Figure 5 Reduced specific viscosity vs. concentration. Copolymer formed from 27.3 mol % MAPTMS in feed: NaCl (●) 0.05N; (O) no NaCl; at 25°C and 14.68 s⁻¹.

bined with HPC (MW 1,150,000) at 0.2 g/dL, a precipitate immediately formed, indicating complexation. Thus, HPC and the above-proposed silanol species show a strong affinity for each other. Others have shown¹¹ a similar interaction between polysilicic acid and laminarin, a linear polysaccharide. It is plausible that the affinity between copolymers of SS(Cs⁺)/MAPTMS, polyMAPTMS, and HPC are subject to the same forces of attraction as the HO(SiO)_nH species and HPC. Whereas copolymers of SS(Cs⁺)/MAPTMS form gels with HPC, the above system forms an insoluble precipitate. This is undoubtedly due to the presence of styrene sulfonate in the copolymer and its strong affinity for water.

As was mentioned above, an attempt will now be made to explain the anomalous behavior of PolyMAPTMS, as seen in Figure 2. Whereas copolymers of SS(Cs⁺)/MAPTMS interact more strongly with HPC in aqueous solution as a function of MAPTMS in the copolymer, PolyMAPTMS shows a decrease in viscosity compared to the 89.3 mol % copolymer. This can be rationalized on the basis of salt repulsions between the sulfonate groups in the copolymer that are absent in the homopolymer of MAPTMS.

Copolymers of SS(Cs⁺)/MAPTMS exhibit the hydrodynamic behavior typical of polyelectrolytes in dilute aqueous solution.^{13,15,16} Figure 5 shows the increasing reduced specific viscosity with decreasing

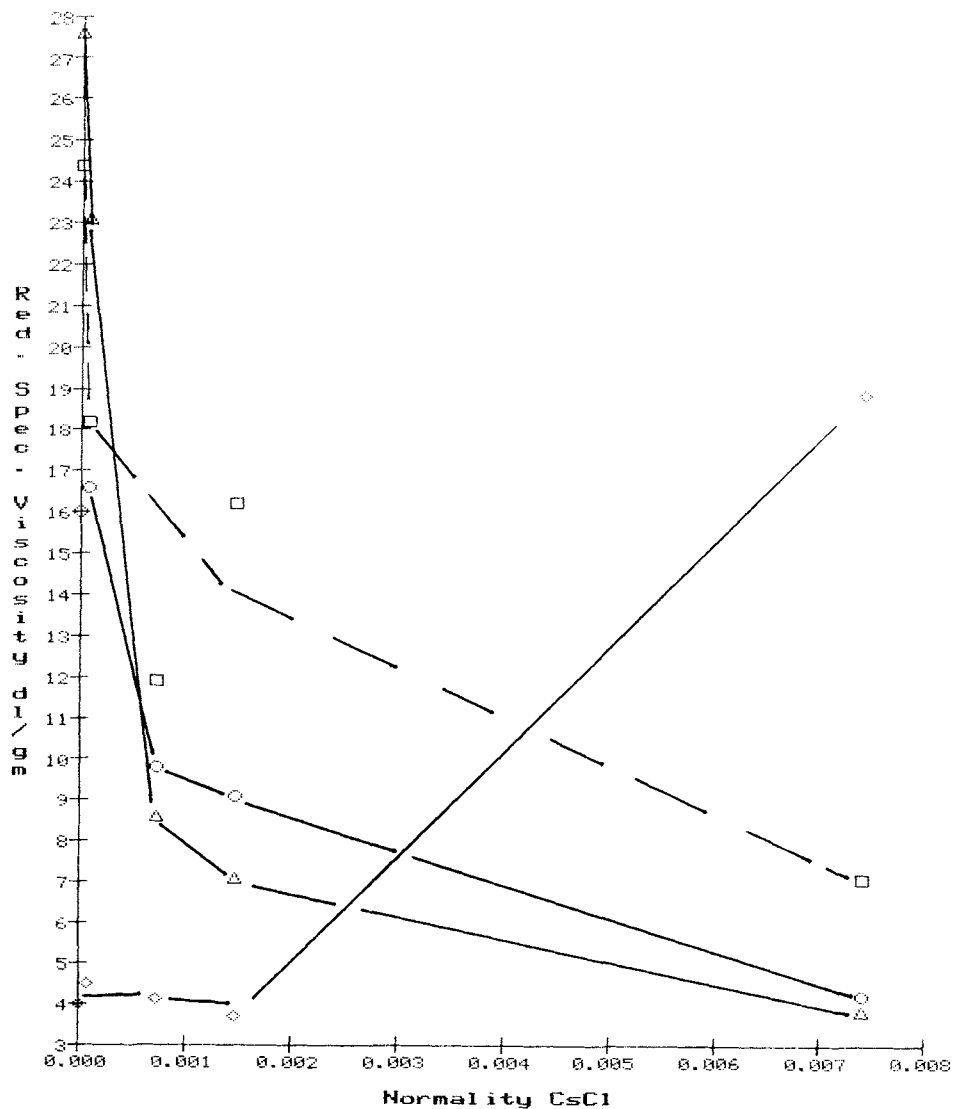


Figure 6 Reduced specific viscosity of 0.05 g/dL polymer vs. concentration of CsCl, 36.71 s⁻¹, 25°C: (○) 27.3 mol %; (□) 89.3 mol %; (◇) 100 mol %; (△) PSS(Cs);

concentration for the copolymer formed from 27.3 mol % MAPTMS in the feed. Upon introduction of electrolyte, the inverse dependency of reduced specific viscosity with concentration diminishes. This is because increasing electrolyte concentration causes the end-to-end distance of the polymer to decrease. Low electrolyte concentration causes the polymer chain to open up, increasing solution viscosity.

Figure 6 shows the effects of electrolyte on the reduced specific viscosity for various copolymers and for polyMAPTMS. As anticipated, the greater the SS(Cs⁺) content, the larger the electrolyte effect. The key to our discussion is that polyMAPTMS

shows no such electrolyte effect at least up to 3×10^{-3} N CsCl. There is, however, a rise in the polyMAPTMS solution viscosity, which corresponds to the onset of a gelatinous precipitate. This is due to a loss of solubility and is unrelated to the above argument.

It is tempting to speculate that polyMAPTMS is a more tightly packed coil in solution than are the copolymers of SS(Cs⁺)/MAPTMS. Thus, the silanol groups would be expected to be less exposed to the solution and less apt to interact with HPC. A 1% solution of polyMAPTMS is turbid and tends to gel at 25°C. Solutions of the copolymers are stable for over 1 year up to 5% (w/w) concentration, thus

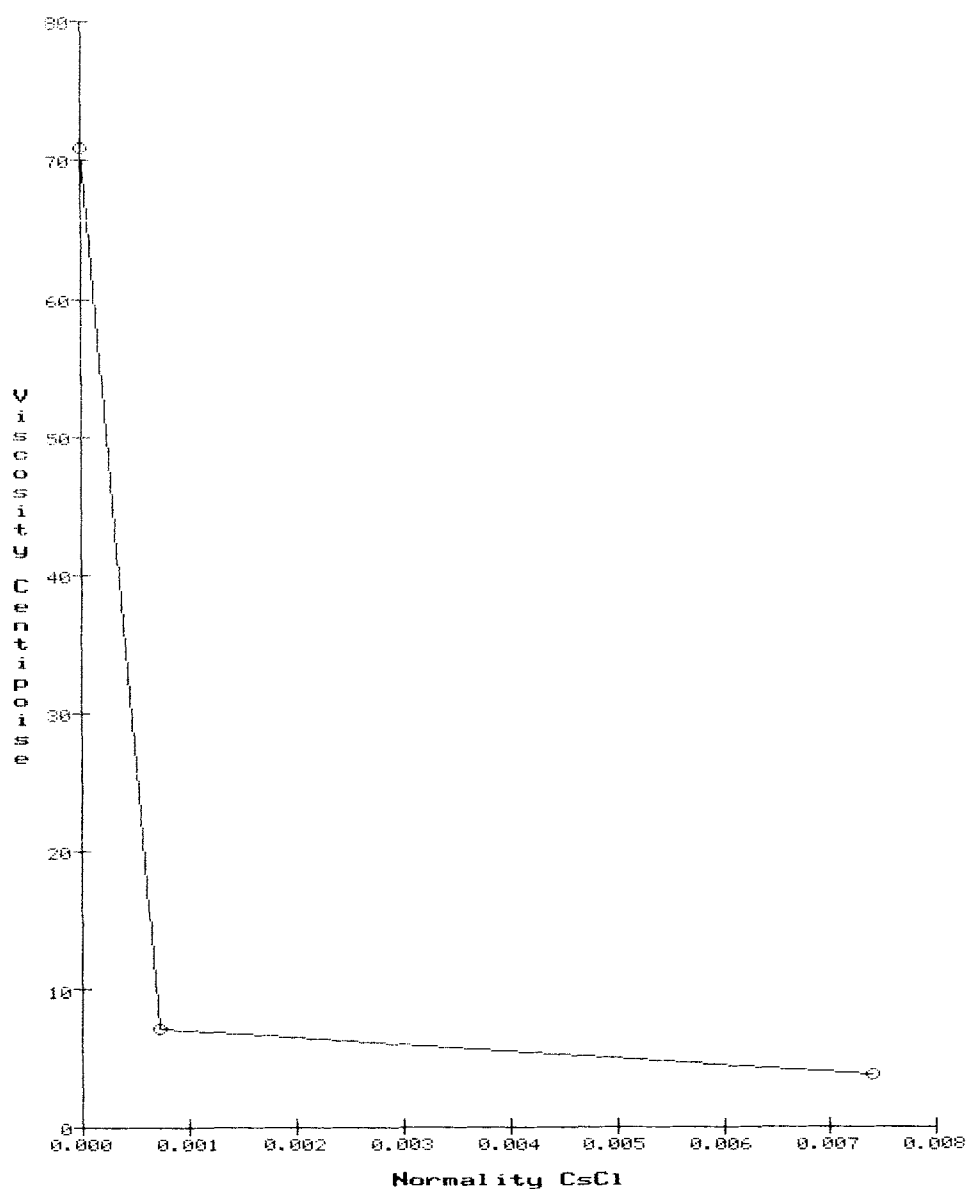


Figure 7 Viscosity of 0.05 g/dL 89.3 mol % copolymer + 0.05 g/dL HPC-H vs. concentration of CsCl, 3.67 s^{-1} , 25°C.

indicating a difference in the solution behavior of the copolymers and polyMAPTMS. The important implication of this is that for maximum interaction between the silanol groups in the copolymer and oxygen atoms in HPC an open structure in the copolymer is required.

Figures 7 and 8 show this by the effect of added salt on the viscosities of solutions of the 89.3 and 27.3 mol % copolymers and HPC-H, respectively. Lower viscosities are observed at salt concentrations corresponding to the falloff in reduced specific viscosity of aqueous solutions of the copolymer alone. Figure 9 demonstrates that the reduced specific vis-

cosity of a HPC-H solution shows no salt dependency.

Therefore, the SS(Cs⁺) and MAPTMS contents show competing effects in regard to HPC complexation. However, MAPTMS content seems to have the overriding effect.

PolySS(Cs⁺) shows no gelation and forms somewhat immiscible blends with HPC. Baring any synergistic effects, salt dipole interactions¹⁷ between copolymers of SS(Cs⁺)/MAPTMS and HPC are probably not the primary cause of gelation and miscibility in the above-mentioned copolymer compositions.

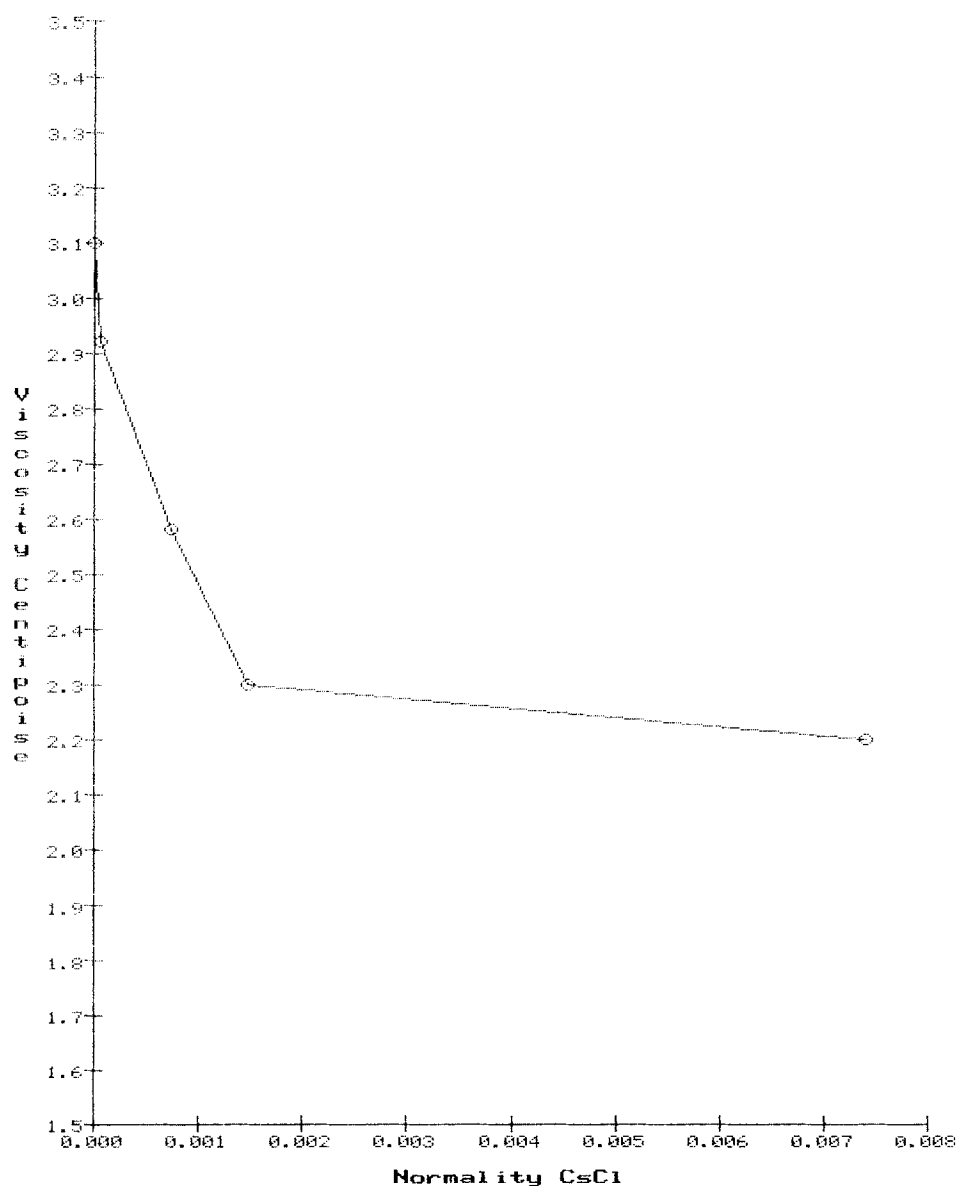


Figure 8 Viscosity of 0.05 g/dL 27.3 mol % copolymer + 0.05 g/dL HPC-H vs. concentration of CsCl, 36.71 s^{-1} , 25°C .

Lastly, something needs to be said about the conformation of HPC in aqueous solutions and its possible role in the observed gelation phenomena. HPC forms anisotropic solutions at 30% in water¹⁰ and is modeled as having a disjointed rod structure in dilute solutions, which suggests some chain rigidity.¹² This would increase the radius of gyration of the molecule over that of a flexible coil opening up its internal surfaces to the solution. The larger dimension of the molecule would also increase its interaction with the copolymer, tending to cause gelation. It would be interesting to study the gelation

properties of less rigid water soluble cellulosics and copolymers of SS(Cs⁺)/MAPTMS.

The topic of polymer complexation has far-reaching implications. The work of Sidney Fox,¹⁸ among others, dramatically demonstrates the likelihood of spontaneous generation of lifelike structures under primordial conditions on earth from monomeric and polymeric materials. It is interesting to consider the role of soluble siliceous materials in the above evolutionary processes as biological macromolecules are water-soluble, tend to be rigid, and have the ability to hydrogen bond. With an eye more

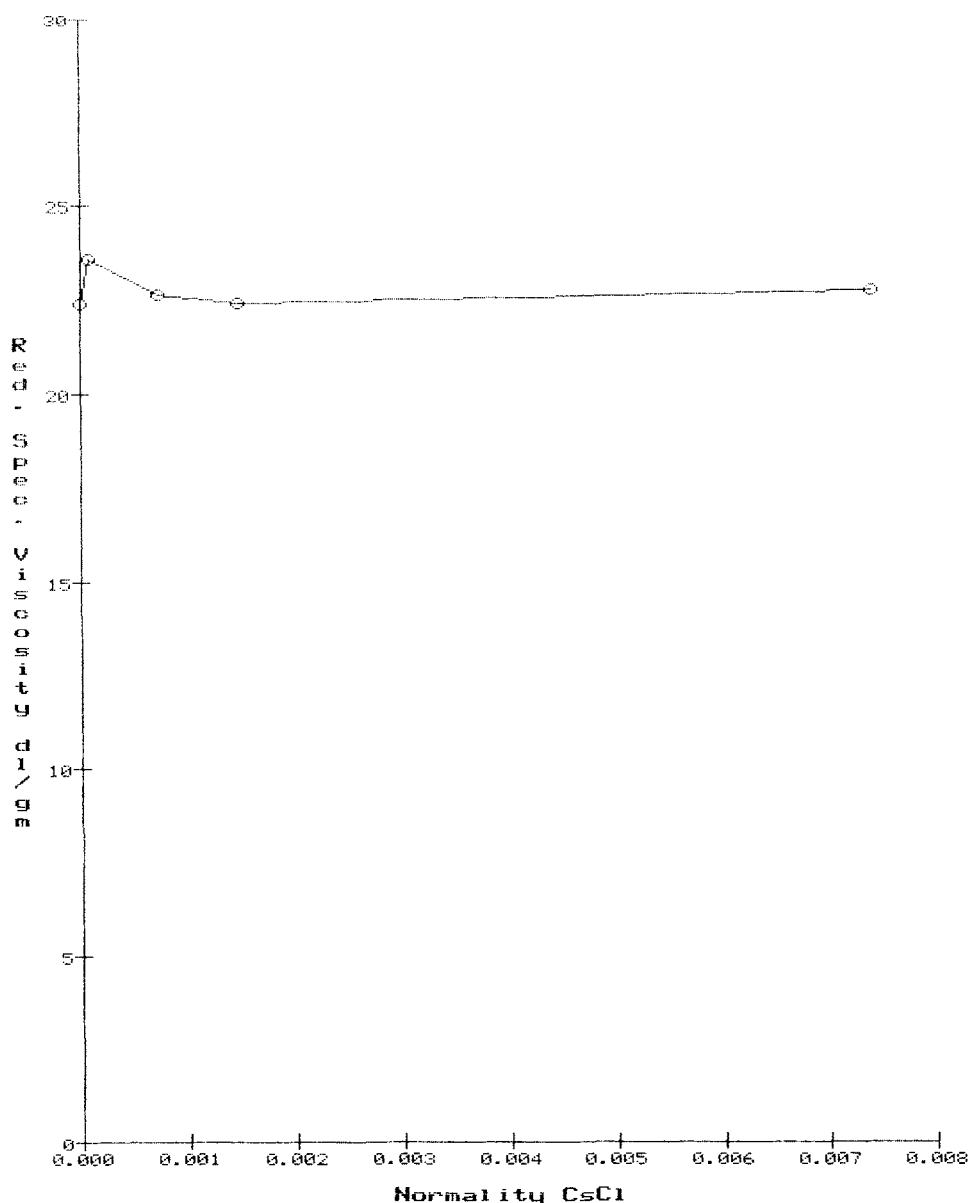


Figure 9 Reduced specific viscosity of 0.05 g/dL HPC-H vs. concentration of CsCl, 36.71 s⁻¹; 25°C.

toward practical applications, silanol groups could play a role in the development of industrially useful polymer-blend materials.

CONCLUSIONS

1. Copolymers of SS(Cs⁺)/MAPTMS and HPC form gels at 0.05 g/dL in aqueous solution. Gel formation is a function of molecular weight of HPC and amount of MAPTMS in the copolymer.
2. Miscibility of blends cast from solutions of the above polymers parallels gel formation.
3. It is proposed that interpolymer association leading to gelation in solution and miscibility in the blend is due to hydrogen bonding between silanol groups present in the copolymer and oxygen atoms in HPC. This may be a generalized reaction, since HO(SiO)_nH shows a strong affinity for HPC in aqueous solution.
4. It is further proposed that the anomalous behavior of polyMAPTMS is due to the absence of SS(Cs⁺) in the chain that if present would tend to cause a more open polymer structure in solution.

Grateful appreciation goes to Phys-Chem Scientific Corp. for sponsoring the studies contained within this article. Special thanks go to Professor E. M. Pearce for his encouragement to pursue these studies and Professor T. K. Kwei for providing me with many valuable insights into the above system. Lastly, grateful acknowledgment goes to Professor Mark M. Green, who, although making no direct contribution to this piece, nevertheless, served to plant the seeds of its conception by communicating to me his sense of wonder in the construction of the physical world.

REFERENCES

1. Tsuchinda and A. Abe, *Adv. Polym. Sci.*, **45**, 1 (1982).
2. M. L. Miller, *The Structure of Polymers*, Reinhold, New York, 1966.
3. J. R. Pennacchia, E. M. Pearce, T. K. Kwei, B. J. Bulkin, and J. P. Chen, *Macromolecules*, **19**, 973 (1986).
4. M. M. Coleman and J. Zarian, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 837 (1979).
5. P. Cousin and R. E. Prudhomme, *Polym. Mater. Sci. Eng.*, **51**, 291 (1984).
6. D. R. Paul and S. Newman, *Polymer Blends*, Academic Press, New York, 1978.
7. L. F. Wang, E. M. Pearce, and T. K. Kwei, *Polymer*, **32**(2), 249 (1991).
8. P. Lin, C. Clash, M. Aponte, E. M. Pearce, and T. K. Kwei, *J. Polym. Sci. Phys. Ed.*, **26**, 603 (1988).
9. E. P. Otocka and F. R. Eirich, *J. Polym. Sci. A-2*, **6**, 895 (1968).
10. R. S. Werbowyj and D. G. Gray, *Mol. Cryst. Liq. Cryst.*, **34**, 97 (1976).
11. P. F. Holt and C. W. Went, *Trans. Faraday Soc.*, **55**, 1435 (1959).
12. R. S. Werbowyj and D. G. Gray, *Macromolecules*, **13**, 69 (1980).
13. R. H. Wiley, N. R. Smith, and C. C. Ketterer, *J. Am. Chem. Soc.*, **76**, 720 (1954).
14. E. Plueddemann, *Silane Coupling Agents*, Plenum Press, New York, 1982.
15. D. T. F. Pals and J. J. Hermans, *Rec. Trav. Chim.*, **T71**, 434 (1952).
16. D. Doty and G. Ehrlich, *Annu. Rev. Phys. Chem.*, **3**, 93 (1952).
17. M. Hara and A. Eisenberg, *Macromolecules*, **17**, 1335 (1984).
18. S. Fox, *Nature*, **205**, 328 (1965).

Received October 16, 1991

Accepted December 17, 1991