Some Water-Soluble Copolymers from Lignin

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Synopsis

The utilization of lignin materials would be enhanced if lignin properties could be altered through chemical modification. Towards this end, lignosulfonate, recovered from spent pulping liquors, was grafted with acrylamide or acrylic acid, using redox initiation. Study was made of the effects of some reaction variables (such as reaction medium, lignin/monomer ratio, and initiator concentration) on the copolymerization efficiency and on the copolymer characteristics. Lignosulfonate having bivalent counterions yielded better copolymerization results than that having univalent cations. Aqueous solutions of graft copolymers displayed high viscosities, and exhibited promising stability during storage and against shearing, suggesting the potential use of copolymers as water-thickening agents.

INTRODUCTION

Ever since valorization of natural resources became a daily slogan, wood chemists have devoted great efforts in searching more complete utilization of the renewable lignocellulosic materials.[1] However, in chemical pulping processes, lignin (constitutes 20–30% of wood) has been considered to be the useless part and removed from the cellulose. Therefore, a great quantity of lignin has been either incinerated to recover some energy and chemicals or discarded into receiving water. Only a very few portion of lignin has been recovered[2]; the recovered lignin has been used in its polymeric form as dispersants, binders, reinforcement agents, etc., or used as low molecular chemical feedstocks. Research has been oriented to the utilization of lignin in polymer material domains as to synthesize thermosetting resins and thermoplastics.

The graft of lignin with vinyl monomers has been studied in the last two decades. Among those who have published results, Koshijima and Muraki reported their work on radical grafting of vinyl monomers onto hydrochloric acid lignin.[3-6] The grafting of hydrochloric acid poplar lignin and reed lignin with vinyl monomers were studied by Simionescu and co-workers.[7,8] Copolymerization of lignosulfonate and methacrylate[9-12] and the grafting of styrene onto various lignin[13-17] were also investigated.

The object of this work was to use commercially available lignin materials in the derivation of useful lignin copolymers by grafting with vinyl monomers. Discussed in this paper are the principal factors (such as the lignin/monomer ratio and initiator concentration) which would affect the synthesis results during the copolymerization of lignosulfonate and acrylamide or acrylic acid. Some viscosities of the copolymer solutions will also be presented, in the light of viscosity stability. It is an intent of this paper to show the promising

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properties of the water-soluble lignin copolymers—the potential use of this type of copolymers as water-thickening agents.

EXPERIMENTAL

Material. A commercial calcium salt of lignosulfonate (LS) (St. Regis Paper Co.), isolated from the spent liquor of sulfite pulping of softwood, was used as the main grafting substrate. Only in a few specific experiments were ammonium and sodium salts employed; these two salts were obtained from the same source. Prior to use, these salts were purified to remove impurities and the low molecular weight LS. The purification was carried out through the ultrafiltration of a 2% water solution, using a Millipore immersible molecular separate kit. Each solution was then dried under vacuum. Acrylic acid (AA) was purified by vacuum distillation, over cupric sulfate and through a copper-ring packed column, to remove the stabilizer. Acrylamide (AM) and other chemicals were all of reagent grade; thus, they were used without further purification.

Graft Copolymerization. The general procedure used to carry out the reactions has been described in detail elsewhere[14]; it will be briefly redescribed in this paper. Graft copolymerization was redox initiated, using the peroxide-ferrous pair, and conducted under nitrogen atmosphere with gentle agitation. Wherever no specification is given, the reaction conditions fixed in this work were as follows: LS = 0.5 g $(7.35 \times 10^{-4}$ mol/L); monomer: AA = 2.5 mL (0.72 mol/L) or AM = 2.5 g (0.70 mol/L); ferrous chloride = 18.5 mg $(2.95 \times 10^{-3}$ mol/L); hydrogen peroxide = 20 mg $(1.18 \times 10^{-2}$ mol/L); reaction medium = 50 mL; temperature: LS–AA, 30°C, and LS–AM, 50°C; reaction time = 2 h.

Reactions were terminated by precipitating the polymeric products in isopropanol; afterwards, copolymers were isolated from homopolymer by extraction with appropriate solvents. For the LS–AA system, ethanol was used to extract the homopoly(acrylic acid), then methanol to extract the copolymer. As for the LS–AM system, the unreacted lignosulfonate was isolated from the reaction mixture by extracting it with dimethyl formamide. Since no suitable solvent has yet been found to separate the homopoly-acrylamide from the poly(AM–LS) copolymer, consequently, the resulting solid mass consisted of the true copolymer and the homopoly(AM) (if there was any). The subsequent viscosity measurement was therefore conducted on the solid mass assuming that it contained only the copolymer.

The terms used to interpret the copolymerization results were defined as follows (on weight base):

$$\text{Total monomer conversion (\%)} = \frac{\text{total polymer formed}}{\text{monomer charged}} \times 100$$

$$\text{Degree of LS reacted (\%)} = \frac{\text{LS grafted}}{\text{LS charged}} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{\text{grafted polymer}}{\text{total polymer formed}} \times 100$$

Solution Viscosity. Viscosity measurement was performed at 25°C using Ubbelohde suspended-level viscometers. In this work, intrinsic viscosity $[\eta]$ was used as a molecular-weight indicator for analogous polymers. This viscosity was determined according to Huggins' expression[18]: $\eta_{sp}/c = [\eta](1 + k'c)$, where η_{sp} stands for the specific viscosity of a solution containing c g/dL of solute. Typical lines of η_{sp}/c vs. c for evaluating the $[\eta]$ values, by extrapolating to $c = 0$, are shown in Figure 1. The upper line was obtained with a commercial polyacrylamide (Cyanamer 250, $\overline{M}_v = 2.4 \times 10^6$) which has served as the reference for comparison purpose throughout this study. The poly(AM–LS) copolymer (ML-23) had an $[\eta]$ value of 5.4 dL/g; this value is equivalent to the $[\eta]$ of polyacrylamide having molecular weight of $\overline{M}_v = 7.1 \times 10^5$.

Stability of solution to shear was preliminarily tested with a shear-testing device (Fig. 2). This device, similar in principle to a screen-shear-tester,[19] essentially consisted of a sampling cylinder fixed with a 50 μm porous stainless steel filter on its bottom. The top of the cylinder was connected to a tee, one side of the tee to a vacuum line and the other to a compressed air line; each side was controlled by a valve. For each shear test, solution was sucked from the bottom to the cylinder by vacuum. After the cylinder was filled up, the vacuum valve was closed, and the compressed air was directed to the cylinder to force the solution passing downward through the filter, where the shearing took place. Different air pressure caused different extent of viscosity degradation; a pressure of 483 kPa (70 psig) was found suitable in this work.
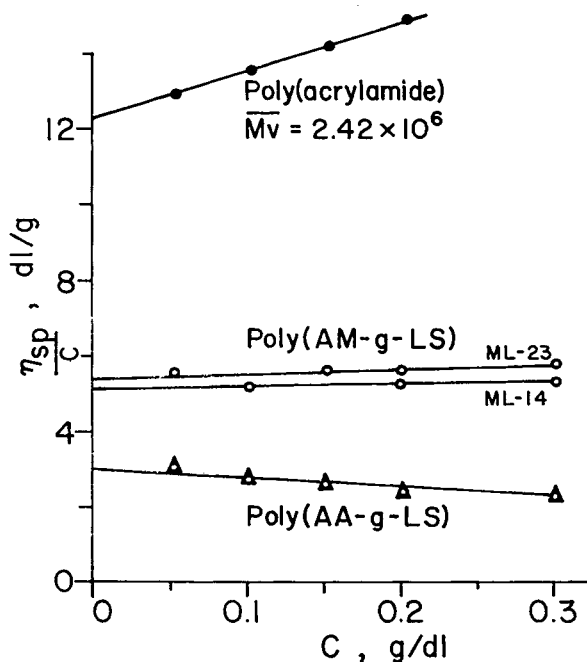

Fig. 1. Reduced specific viscosity, η_{sp}/c, vs. solute concentration for poly(AM) (●), poly(AM–LS) (○), and poly(AA–LS) (△), in 0.001M NaCl solution.
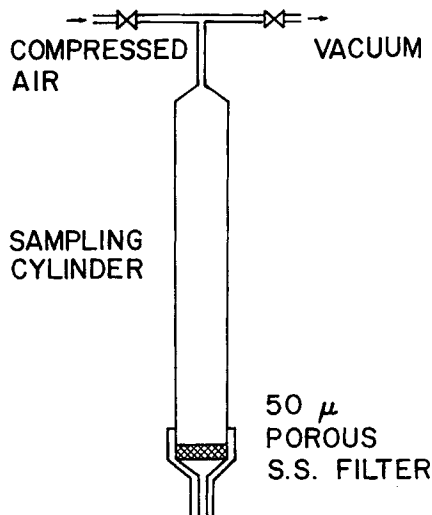
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Fig. 2.   Schematic diagram of the shear-testing device.

RESULTS AND DISCUSSION

Medium Effect

When LS was grafted with vinyl monomers, the effect of reaction medium on the copolymerization varied from one monomer to another. In the case of LS reacting with a monomer which possesses electropositive (i.e., electron-releasing) substituent, such as styrene, a better copolymerization result was obtained using methanol than using water as the reaction medium.[14] In a system involving a monomer possessing electronegative (i.e., electron-attracting) substituent, such as acrynitrile or methyl methacrylate, water was the preferable medium as compared to methanol.[9] These results deduced that the reaction medium suitable for these two acrylic monomers would also be suitable for the LS–AA and LS–AM systems. In fact, this deduction was true and the kinetic curves for the reaction of LS–AA in three media, commonly used in lignin study, are illustrated in Figure 3. As expected, water was the best medium in which about 94% of AA converted to polymer after 1 h of reaction. On the other hand, only 41% of AA polymerized in methanol in the first hour and the conversion levelled off around 60% after 3 h of reaction.

In the LS–AM system, it was found that over 90% of AM could polymerize in water before 1 h of reaction. However, when using methanol as the medium, no polymerization could be detected during the first few hours and only 1.5% conversion was observed even after 24 h of reaction. From the above observations, water was evidently the best reaction medium and was used hereafter in this study.

Ratio of LS / Monomer

Being a macromolecule having quinonoid structure and carrying stable free radicals, LS might act as an inhibitor in vinyl polymerization. However, in both the LS–AA and LS–AM systems, such inhibiting effect of LS was not evident. On the contrary, the presence of LS considerably accelerated the
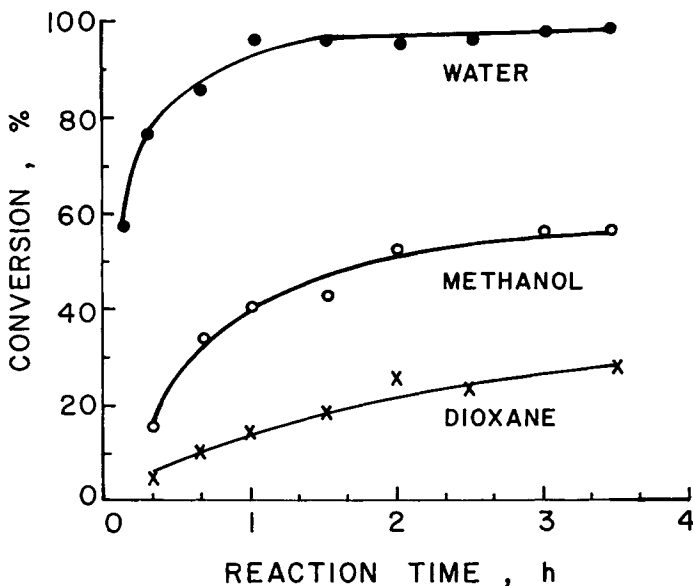
Fig. 3.   Variation of the total monomer conversion with reaction time for the LS–AA system, at 30°C, in water (●), methanol (○), and dioxane (×): LS 10 g/L; AA, 50 mL/L.

initial rate of polymerization, indicating the participation of LS in copolymerization immediately from the beginning of the reaction. When the concentration of LS was fixed and that of monomer varied, the amount of LS participated in copolymerization would decrease if monomer concentration decreased, as shown in Figures 4 and 5 for the systems of LS–AA and LS–AM, respectively. In Figure 4, when the LS/AA ratio varied from 0.1 to 0.5 (wt/wt), the percentage of the reacted LS decreased almost proportionally from 90 to 62, and the grafting efficiency moderately increased from 41% to 52%, while monomer conversion kept practically unchanged. The decreasing amount of the reacted LS could be explained by the decreasing chance of collision between the LS radical and monomer molecules. When the LS/AA ratio increased, one LS radical would be surrounded by fewer number of AA molecules, thus having more chance to annihilate its active center by disproportionation with another nearby LS radical. As a consequence, those LS macromolecules which lost their activity remained in their ungrafted state. For the same reason, if the LS radical succeeded in initiating the addition of monomers, the amount of monomer which eventually grafted onto one LS molecule would be less at a higher than at a lower LS/AA ratio. These statements were supported by the fact that the copolymer size, expressed in terms of intrinsic viscosity [η], decreased as LS/AA increased. The LS–AM system exhibited the similar results (Fig. 5), except that the amount of LS grafted did not decline until the LS/AM ratio reached around 0.3 (wt/wt).

Peroxide Concentration

When peroxide-ferrous was employed in an LS–vinyl monomer system, copolymerization was thought to occur through an LS macroradical intermediate.[10, 12] This LS macroradical might be generated by the freshly oxidized
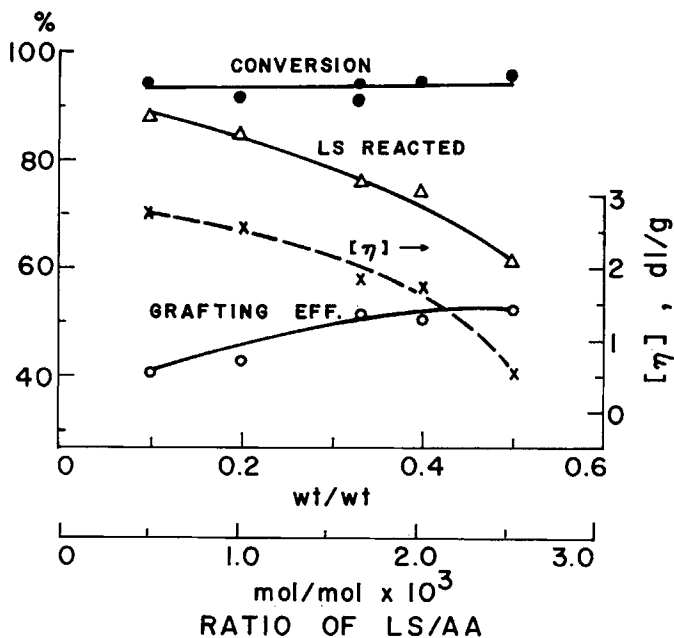
Fig. 4. Effect of the LS/monomer ratio on the total conversion (●), degree of LS reacted (△), grafting efficiency (○), and intrinsic viscosity of copolymer (×), for the LS–AA system in water medium at 30°C: LS 7.35×10^{-4} mol/L (10 g/L); H_2O_2 1.18×10^{-2} mol/L.
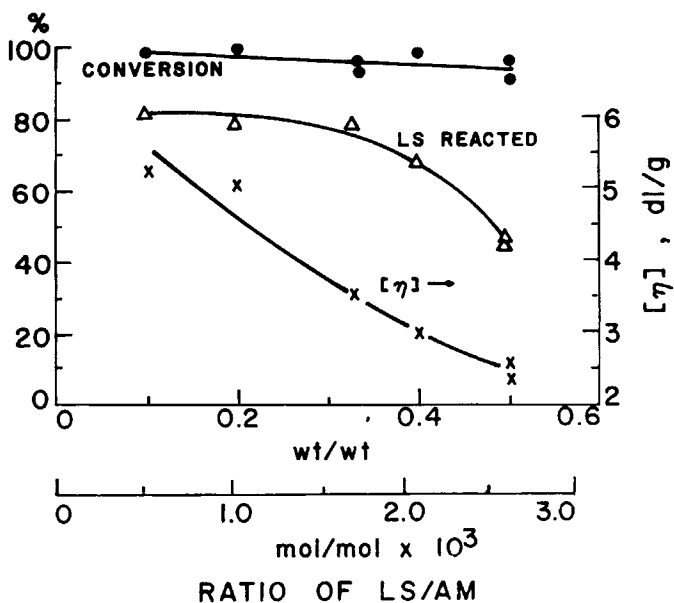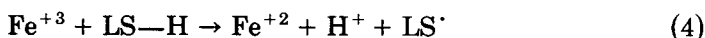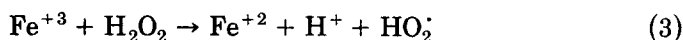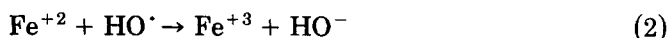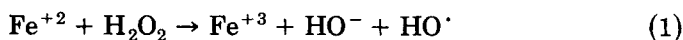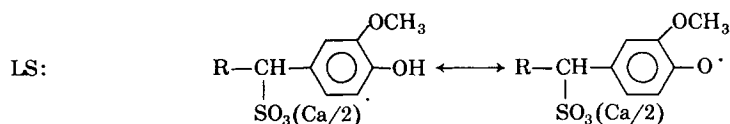

Fig. 5. Effect of the LS/monomer ratio on the total conversion (●), degree of LS reacted (△), and intrinsic viscosity of reaction product (×), for the LS–AM system in water medium at 50°C: LS 7.35×10^{-4} mol/L (10 g/L); H_2O_2 1.18×10^{-2} mol/L.
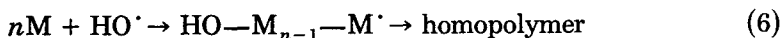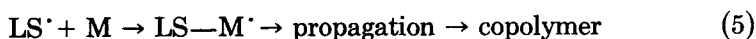
ferric ions according to some cyclical equilibriums:

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + HO^- + HO^{\cdot} \tag{1}$$

$$Fe^{+2} + HO^{\cdot} \rightarrow Fe^{+3} + HO^- \tag{2}$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + H^+ + HO_2^{\cdot} \tag{3}$$

$$Fe^{+3} + LS{-}H \rightarrow Fe^{+2} + H^+ + LS^{\cdot} \tag{4}$$

where

LS:

$$R{-}\underset{\underset{SO_3(Ca/2)}{|}}{CH}{-}\overset{OCH_3}{\underset{}{\bigcirc}}{-}OH \longleftrightarrow R{-}\underset{\underset{SO_3(Ca/2)}{|}}{CH}{-}\overset{OCH_3}{\underset{}{\bigcirc}}{-}O^{\cdot}$$

With the presence of vinyl monomers M,

$$LS^{\cdot} + M \rightarrow LS{-}M^{\cdot} \rightarrow propagation \rightarrow copolymer \tag{5}$$

$$nM + HO^{\cdot} \rightarrow HO{-}M_{n-1}{-}M^{\cdot} \rightarrow homopolymer \tag{6}$$

The simultaneous existence of reactions (5) and (6) was supported by the evidence that the presence of LS accelerated the initial rate of monomer disappearance.

Based on the above cyclical reactions [reactions (1) to (4)] ferrous ions can be considered to act in this graft reaction as a catalyst, and peroxide as the initiator. Therefore, the concentration of peroxide played an essential role in the control of copolymerization. Figure 6 illustrates the reaction results of the LS–AM system as a function of peroxide concentration. It can be seen that monomer conversion increases as peroxide concentration increases until the latter reaches 6 mmol/L; then the conversion levels off around 98%.

From the lines (Fig. 6) representing, respectively, the degree of LS reacted and the copolymer size (in terms of $[\eta]$), two regions can be observed. In the region where the peroxide concentration was less than 6 mmol/L, both the degree of LS reacted and the copolymer intrinsic viscosity augmented only slightly with H_2O_2 concentration. In the second region where H_2O_2 concentration changed from 6 to 11.8 mmol/L, both parameters climbed rapidly, and the percentage of LS reacted increased from 34 to 82 and the intrinsic viscosity from 0.64 to 5.4 dL/g. These results implied that reaction (6) was the predominant reaction if the amount of initiator was not sufficient. Increasing the peroxide concentration could generate more LS macroradical, thus increasing the competitivity between reactions (5) and (6). Besides, within this range, higher peroxide concentration seemed to stimulate more active sites on each LS macromolecule, which could thus be grafted with more polyacrylic branches. Consequently, the copolymer became larger in size and displayed a higher intrinsic viscosity.

It was noteworthy that when the peroxide concentration was further increased (i.e., higher than 11.8 mmol/L), rapid gelation occurred in the
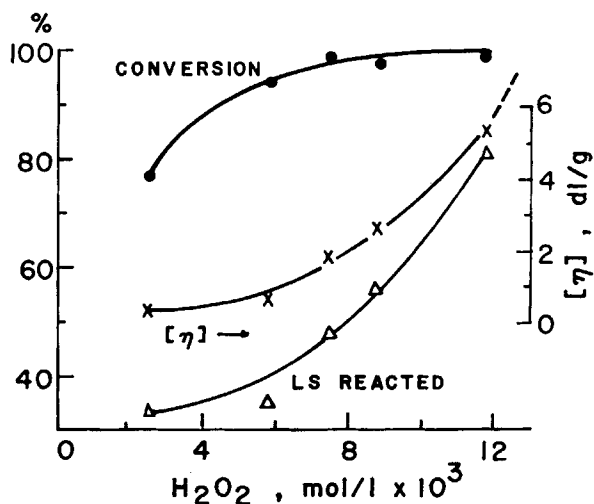
Fig. 6. Effect of peroxide concentration on the total conversion (●), degree of LS reacted (△), and intrinsic viscosity of reaction product (×), for the LS–AM system in water medium at 50°C: LS 10 g/L; acrylamide 50 g/L; reaction time 2 h.

reaction, and the resulting product became insoluble in water or other ordinary solvents. The formation of crosslinked copolymer was thought to be responsible for the insolubility of the product. However, this was only a speculation which should be verified through further detail studies.

LS Salts

Three kinds of salts (Ca^{+2}, Na^{+1}, and NH_4^{+1}) of lignosulfonate were copolymerized with acrylamide. Results (Table I) showed that the monomer conversion reduced 6% (from 98.7 to 92.7%) when NH_4–LS replaced Ca–LS in the reaction. Meanwhile, the degree of LS reacted dropped from 82 to 48% and the intrinsic viscosity of product changed from 5.4 to 4.4 dL/g. This indicated the superiority of the calcium salt in graft affinity; i.e., the Ca–LS macromolecule was more capable of participating in the reaction than NH_4–LS (or Na–LS). Furthermore, the larger molecular size (expressed in terms of intrinsic viscosity) of Ca–LS copolymer implied a larger amount of polyacrylic

TABLE I
Copolymerization of Acrylamide with Different Salts of Lignosulfonate[a]

Cation of LS salt	Total monomer conversion (%)	Degree of LS reacted (%)	Intrinsic viscosity of product (dL/g)
NH_4^{+1}	92.7	48.1	4.4
Na^{+1}	94.6	61.5	4.6
Ca^{+2}	98.7	82.2	5.4

[a]All three salts showed the same molecular-weight-distribution on GPC. LS = 0.74 mmol/L; AM = 1.40 mol/L; H_2O_2 = 11.8 mmol/L; 2 h of reaction in water, at 50°C.

chains on Ca–LS than on NH_4–LS molecule. In other words, more active sites for grafting had been formed on the surface of the Ca–LS molecule. The reason for this might be as follows: The bivalent counter ions, such as Ca^{+2}, might be sandwiched between two LS anions, thus making accessible to initiator some nonelectrically shielded area on the outer surface of the "sandwich." On the other hand, the univalent cations, such as Na^+ or NH_4^+, likely distributed around one LS molecule in all directions. These cations would attract electrically some water molecules to their surrounding; these water molecules could thus become more or less obstacles to the approaching initiator or monomer radicals. Consequently, LS salts with bivalent counterions would have more chance to be stimulated than those with univalent cations.

Solution Viscosity

The aqueous solutions of poly(AM–LS) or poly(AA–LS) exhibited high viscosities as shown in Figure 7, where viscosity is plotted against polymer concentration. It is obvious that, at a given concentration, the solution viscosity of the poly(AM–LS) copolymer is much less than that of the commercial poly(AM) ($M_v = 2.4 \times 10^6$); taking 1% solution as an example, the viscosities of poly(AM–LS) and poly(AM) are 14 and 72 cp, respectively. The viscosity of poly(AM–LS) which is lower could be increased by using double amount of this polymer; e.g., a 2.2% solution would have 72 cp.

For most polyelectrolytes, the presence of alkaline ions (e.g., Na^+, Ca^{+2}) would suppress the extension of molecular chains in aqueous solution, result-
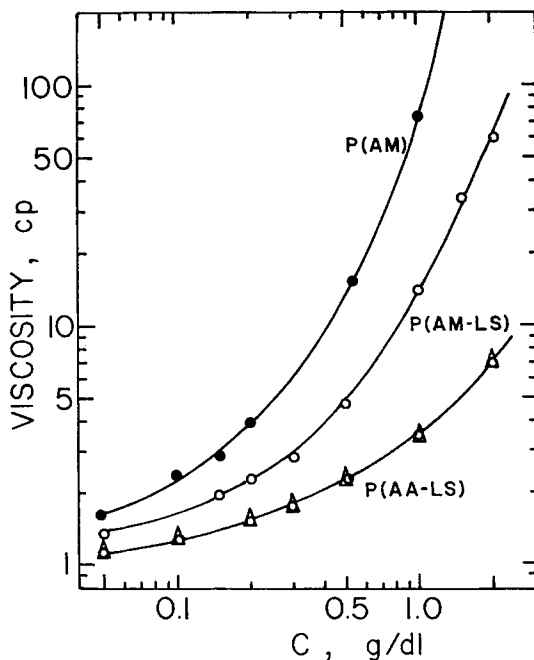
Fig. 7.   Variation of viscosity with polymer concentration for poly(AM) (●), poly(AM–LS) (○), and poly(AA–LS) (△).

ing in a reduction in solution viscosity. The same phenomenon was observed for the poly(AM–LS) solutions. When solution salinity rose from 0.001 to 0.02M NaCl, the viscosity of a 1500 ppm poly(AM–LS) solution dropped from 1.92 to 1.55 cp, while that of poly(AM) solution from 2.85 to 2.14 cp. The percentage reduction of the former (i.e., 20%) was smaller than that of the latter (i.e., 25%). In other words, poly(AM–LS) was less sensitive to the salt concentration than poly(AM); the calcium ion already existed in the LS moiety was considered to be the cause.

The solution stability upon storage at room temperature for poly(AM–LS) was found comparable to that of poly(AM). Both solutions, containing 1500 ppm of solute, were kept hermetically in flasks (after thoroughly purged with nitrogen) for a period of 3 weeks; then their viscosities were checked. Drop of 4–6% in viscosity was observed for both cases.

Knowing that shearing causes scission and disentanglement of polymeric chain, resulting in lower viscosity, an attempt was made to study the solution stability in shearing by conducting preliminary tests with the shear-testing device shown in Figure 2. Each time after the solution had passed through the filter, its viscosity was measured, and the percentage retaining was calculated. The results for the poly(AM–LS) copolymer and poly(AM) are presented in Figure 8, in which the percentage of original viscosity retained was plotted against the shearing cycle. As observed, the first shearing causes 8.5 and 11.7% viscosity degradation in the poly(AM–LS) and poly(AM) solutions, respectively. After 20 times of shearing, poly(AM–LS) could still retain 75% of its original viscosity, while poly(AM) retain 64%, thus poly(AM–LS) copolymer demonstrating its more stable molecular structure against shearing than poly(AM). The stability of the copolymer might attribute to the very rigid LS backbone as well as to the rather short grafting polyacrylic chains. On the other hand, the commercial poly(AM) is normally a linear polymer, whose possibility in chain entanglement and whose easiness in chain cleavage by shearing is higher as compared to a branch polymer.

When the ratio of viscosities after and before shearing, η/η_0, was plotted against the cycle of shearing on a log–log scale, a linear relationship was
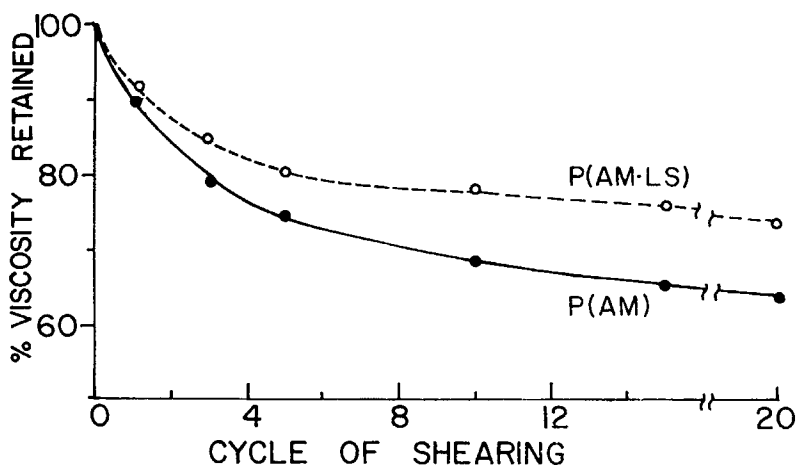

Fig. 8. Viscosity retained as a function of shearing cycle for poly(AM) ($\bullet$, η_0 = 3.20 cp) and poly(AM–LS) ($\bigcirc$, η_0 = 1.96 cp); 1500 ppm of polymer in 0.001M NaCl solution.
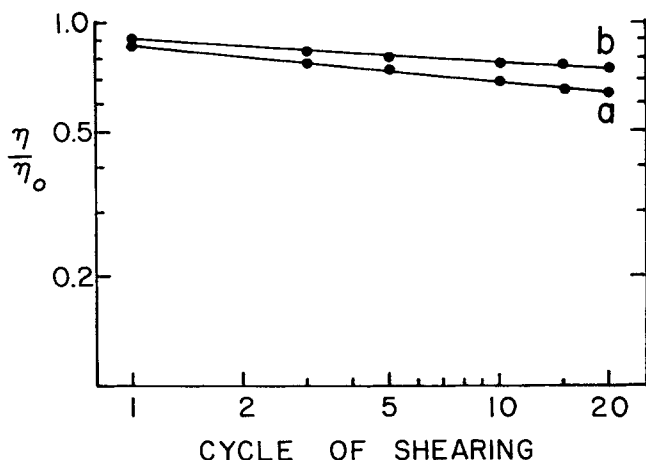
Fig. 9. Relationship between the fraction of viscosity retained, η/η_0, and cycle shearing on log–log scale for poly(AM) (a) and poly(AM–LS) (b); 1500 ppm of polymer in $0.001M$ NaCl solution.

obtained (Fig. 9). This relationship could be written in the form of

$$\eta/\eta_0 = \alpha S^\beta$$

where S is the cycle of shearing; α and β are two curve-fitting constants which can be evaluated from the intercept and slope of the straight line established. With this expression, it seems possible to predict the viscosity degradation upon shearing in our work.

CONCLUSION

Commercial lignosulfonate can be effectively copolymerized with acrylic acid and acrylamide, through the peroxide-ferrous redox initiation in water. Copolymer size could be controlled by the lignin/monomer ratio and peroxide concentration. Calcium salt of lignosulfonate yielded much better copolymerization results than sodium or ammonium salt. Aqueous solutions of graft copolymers displayed high viscosities and exhibited promising stability during storage and upon shearing, suggesting the potential use of this kind of copolymers as water-thickening agents. However, the copolymers obtained were still not large enough in size as compared to the commonly used polyacrylamide. Further research concerning the development of larger size copolymers and their application should be pursued.

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