Characterization of viscoelastic properties of polyacrylamide/Cr(III) hydrogels

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Summary

The viscoelastic properties of polyacrylamide/Cr(III) hydrogels were characterized with the help of oscillatory shear rheometer. The serrated-plate geometry rather than the cone-plate geometry was used in order to avoid the slip effect. The dynamic storage modulus (G') increased with increasing polyacrylamide and/or Cr(III) concentrations. The mean molecular weight of the chains adjoining adjacent crosslinks (M_c), calculated according to the elastic rubber theory, exhibited the same order of the primary polymer. G' decreased with increasing monovalent salt concentration, owing to the polyelectrolyte effect.

Introduction

Polyacrylamide (PAM) in aqueous solution may react with chromium originally in its +3 valence state to form a hydrogel. The controllability of gelation rate by adding the organic complexing agents such as propionate, acetate, malonate makes the gel system of great interest for the application in petroleum production industry, especially for reservoir profile modification(1-3).

Otherwise, this gel system provides variable gel strengths, from weak gels to strong gels, to meet the need for the conditions of different strata. A particular attention is then paid to the mechanical performance in response to viscoelastic properties that can be determined by means of oscillatory shear measurement. According to the rheological theory(4), the storage modulus (G') and the loss modulus (G") vary with excitation frequency (ω). For linear polymer solution, the double logarithmic plot of G' and G" is characterized by low frequency slopes of 2 and 1 respectively, whereas for gels, G' and G" are independent of ω. Moreover, the magnitude of viscoelastic parameters is closely related to the feature of gel network.

Based on our previous work on sol/gel phase diagrams and gelation kinetics (5,6), we report here studies on the viscoelastic behaviors of polyacrylamide/Cr(III) hydrogels with the help of oscillatory shear rheometer, which may lead to a good understanding of strength and structure of the hydrogels.

Experimental

The polyacrylamide used in this work was provided by the No 6 Chemical Factory at Fusun, China. The weight-average molecular weight was 3.6×10^6 g mol^{-1} as mesured by low angle laser light scatting (KMX-6) and the intrinsic viscosity was 770 ml g^{-1} determined by low shear viscosity mesurement (Contraves). The hydrolysis degrees of polyacrylamdes were determined by IR study with IFS-113V FT-IR spectrophotometer (Bruker). The absorbent ratio (R) of the peak at 1677 cm^{-1} to that at 1610 cm^{-1} was related to the hydrolysis degree (τ , in percentage) as follows(13):

$$R = 2.236 - 0.021 \ \tau$$

The stock polymer solutions were prepared by gentle stirring in distilled water containing certain amount of NaCl. The stock solution of Cr(III) with a concentration of 2×10^{-3} g ml^{-1} was prepared from CrCl$_3$.6H$_2$O, chemical grade.

The 10-ml samples were prepared by mixing of desired quantities of polyacrylamide, Cr(III), and solvent. They were stirred and then allowed to rest in an oven at 70°C for 24 hours.

Dynamic viscoelastic properties were measured by CS-50 Rheometer (Bohlin) equipped with serrated parallel plates (2cm). One exception with cone-plate (4cm and 2°) was indicated in the context. The excitation frequency of oscillatory shear ranged from 0.01 to 10 rad s^{-1}. The temperature was maintained at 26°C using a thermostat circulating silicon oil.

Results and Discussion

The rheological properties of a series of polyacrylamide/Cr(III) hydrogels were measured by means of oscillatory shear rheometer with serrated parallel plate in the frequency range of $10^{-2} \sim 10^1$ rad s^{-1}. Fig.1 illustrates the dependence of dynamic storage moduli G' and loss moduli G" on the excitation frequencies (ω).
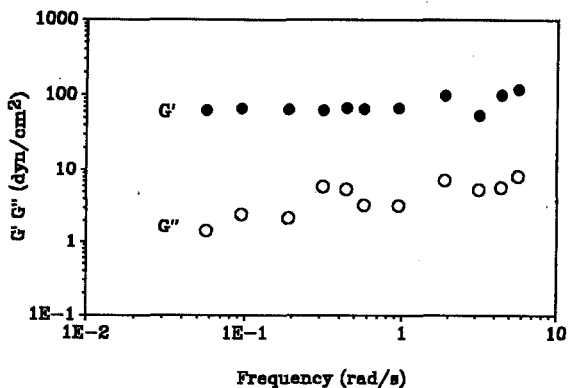

Fig.1   Variation of G' and G" with Frequency
PAM: 8×10^{-3}g ml^{-1}; Cr(III): 5×10^{-5}g ml^{-1}; NaCl: 5×10^{-3}g ml^{-1}

It is shown that the plateau of G' is extended to low frequency (10^{-2} rad s^{-1} or less)

and superior to the plateau of G"(Fig.1). This phenomenon suggests that the hydrogels be considered as rubber-like materials. G', which represents the elasticity of polymer network, is virtually related to the strength of the hydrogels. Moradi-Araghi et al. indicated that a G' superior to 100 dyn cm^{-1} represents a strong gel, whereas a G' inferior to 10 dyn cm^{-1} a weak gel (7). The strength of a gel is one of the important parameters for the determination of suitability of the gel for a given application.

It was reported by some researchers that the gelation kinetics could be followed by rheometer equipped with parallel plate or cone-plate geometries (8-10). G' might augment with the gelation process and reach its maximum that indicated the equilibrated state of hydrogels. However, the measurement of a separately prepared gel seems not accurate using parallel plate or cone-plate geometries. With our experiences, the occurrence of slip effect makes the value of G' much small (Fig.2, for comparison) and gives the same value of G' for different gels. Therefore, it seems necessary to use serrated parallel plate to characterize this kind of formed hydrogels.
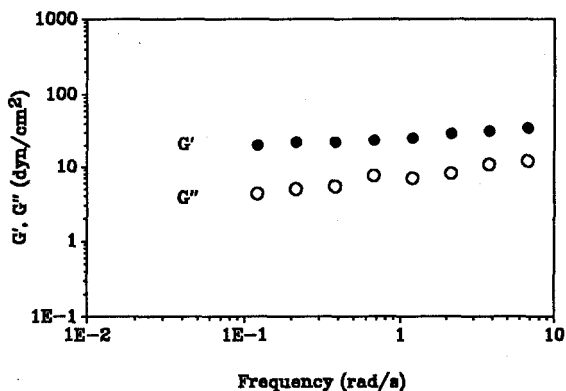

Fig. 2. Variation of G' and G" with Frequency Using Cone-Plate Geometry
PAM: 8 × 10^{-3}g ml^{-1}; Cr(III): 5 × 10^{-5}g ml^{-1}; NaCl: 5 × 10^{-3}g ml^{-1}
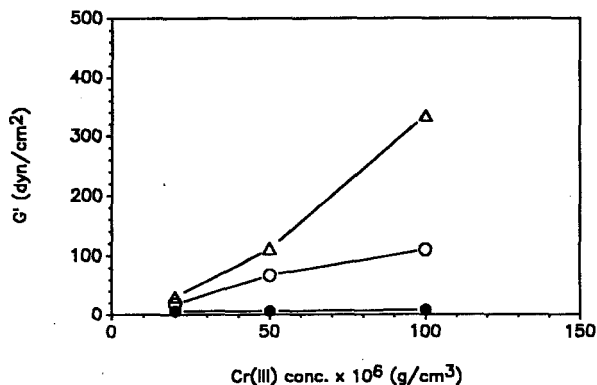
Fig.3.   Dependence of G' on Cr(III) Concentration
PAM: •4 × 10^{-3}, o 8 × 10^{-3}, △12 × 10^{-3} g ml^{-1}, NaCl: 5 × 10^{-3}g ml^{-1}

The dependence of G' on crosslinker concentration for different polymer concentrations is shown in Fig.3. As can be seen from Fig.3, G' increases with increasing polymer and/or crosslinker concentrations. The value of G' ranges from several to several hundreds dyn cm^{-2}.

The magnitude of G' corresponds to the network structure of hydrogels. According to the elastic rubber theory (11), G' may be presented as

$$G' = (\Phi C_p RT/M_c)(1-2M_c/M_w) \qquad (1)$$

in which Φ is the front factor ranging from 1 to 10, C_p the polymer concentration, R the gas constant, T the absolute temperature, M_c the average molecular weight of the chains adjoining adjacent crosslinks, and M_w the average molecular weight of primary polymer. With the help of Eq.(1), M_c can be calculated from G'. Fig.4 presents that the calculated M_c decreases slightly with increasing crosslinker concentration. In other words, the crosslinking density increases with crosslinker concentration. As can be seen from Fig.4, M_c is in the range 0.8 ～ 1.7 × 10^6 g mol^{-1}, which is in the same order of the primary polymer (3.6 × 10^6 g mol^{-1}). This feature, analogous to that found for xanthan/Cr(III) hydrogels by Lund et al.(10), suggests that there be only several crosslinking junctions per primary polymer.
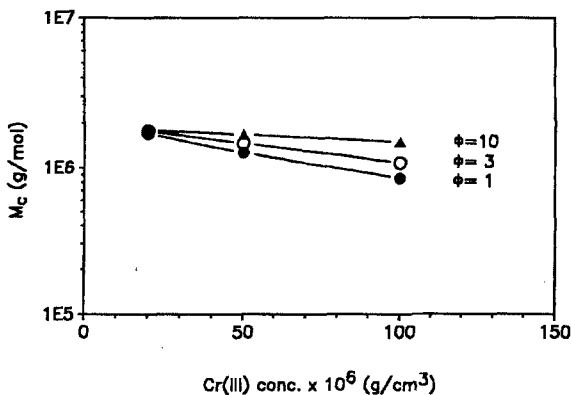

Fig.4.   Correlation between M_c and Cr(III) Concentration with Different Φ
PAM: 12 × 10^{-3}g ml^{-1}; NaCl: 5 × 10^{-3}g ml^{-1}

Fig 5 shows that the influence of monovalent salt (NaCl) on G' of hydrogel. This is related to the polyelectrolyte properties of polymer network, for under the reaction temperature 70 °C for 24 hours, polyacrylamide hydrolyzes to partially hydrolyzed polyacrylamide with a portion of carboxyl groups (about 40%). As a polyelectrolyte, the conformation is strongly influenced by ionic strength(12). At low ionic strength, Na$^+$ is not enough to screen the electrostatic repulsion among carboxyl groups. G' is greater owing to the potential of network expansion. G' decreases with increasing NaCl concentration. After a NaCl concentration of around 0.05 M, the carboxyl groups seem

concentration. After a NaCl concentration of around 0.05 M, the carboxyl groups seem to have been saturated with Na$^+$ and G' decreases slightly with increasing NaCl concentration. It is worthwhile to further study on the salt effect on viscoelastic properties of the hydrogels.
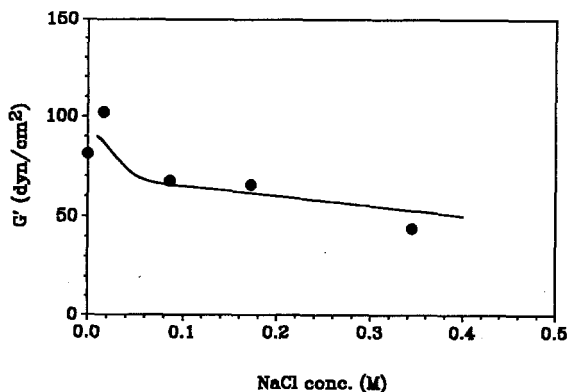

Fig.5.   Influence of Monovalent Salt Concentration on G'
PAM: 8 × 10^{-3}g ml^{-1}; Cr(III): 5 × 10^{-5}g ml^{-1}

Acknowledgment

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