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Diallyl ammonium salts and Sulfur dioxide**

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Rheological Behavior of pH Responsive Associating Ionic Polymers of Diallylammonium salts and Sulfur dioxide

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Abstract

In this study, the viscoelastic behavior of hydrophobically modified polyelectrolytes obtained from hydrolysis of cationic acid salt (CAS) as a function of zwitterions (x) and anions (z) fraction was studied. The dynamic viscosity, η' , dependence on frequency of a polymer solution of polybetaine (PB)/ Associating Polyelectrolyte (APE) having various compositions of x and z fractions in 0.1 N NaCl showed typical shear thinning behavior. η' of a solution of CAS 4 (M_2-4) with x:z ratio of 33:67 attained a maximum value in the presence of 1.67 equivalent of NaOH and decreased upon further addition of NaOH. The maximum is suggested to be a result of a combined effect of coil expansion and hydrophobic association. η' of CAS 4 (M_2-4) treated with 1.67 equivalent of NaOH increased gradually as temperature increases due to the increase in hydrophobic bonding. The association effect is retarded at temperatures higher than 50°C. Rheology of CAS 4 (M_2-4) samples treated with 1.67, 1.81 and 2.0 equivalent of NaOH suggested a reversible network. However, for APE 7 (M_2-5) elastic behavior is dominant and formation of highly interconnected three dimensional networks was suggested. At lower x/z ratios, the effect of coil expansion due to a higher APE fraction is more than counterbalanced by the lower degree of intermolecular hydrophobic associations, whereas at higher x/z ratio the coil contraction becomes the predominant effect.

1. Introduction

Associating water soluble polymers have been the subject of extensive research during the past decades because of their interesting rheological behavior in aqueous solution¹⁻³ (see references cited in reference #3). These are amphiphilic polymers containing a small proportion of hydrophobic groups incorporated in hydrophilic polymer chains. Above a certain polymer concentration (concentration required for hydrophobic association C^*_{HA}) intermolecular association of the hydrophobic groups leads to reversible formation of three dimensional physical cross-links of polymer chains in aqueous solution. While regular polymers build viscosity through a combination of concentration and molecular weight, associating polymers depend on the formation of physical network. The most salient features of such network are their significant enhancement of viscosity and elastic behavior compared to that of polymers without associating groups.

One reason for using associative polymers as rheology modifiers is that mechanical degradation is reversible. The physical links in the networks may be disrupted when the strain rate is high and sustained, but reform when the imposed stress drops. The primary advantage of associative polymers is that they contribute less elasticity than regular linear high molecular weight polymers, which is desirable in some coating processes⁴. The shear thinning feature associated with the reversible nature of these physical cross links led to their applications as rheology modifiers (particularly thickening agents) especially in aqueous based formulations within numerous industrial domains such as water-borne coatings, paints, cosmetics and enhanced oil recovery⁵⁻⁸.

The increase in viscosity can be enhanced by using charged monomers, because intermolecular charge repulsions lead to coil expansion. In contrast with polymers containing neutral hydrophilic and neutral hydrophobic groups, the presence of ionic sites of similar charges along the hydrophilic backbone of associating polyelectrolytes leads to a great variety of interesting behaviour⁹ (see references cited in reference #9). In partially hydrolyzed hydrophobically modified polyacrylamide, the electrostatic repulsion between the negative charges of carboxylate groups causes the polymer chains to extend and this extension can effectively enlarge the hydrodynamic volume of the polymer chain, hence increase the viscosity.¹⁰ The physics behind hydrophobic self association in hydrophobically associating ionic polymers is that hydrophobic interactions compete with electrostatic repulsion within the same polymer chain and/or between different polymer chains. Thus, the balance between hydrophobic interactions and electrostatic repulsions determines whether the polymer will undergo hydrophobic self association or not. Primarily, this balance is a function of the charge density and hydrophobe concentration in the polymer as well as the size and arrangement of the hydrophobe.¹¹

In addition to forming highly viscous solutions, aqueous systems containing hydrophobically modified water soluble polymers may organize into viscoelastic hydrogels. The hallmark of viscoelastic material is the presence of a so called rubbery plateau in its dynamic modulus spectra. This means that under oscillatory shear, there exists some range of applied frequency, ω (s^{-1}), over which the material behaves more like an elastic solid than a viscous fluid, and its response is independent of applied frequency. Thus the dynamic storage (or “elastic”) modulus, G' , exceeds the dynamic loss (or “viscous”) modulus G'' , and G' is invariant with applied frequency, ω . In

contrast, in polymer solutions G'' , is greater than G' over the entire frequency range. Thus the physical distinction between a hydrogel and a polymer solution is that the intermolecular linkage points in a gelled network are mechanically stable over some range of applied shear stress, while those in a solution are not.¹²

Since the discovery that free radical polymerization of diallyl quaternary ammonium salt yields water soluble cyclopolymers instead of cross-linked polymers¹³, numerous homo and co-cyclopolymers of scientific and technological interest have been synthesized from various diallyamine compounds.¹⁴⁻²¹ There are, however, only a few reports, which describe the synthesis of associating ionic copolymers prepared by Butler's cyclopolymerization technique²²⁻²⁴.

Recently, we reported²⁵ the synthesis and solution properties of a series of cycloterpolymers of sulfur dioxide, *N,N*-diallyl-*N*-carboethoxymethylammonium chloride **1** with varying amounts of hydrophobic monomers *N,N*-diallyl-*N*-alkylammonium chloride **2** (with alkyl lengths of 12 and 18 carbons) (scheme 1). Incorporation of small amounts of the hydrophobic comonomer has dramatically enhanced the viscosity values in the C₁₈ polymer series, whereas the presence of even a large amount of C₁₂ (0-10 mole %) failed to achieve association in the studied concentration range (0.0625-2 g/dL). The electrostatic repulsive forces between the chains do not permit them to approach each other to a safe distance required for the dodecyl pendants (C₁₂H₂₅) to manifest interchain association. The octadecyl pendants (C₁₈H₃₇) can associate intermolecularly because the extended length of the pendants allows them to mingle with each other without exposing the chains to experience the adverse effect of electrostatic repulsions. The low C^*_{HA} (~1 g/dL) observed for the C₁₈

polymer series is indeed a notable improvement over the C^*_{HA} of 15-17 g/dL for the similar cyclopolymers having $\sim C_{11}$ pendants²⁶ (see references cited in reference #26).

Our present study, examines the viscoelastic behavior of hydrophobically modified polyelectrolytes obtained from hydrolysis of Cationic acid salt (CAS) **4** as a function of zwitterions (x) and anions (z) fraction. CAS **4** samples are completely converted to corresponding anionic polyelectrolyte (APE) **7** in the presence of 2.0 equivalent of NaOH. Whereas, treatments of CAS **4** (M_2-4), (containing 4 mole% hydrophobe) with 1.5, 1.67, and 1.8 equivalents of NaOH afford corresponding polybetaine (PB) / APE **6** having different fractions of zwitterions (x) and anions (z) (scheme 1). The rheological behavior of this system is pH sensitive. Dynamic rheology of APE **7** as function of hydrophobe content was also examined. In addition, influence of concentration of CAS **4** (M_2-4) treated with 1.67 equivalent of NaOH is studied in the range 2-3 g/dL.

2. Experimental

2.1 Materials

The polymers used in this study were prepared by free radical cycloterpolymerization of sulfur dioxide and *N,N*-diallyl-*N*-carboethoxymethylammonium chloride **1** with hydrophobic comonomer *N,N*-diallyl-octdecylammonium chloride **2** to afford water soluble cationic polyelectrolyte **3** (CPE). The CPE **3** upon acidic (HCl) hydrolysis of the pendent esters groups gave the corresponding cationic acid salt (CAS) **4** which was hydrolyzed with NaOH to introduce carboxylate pendent on the polymer backbone. Details of their synthesis, characterization and aqueous solution properties are reported elsewhere²⁵. All the polymers used in this

study have linear alkyl side chains composed of 18 carbons, hydrophobe levels of 4 and 5 mole%, and the weight average molecular weight (M_w) is $(3.7 \pm 0.4 \times 10^5 \text{ g mol}^{-1})$ for the 4 mole% hydrophobe polymer. The molecular weight was determined using a Wyatt static light scattering DAWN instrument with 18 angle detection. The molecular weight measurement was carried out in methanol to minimize electrostatic interactions. Hydrolysis levels range from 1.5 to 2.0 NaOH equivalent for CAS 4 (M_{2-4}) and 2.0 NaOH equivalent for CAS 4 (M_{2-5}).

2.2 Conversion of CAS 4 to PB/APE 6 and APE 7 by basification and its use in rheology measurements

The CAS 4 (M_{2-4}), (which contains 4 mole% hydrophobe) were converted to the corresponding PB/APE 6 ($x = z = 0.48$; $y = 0.04$) by adding 1.5 equivalents of aqueous NaOH, and the resultant solutions were used for rheology measurement in 0.1N NaCl. A solution of the above PB/APE 6 (M_{2-4}) was prepared by dissolving 0.400 g (1.418 mmol) of CAS 4 (M_{2-4}) (in NaOH solution containing 2.099 (i.e., $1.418 + 1.418 \times 0.96 \times 0.5$) mmol of NaOH [9.8 cm³ of 0.2137 N NaOH was used for the purpose]. The release of 1.418 mmol of NaCl thus made the system 0.144 N NaCl. The solution was then diluted to 14.2 cm³ with deionized distilled water to make the solution 0.1 N NaCl. Further dilution with 0.1 N NaCl to 20 cm³ made the concentration of CAS 4 (M_{2-4}) in the presence of 1.5 equivalents of NaOH as 2 g/dL in 0.1 N NaCl. [CAS (4.1H₂O) and APE (7.2H₂O) have very similar molar masses of 273.73 and 277.27, for the repeating units, respectively].

Likewise, the solutions of 2 g/dL of the CAS 4 (M_{2-4}) in the presence of 1.67, 1.8, and 2.0 equivalents of NaOH were prepared by treating 0.400 g (1.418 mmol) of CAS 4

(M₂-4) as above with (1.418+1.418x0.96x0.67), (1.418+1.418x0.96x0.80) and (1.418+1.418x0.96x1) equivalents of NaOH to obtain solution of APE/PB 6 (x = 0.32; z = 0.64; y = 0.04), APE/PB 6 (x = 0.19; z = 0.77; y = 0.04) and APE 7 (x = 0.96; y = 0.04), respectively. A stock solution of 3 g/dL CAS 4 (M₂-4) and 2 g/dL solution of CAS 4 (M₂-5) (derived from CPE 3 M₂-5) in the presence of 1.67 and 2.0 equivalents of NaOH respectively, were prepared in a similar way. To ensure complete dissolution, the solutions were left at room temperature for 24 hours and vigorously stirred with magnetic stir bar for 1 hour to obtain homogeneous solution.

2.3 Rheological measurements

Dynamic shear measurements of polymer solutions over a wide range of oscillation frequencies were conducted using a constant strain Advanced Rheometric Expansion System (ARES) fitted with a stainless steel cone and plate sample cell operating in oscillatory mode. The radius of the plate is 50 mm, cone angle is 0.1 rad and the gap between the cone and plate was set to 0.0483 mm. A shear strain amplitude (γ°) of 10% was used, after a strain sweep test on selected samples showed that this γ° was sufficiently small to produce dynamic properties in the linear viscoelastic region. Reproducibility of frequency sweep measurements is shown in Figure 1 for CAS 4 (M₂-5) sample. The displayed results represent two independent measurements on fresh loadings of the same sample. Excellent agreement of both dynamic viscosity and storage (or “elastic”) modulus, G' shows the degree of reproducibility of these measurements. All experiment were conducted at $25 \pm 0.1^{\circ}\text{C}$ and performed in a descending ω order from 10^2 to 10^{-2} rad/s.

3. Results and Discussion

The Cationic polyelectrolyte **CPE 3** was synthesized via cycloterpolymerization of sulfur dioxide, *N,N*-diallyl-*N*-carboethoxymethylammonium chloride **1** and the hydrophobic monomer *N,N*-diallyl-*N*-octadecylammonium chloride **2** following the procedure earlier reported.²⁵ The **CPE 3** were hydrolyzed in 6 N HCl to produce the water-insoluble cationic acid salt **CAS 4 (M₂-4)** which, on treatment with 1.5, 1.67, 1.80 and 2.0 equivalents of NaOH, afforded the solution of **PB/APE 6** and **APE 7** in approximate **PB/APE** ratios of 50:50, 33:67, 20:80 and ~0:100 respectively. Prior to addition of alkali, the **CAS 4** polymer contains insoluble carboxylic acid groups in the form of latex particles. The addition of NaOH solution neutralizes the acid group (-COOH) on the polymer chain, and as a result the carboxylic acid groups are converted to the ionized carboxylate form which has higher solubility in water.

CAS 4 (M₂-4) terpolymer containing 4.0 mole% hydrophobe as well as its corresponding **PB 5** (obtained by treating **CAS 4 (M₂-4)** with 1 equivalent of NaOH) was found to be insoluble in salt-free or salt-added solutions.²⁷ Critical NaOH equivalent required for the solubility of **CAS 4 (M₂-4)** was around 1.25; this amount of NaOH would result in the formation of **PB/APE 6** with a x:z ratio of approximately 75:25 (Scheme 1). As for the **CAS 4 (M₂-5)** terpolymer containing 5.0 mole% hydrophobe, the critical NaOH equivalent was around 1.50, treatment with 1.67 equivalent NaOH giving a cloudy solution.

Figure 2 shows dynamic viscosity η' dependence on frequency of 2 g/dL polymer solution of **PB/APE 6 (M₂-4)** having various compositions of PB (x) and APE (z) fraction in 0.1 N NaCl. The viscosity values generally decreases with increase in oscillation

frequency, a typical shear thinning behavior of associative polymers. As the oscillation frequency increases, the intermolecular hydrophobic associations are disrupted and this results in a decrease in the viscosity. It is interesting to note that no Newtonian plateau was observed even at very low frequencies. This indicates that the network links are very sensitive and disrupt under the slightest shear. This might be caused by the high electrostatic repulsion, the highly swollen nature of the network and the slight hydrophobic overlap resulting from the strong repulsion.

Variations of dynamic viscosity, η' of a 2 g/dL solution of CAS 4 (M_2-4) is shown in Figure 3 at various oscillation frequencies in the presence of various equivalents of NaOH in 0.1 N NaCl. η' attains its maximum value in the presence of 1.67 equivalent of NaOH, and decreases upon further addition of NaOH. Addition of 1.67 equivalent of NaOH will transform the CAS 4 (M_2-4) to its corresponding PB/APE 6 having an approximate composition of 33:67 for the zwitterionic (x) and anionic (z) parts, respectively²⁶. As mentioned earlier, CAS 4 as well as PB 5 (obtained from CAS 4 on treatment with 1 equivalent of NaOH) are insoluble in water. Internal neutralization of the charges in polybetaines is known to lead the polymer backbone to adapt a collapsed coil conformation as a result of intra-chain interactions.^{28,29} When the net charge of an ionic polymer approaches zero, attraction between oppositely charged units lead to a globule-like conformation, and most often to insolubility in pure water.

As the pH increases, the anionic fraction increases and the PB fraction decreases, as a result the intramolecular aggregates are progressively destroyed because the anionic charge density on the polymer backbone is increased. While the presence of ionic sites of similar charges (CO_2^- groups in the APE fraction) along the hydrophilic backbone can

lead to a better solubility in water and a stronger thickening efficiency due to coil expansion, intermolecular electrostatic repulsions lead to a lowering of the degree of hydrophobic association. Synergistic effect may be observed where the electrostatic repulsions can result in chain expansion and the hydrophobic groups may also maintain interpolymer association. At a x/z ratio of 33:67, combined effect of coil expansion and hydrophobic association was found to lead to a maximum viscosity value (Figure 3). At high pH CAS samples are completely converted to anionic polyelectrolyte (APE) and the electrostatic repulsion causes the chain to lose flexibility and thus hydrophobic groups are less capable of associating with each other to form viscoelastic network. Thus at lower x/z ratios, the effect of coil expansion due to a higher APE fraction is more than counterbalanced by the lower degree of intermolecular hydrophobic associations, whereas at higher x/z ratio the coil contraction becomes the predominant effect.

Figure 4 displays the effect of temperature on dynamic viscosity of 3 g/dL solution in 0.1N NaCl of CAS 4 (M₂-4) treated with 1.67 equivalent of NaOH. Over the entire frequency range studied, η' increases gradually as temperature increases. Hydrophobic effect can be regarded as a process of entropy increase, which means that as temperature increases, the hydrophobic effect increases. The dynamic viscosity increase observed upon heating, is consistent with an entropy driven increase in hydrophobic bonding.^{30,31} On the other hand, the association effect is retarded at high temperature presumably as a result of changes in hydration spheres of the hydrophobic groups and the strong thermal vibration of water molecules.

Viscoelastic properties of concentrated or semi dilute polymer solutions are described by two functions; the dynamic storage modulus G' , which represents the

elasticity of the network and the loss modulus G'' , which accounts for the lost energy due to friction. Figures 5-7 show frequency dependence of the storage modulus G' and the loss modulus G'' , respectively for 2 g/dL polymer solution of the CAS 4 (M_2-4) samples treated with 1.50 and 1.67 equivalent NaOH obtained at 25°C. The G' of CAS 4 (M_2-4) treated with 1.5 equivalent NaOH is consistently lower than G'' over the entire frequency range studied. Both moduli are highly frequency dependent and increase in a parallel manner with increasing ω , thus no cross over frequency could be obtained. On the other hand, CAS 4 (M_2-4) samples treated with 1.67, 1.81 and 2.0 equivalent of NaOH show transition from an elastic dominated response ($G' > G''$) at high frequencies to a viscous-dominated response at lower frequencies. These data are reminiscent of a reversible network wherein interchain interactions are transient.³² A weak gel-like system is obtained with high frequency dependence of G' and up to crossover frequency, ω_{cross} beyond which G'' is relatively less frequency dependent while G' shows a progressive increase with frequency and no plateau value is obtained in both cases. The lack of a plateau can be attributed to the rapid relaxation process.³³ Hydrophobically modified polymers such as galactomannan ether³⁴, galactomannan/borate³⁵ and polyvinylalcohol/borate³⁶ are reported to exhibit similar viscoelastic behavior. The $G'(\omega)$ and $G''(\omega)$ curves cross each other at a particular frequency designated as ω_{cross} and at critical modulus G_c . The critical modulus, G_c of CAS-4 samples treated with 1.67, 1.80 and 2.0 equivalent of NaOH were found to be 2.7, 1.7 and 2.8 respectively.

Frequency dependence of the storage (G') and the loss (G'') moduli obtained at 20° C for 2.5 g/dL and 3 g/dL polymer solutions of the CAS 4 (M_2-4) samples treated with 1.67 equivalent of NaOH show an elastic behavior in which G' is consistently

greater than G'' across the frequency range studied, suggesting the formation of highly interconnected three dimensional network. G' shows high frequency dependence at low frequency and relatively less frequency dependence at high frequency with no plateau value, while G'' remains relatively constant and reaches a plateau, denoting a constant viscous relaxation. No cross over frequency could be obtained for 2.5 g/dL and 3 g/dL polymer solutions of the CAS 4 (M_2-4) samples treated with 1.67 equivalent of NaOH.

Beside the earlier mentioned ionic charge density effect, the polymer concentration and hydrophobe content are certainly other factors that affect the rheological properties of polymer solutions. Figure 8 shows (G') and (G'') as a function of frequency for 2.0 g /dL of APE 7 (M_2-4) and APE 7 (M_2-5). The APEs are obtained by treatment of the corresponding CAS 4 with 2.0 equivalents of NaOH. As mentioned earlier, APE 7 (M_2-4) shows a transition from an elastic dominated response ($G' > G''$) at high frequencies to a viscous-dominated response at lower frequencies, suggesting a reversible network behavior wherein interchain interactions are transient. Whereas APE 7 (M_2-5) clearly exhibits elastic behavior in which G' is consistently greater than G'' across the frequency range studied, suggesting the formation of highly interconnected three dimensional networks.

Conclusion

In this study, the viscoelastic behavior of hydrophobically modified polyelectrolytes obtained from hydrolysis of Cationic acid salt (CAS) 4 and CAS 4 (M_2-4) treated with 1.67 equivalent of NaOH are investigated. The rheological behavior of this system is pH sensitive. The addition of NaOH solution neutralizes the acid group (-COOH) on the polymer chain, and as a result the carboxylic acid groups are converted to

the ionized carboxylate form which has higher solubility in water. Here are the main conclusions:

1. The dynamic viscosity η' dependence on frequency of 2 g/dL polymer solution of PB/APE 6 (M_2-4) having various compositions of PB (x) and APE (z) fraction in 0.1 N NaCl showed a typical shear thinning behavior of associative polymers.
2. The dynamic viscosity, η' , of a 2 g/dL solution of CAS 4 (M_2-4), corresponding to a composition of 33:67 for the zwitterionic (x) and anionic (z) parts, in the presence of various equivalents of NaOH in 0.1 N NaCl attains a maximum value in the presence of 1.67 equivalent of NaOH and decreases upon further addition of NaOH. The maximum is a result of a combined effect of coil expansion and hydrophobic association.
3. At lower x/z ratios, the effect of coil expansion due to a higher APE fraction is more than counterbalanced by the lower degree of intermolecular hydrophobic associations, whereas at higher x/z ratio the coil contraction becomes the predominant effect.
4. The dynamic viscosity of 3 g/dL solution in 0.1N NaCl of CAS 4 (M_2-4) treated with 1.67 equivalent of NaOH' increased gradually as temperature increases consistent with an entropy driven increase in hydrophobic bonding^{30,31}. The association effect is retarded at temperatures higher than 50°C.
5. Rheology of CAS 4 (M_2-4) samples treated with 1.67, 1.81 and 2.0 equivalent of NaOH suggest a reversible network wherein interchain interactions are transient.³²
6. The critical modulus, G_c of CAS-4 samples treated with 1.67, 1.80 and 2.0 equivalent of NaOH were found to be pH dependent.

7. The rheology of APE 7 (M_2-5) clearly exhibits elastic behavior in which G' is consistently greater than G'' suggesting the formation of highly interconnected three dimensional networks.

Acknowledgement

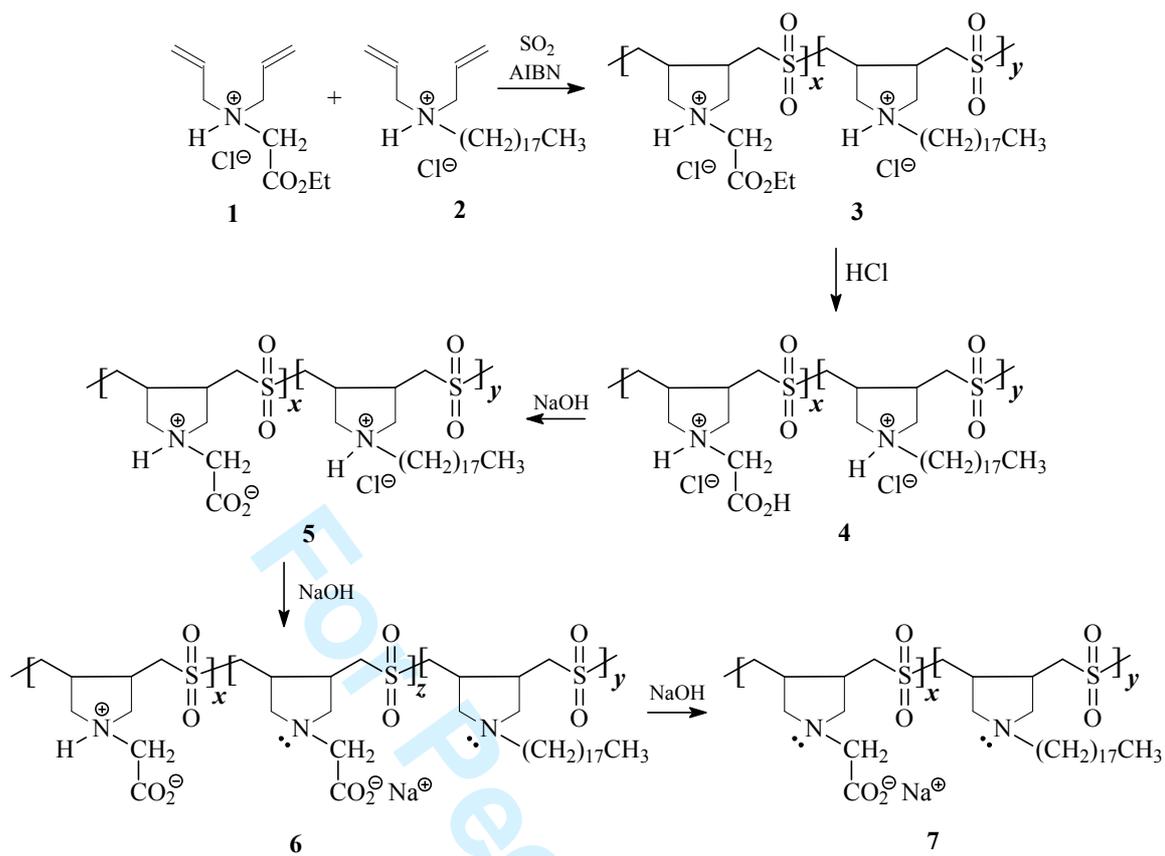
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Scheme 1.

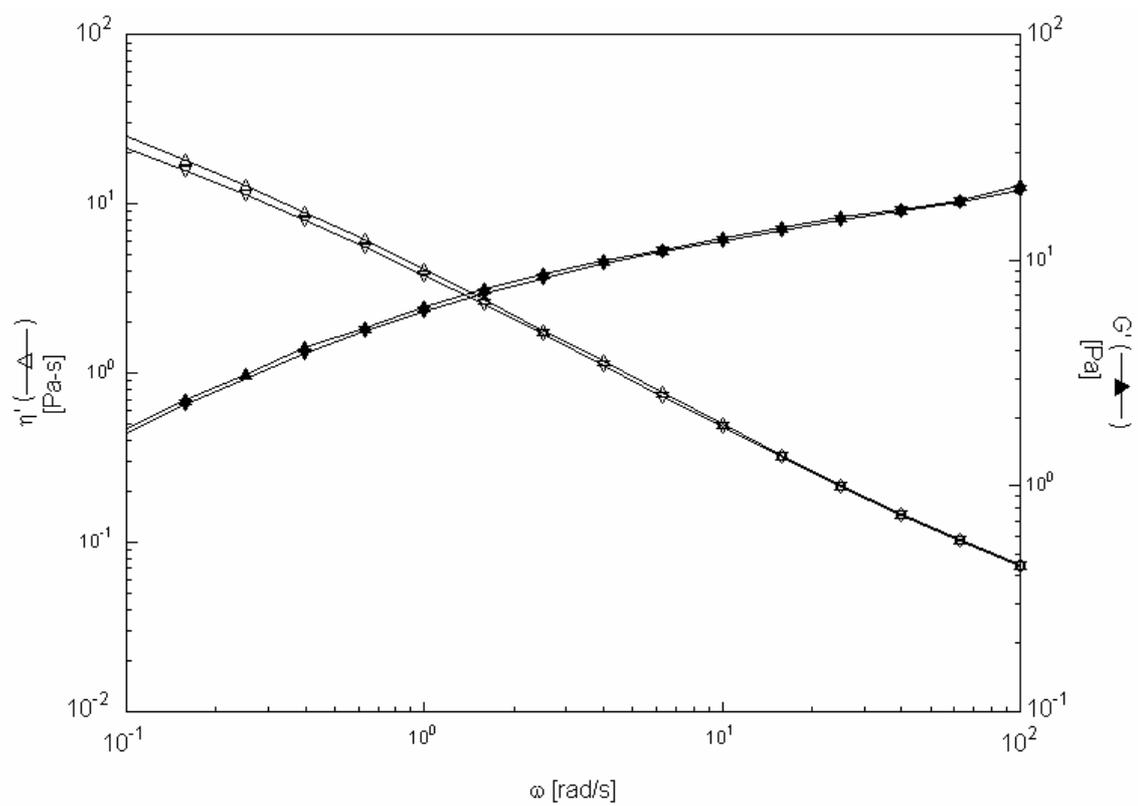


Figure 1: Reproducibility of $\eta'(\omega)$ and $G'(\omega)$ data of CAS 4 (M_2-4) treated with 1.67 equivalent NaOH

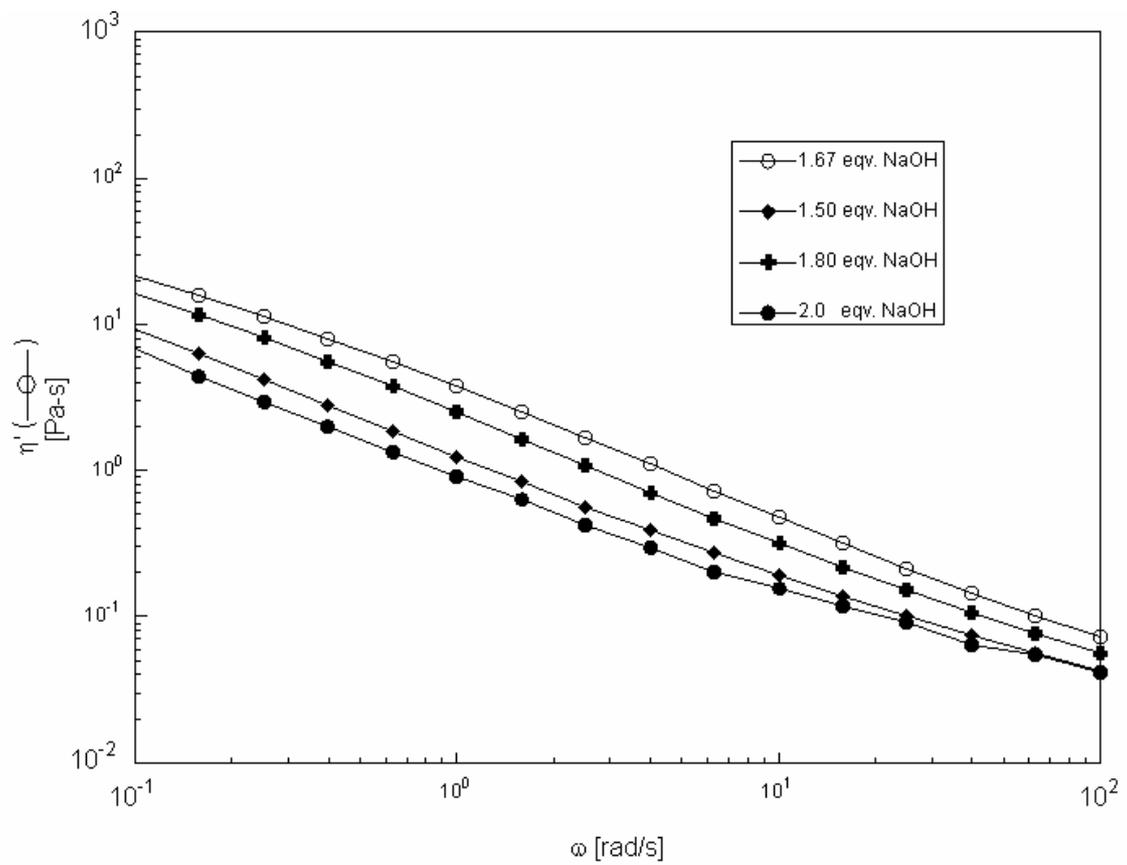


Figure 2: Dynamic viscosity as a function of frequency for CAS sample treated with different equivalents NaOH at 25° C.

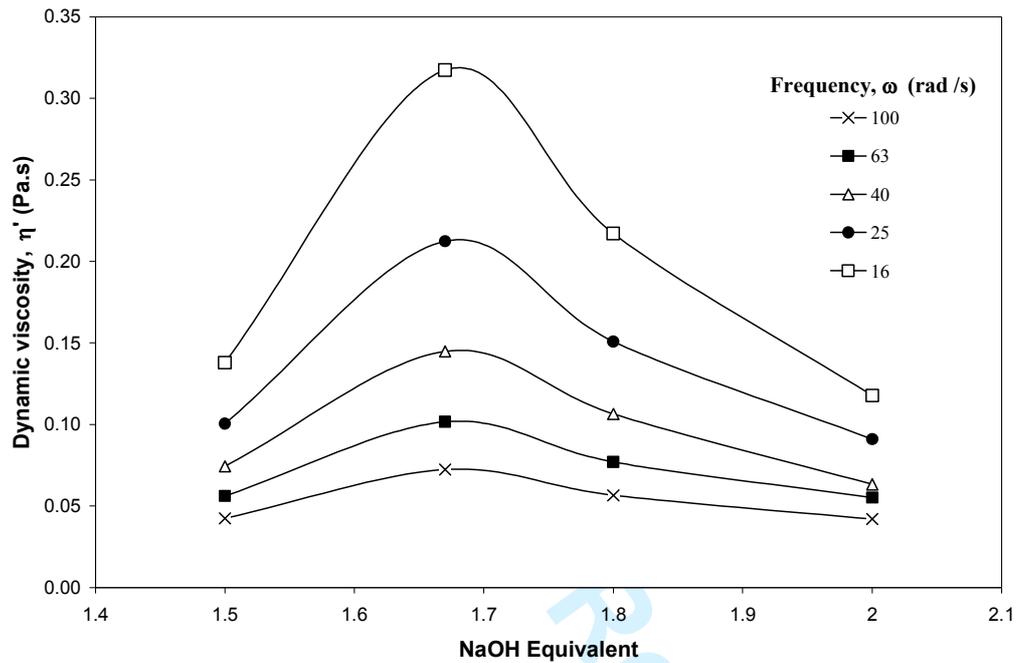


Figure 3: Variation of dynamic viscosity of 2 g/dL solutions of CAS 4 (M_2-4) at various oscillation frequencies in the presence of various equivalent of NaOH in 0.1N NaCl at 25°C

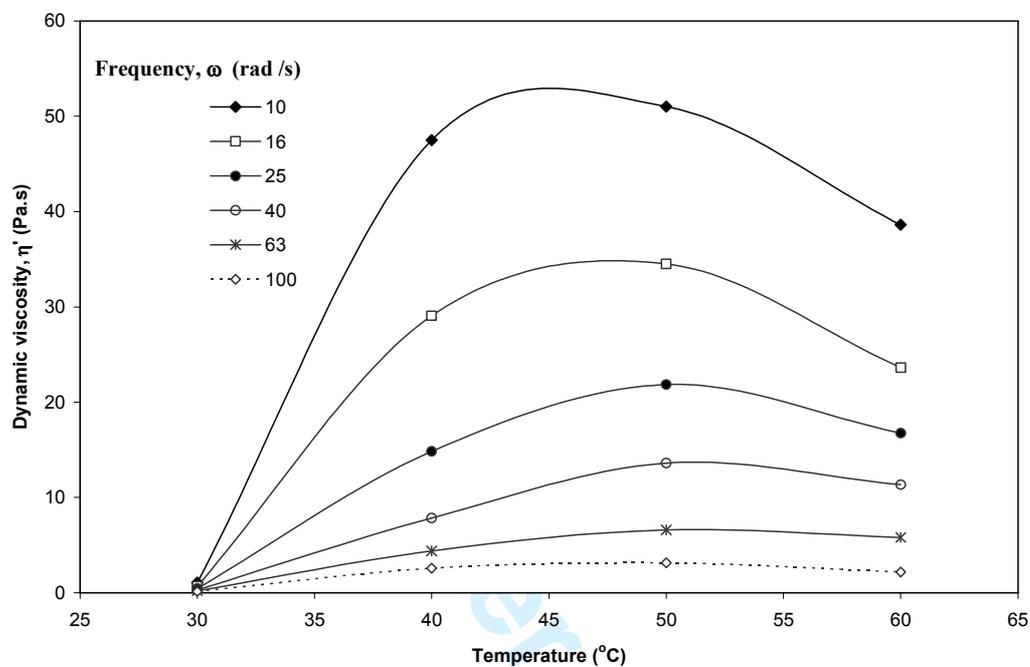


Figure 4: Variation of dynamic viscosity with temperature of 3 g/dL solutions of CAS 4 (M_2-4) treated with 1.67 equivalent of NaOH in 0.1N NaCl at various oscillation frequency

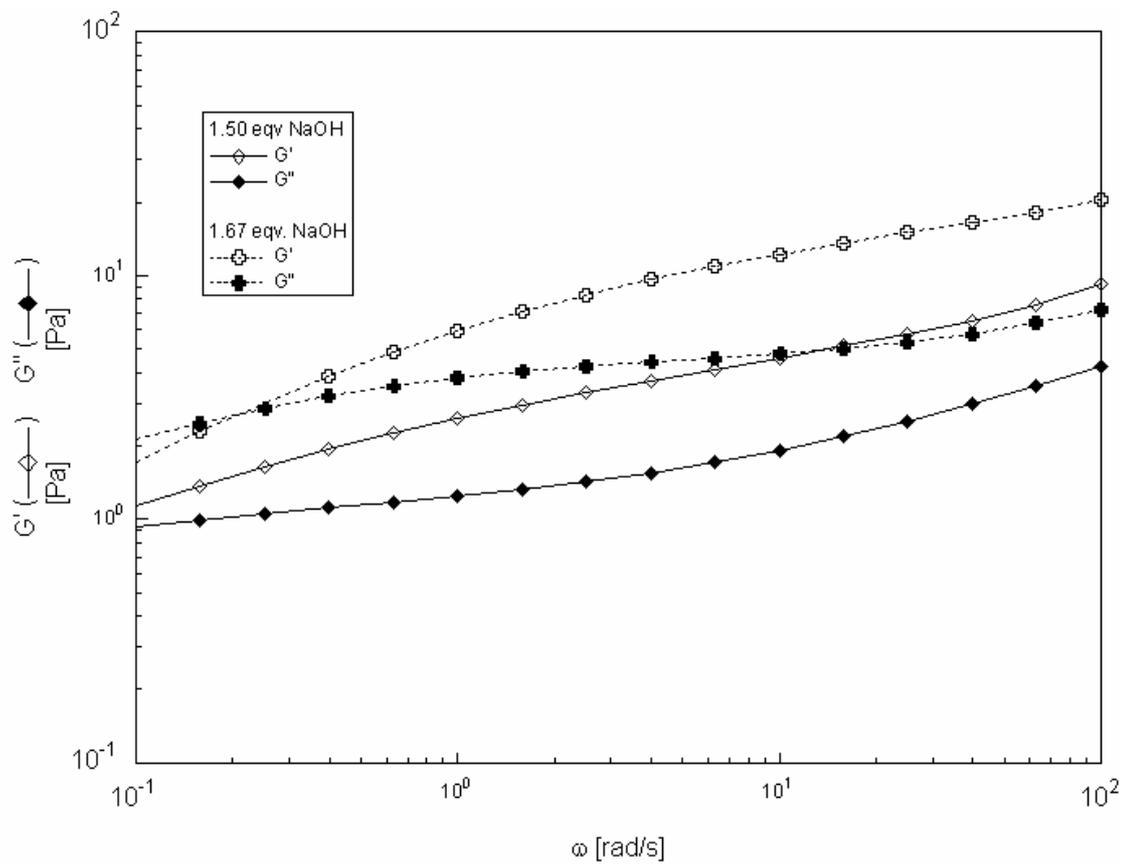


Figure 5: Storage (G') and loss (G'') moduli as a function of frequency for CAS 4 (M_2-4) sample treated with 1.5 and 1.67 equivalent of NaOH at 25° C

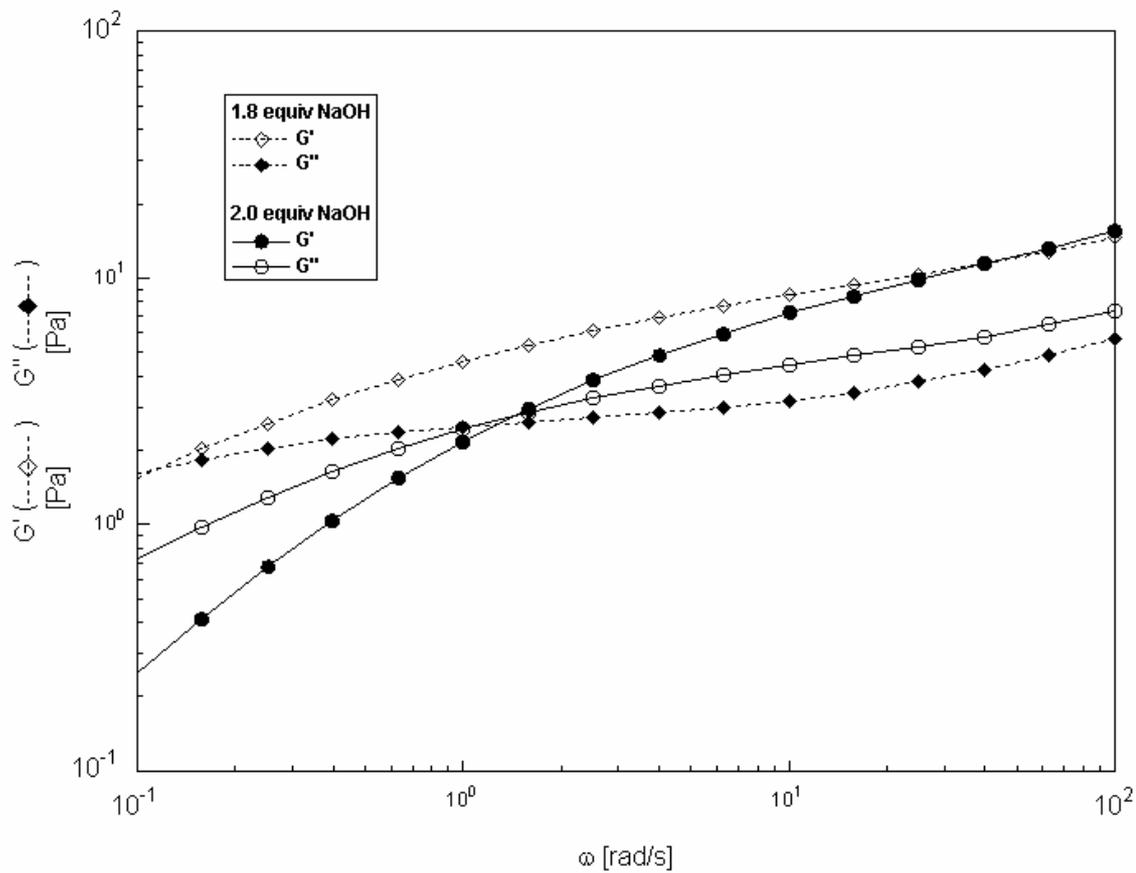


Figure 6: Storage (G') and loss (G'') moduli as a function of frequency for CAS 4 (M_2 -4) sample treated with 1.80 and 2.0 equivalent of NaOH at 25° C

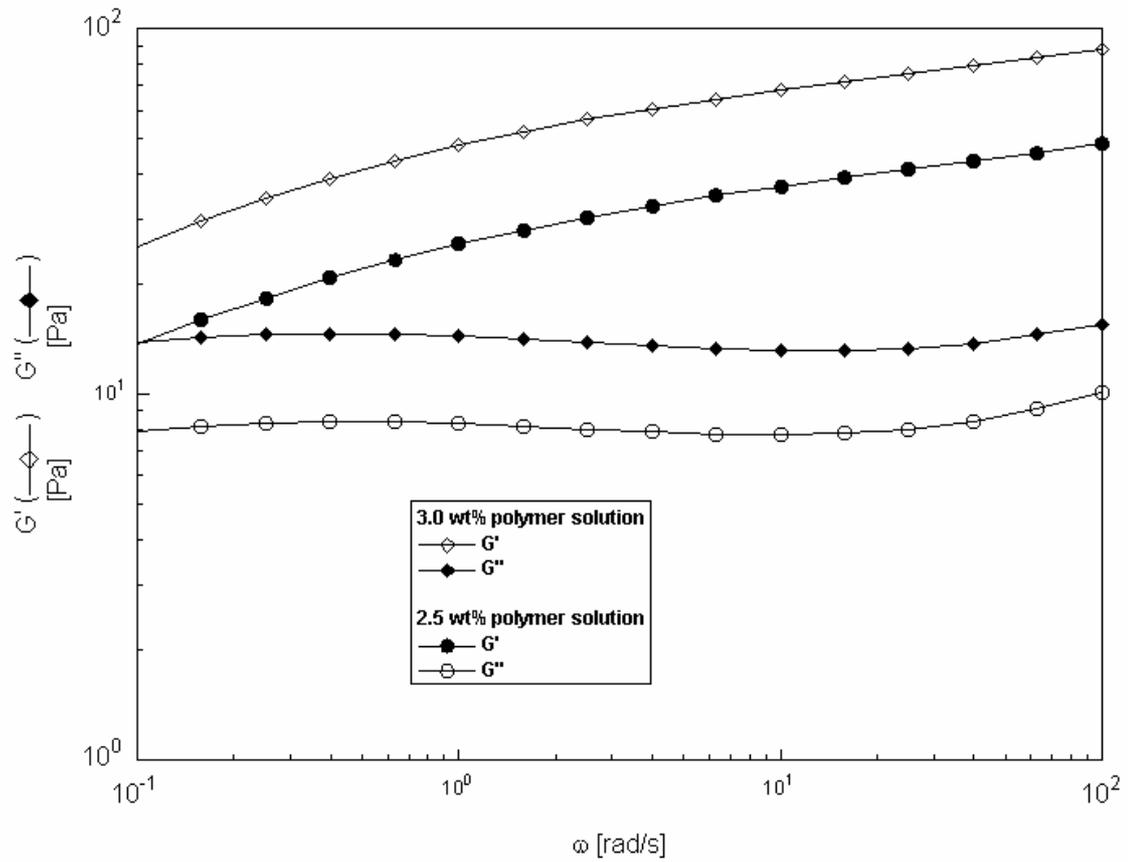


Figure 7: Storage (G') and loss (G'') moduli as a function of frequency for CAS 4 (M_2 -4) sample treated with 1.67 equivalent of NaOH at 25° C

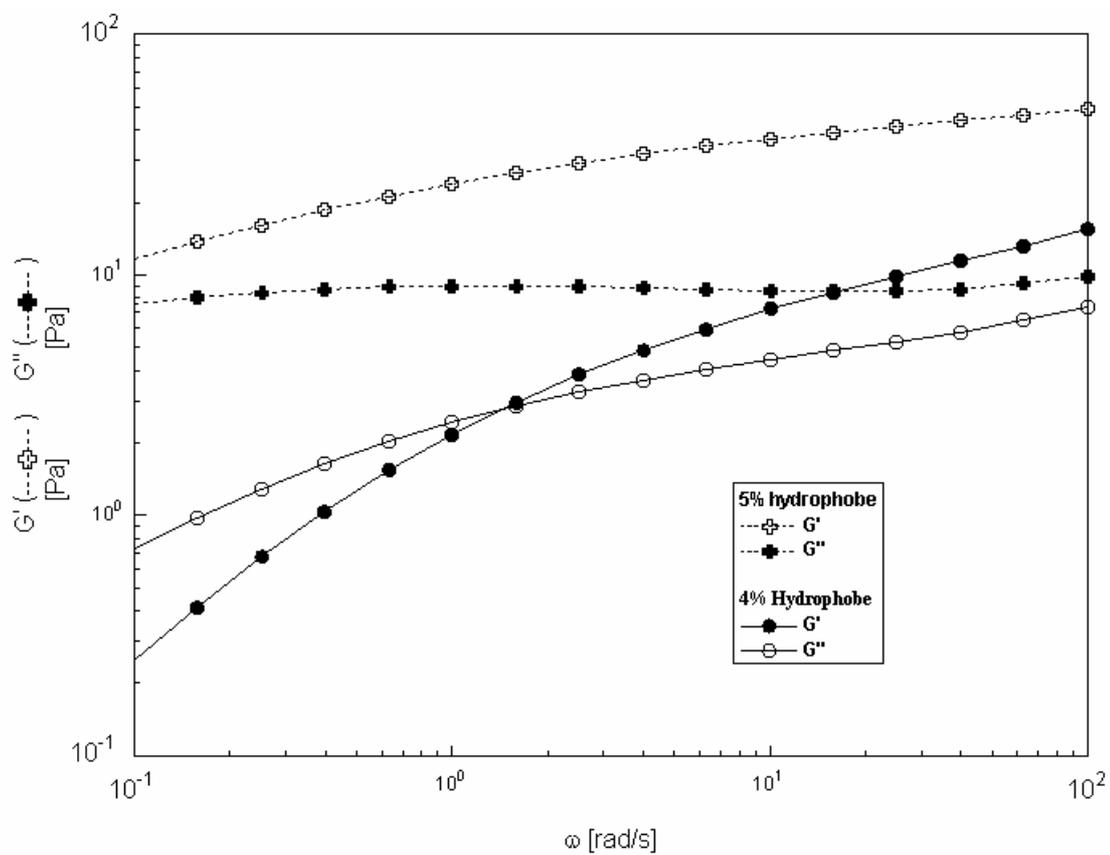


Figure 8: Storage (G') and loss (G'') moduli as a function of frequency for CAS 4 (M_2-4) and CAS 4 (M_2-5) samples treated with 2.0 equivalent of NaOH at 25° C.