Atomic Force Microscopy Studies on Hydroxypropylguar Gels Formed under Shear

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ABSTRACT: Atomic force microscopy (AFM) is used to image hydroxypropylguar gel structures formed under quiescent conditions as well as gels formed under varying levels of steady shear. Hydroxypropylguar (HPG) in aqueous solution is representative of a high molecular weight, flexible polysaccharide. HPG readily cross-links with borate ions to form a gel network. The steady-state rheological properties of borate cross-linked HPG gels are shown to be dependent on the shear rate applied during the gelation reaction. The storage modulus is used as an indication of the gel strength. The gel strength is shown to be enhanced under moderate shear conditions and is seen to decrease under high shear during gelation. AFM images show an aligned, ordered structure is present in the high gel strength material (low preshear rate), with a random network structure present in the gel formed under quiescent conditions. A material composed of globular structures is apparent in the gel formed under high shear. The variation in the observed microstructure and rheological data with preshear rate is discussed in relation to alignment of polymer molecules in shear fields.

Introduction

Hydroxypropylguar (HPG) is a high molecular weight polysaccharide which displays semi-flexible behavior in distilled water.[1] A gel is formed when borate ions are added to an HPG solution. The borate−HPG cross-links are in a state of dynamic equilibrium, where the cross-link bonds are continually breaking and re-forming.[2] As a result of the dynamic equilibrium of the cross-links, gelling the fluid under shear does not result in irreversible shear degradation of the gel structure. The recovery of the cross-links makes the HPG−borate system an ideal fluid to study the effects of polymer orientation and alignment in shear. At the cessation of the steady shear phase of an experiment, it is expected that the cross-linking should freeze the polymer molecules in their shear-induced state and allow the resultant gel structure to be probed using the AFM technique.

A limited number of studies have been conducted to probe the behavior of polymer molecules in dilute solution under shear using scattering techniques.[3−5] These methods are generally not applicable to semidilute solutions, as the presence of multiple scattering obscures interpretation of the results. It is anticipated that the behavior of polymers in semidilute solution under shear varies significantly from that of dilute polymer solutions under shear due to the presence of interactions. AFM imaging of gels formed under controlled shear conditions presents a novel method for observing the resultant gel structures and should contribute to the level of knowledge of the behavior of semidilute polymer solutions in shear. In recent times the AFM surface imaging technique has been applied to a number of biopolymer systems to image the molecular structure of single molecules and polymers in solution with great success.[6−8] We present images obtained for gels formed under different shear conditions which enable insight into the molecular behavior under shear to be inferred.

Experimental Section

The molecular weight of the HPG sample used in this study has been calculated, using the intrinsic viscosity of 20.2 dL/g and literature values of the Mark−Houwink equation to be 3.5×10^6.[1] All polymer solutions tested were prepared in distilled water at a concentration of 0.48 wt %. The overlap concentration, given as the boundary between dilute and semidilute behavior, was determined to be 0.164 d/L for HPG with a molecular weight of 3.5×10^6 in distilled water. Boric acid is used as the source of the borate ions. The gel reaction is initiated through the addition of hydroxide ions which shift the equilibrium illustrated in eq 1 in favor of the borate

$$H_3BO_3 + OH^- \rightleftharpoons B(OH)_4^- \quad (1)$$

species. The concentration of boric acid used is 0.36 d/L and 0.26 d/L of NaOH is added to initiate cross-linking. The pH of a 0.48 wt % HPG solution with 0.36 d/L of boric acid is approximately 6.2 at 20 °C. At this pH the concentration of borate ions is effectively zero. Upon the addition of 0.26 d/L of NaOH the pH shifts to 11 where the concentration of borate ions approaches a maximum.

All rheological characterization has been performed using a controlled strain rate Weissenberg Rheogoniometer in a cone-and-plate configuration. The cone-and-plate geometry is used to ensure that the entire fluid sample in the rheometer experiences a constant, well-defined shear field.[9] Other rheometer geometries, such as parallel plate and couette geometries, place a shear gradient across the fluid sample which is often ill-defined for structured fluids.[10] The rheometer has been modified, as illustrated in Figure 1, such that the gel components can be injected directly into the rheometer to allow cross-linking to occur in situ while the instrument is operating in steady shear.

Borate cross-linked HPG gels are highly elastic and, combined with their structured nature, may develop flow instabilities which result in the sample being displaced from the

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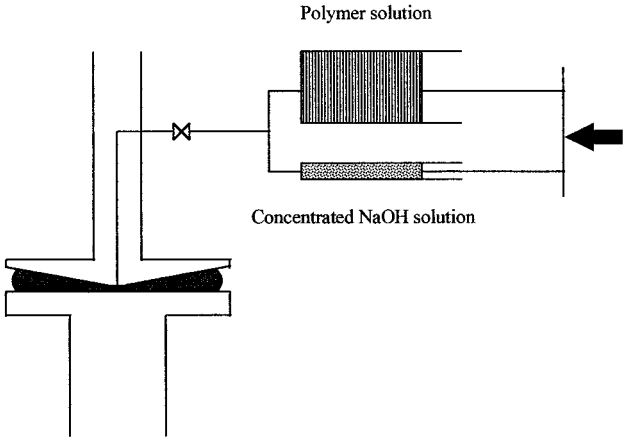

Figure 1. Modified Weissenberg Rheogoniometer for in situ gelation under quiescent and steady shear conditions.

rheometer gap when a steady shear rate is applied, unless the sample gap is underfilled. Underfilling the gap prevents the fluid from displacing out of the gap during the steady shear phase of the experiment. The steady shear phase of the experiment is initiated prior to injecting the fluid into the gap and then continued for a period of 10 min after loading the sample into the rheometer. The reacting components of the gel are assumed to be well mixed due to a combination of a T-joint in the injection system, the impingement of the components onto the base plate of the rheometer and the action of the constant shear. After 10 min of applied shear, the steady shear was stopped and the rheometer operation was switched to oscillatory mode where the storage modulus was monitored as a function of time for a period in excess of 8000 s or until the data approached a steady-state value. Between the switch from steady shear operation to oscillatory operation the exposed edges of the fluid were covered with silicon oil to prevent drying of the sample during the oscillatory testing phase of the experiment. At all times the oscillatory measurements were made in the linear viscoelastic region of the fluid.

The procedure for preparing the AFM samples was similar to that used by Kirby et al.[6] and is outlined as follows. The HPG gel samples were removed from the rheometer with minimal disturbance and placed on freshly cleaved mica, which provides an atomically flat surface, and then dried in air for 24 h to remove the solvent. For the samples which were sheared, the cone was separated from the lower plate at the cessation of the shearing phase and mica was placed under the gel sample and then left to dry. Care must be taken at this point to ensure both the face of the gel and the internal structure are not damaged or altered in any way.

The AFM used to probe the gel structure was a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA). It is possible to operate the instrument in two modes; contact and Tapping-mode. The contact mode drags the sample across the AFM tip and essentially maintains contact between the tip and the sample at all times. The contact method applies a far greater force to the sample and can lead to poor images and distortion of the sample by the tip for soft samples.[8] Alternatively, the Tappingmode method operates in a manner where the scanning tip is mechanically oscillated at its resonant frequency. In the Tappingmode method, the tip intermittently contacts the surface at the lowest point in the oscillation and thus is not in constant contact with the sample. This technique significantly reduces the forces exerted by the tip on the sample compared to the conventional contact mode of operation, thereby reducing sample damage. Both contact and Tappingmode methods were evaluated, operating in air and under butanol. Imaging HPG samples dried in air using the Tappingmode method was found to give the best images. Integrated silicon cantilevers were used. The cantilevers were oscillated at or slightly below their resonant frequency, which was between 300 and 500 kHz. "Soft" tapping of the surface was achieved by maximizing the tapping mode setpoint, such

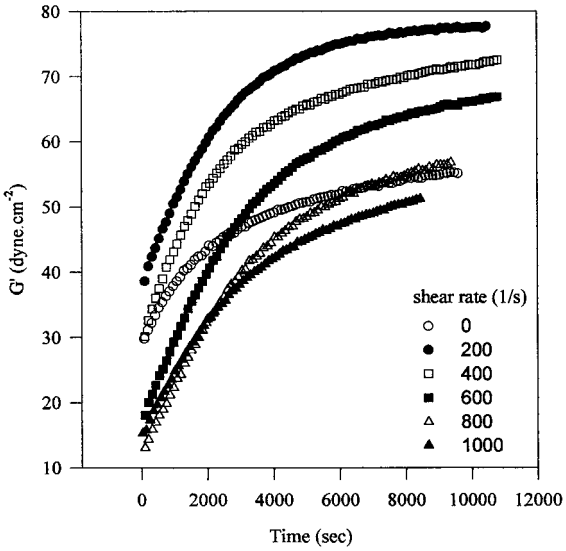

Figure 2. Storage modulus as a function of time for fluids gelled under various levels of shear applied for a period of 10 min.

that it was just below the value required to completely withdraw the tip from the sample. In this way, imaging of the surface layers only was achieved.

Discussion

Figure 2 illustrates the variation of gel strength with time, as indicated by the storage modulus G', for gels which have experienced varying levels of shear for a period of 10 min after injection into the rheometer. In a more comprehensive set of experiments both the time of preshear and the intensity of the preshear have been varied.[1] The fluid sheared at 200 s^{-1} can be seen to have the highest storage modulus data for times beyond 8000 s, as demonstrated in Figure 2. As the shear rate is increased the value of the storage modulus data decrease. For shear rates higher than 1000 s^{-1}, the storage modulus data as a function of time essentially become constant and no further decrease in G' was observed. A gel of intermediate strength results when no shear was applied to the fluid as it gels. Stronger gels may be produced at shear rates below 200 s^{-1}, but this could not be evaluated as the sample could not be held in the rheometer gap at shear rates lower than 200 s^{-1}.

Gels formed with shear times of 10 min at shear rates of 200 and 1000 s^{-1} were chosen for AFM studies as these conditions produced the greatest difference in the rheological data. In the context of this work a shear rate of 200 s^{-1} is referred to as moderate while 1000 s^{-1} or higher is considered as a high shear rate.

Atomic force microscopy (AFM) was used as a method to probe the molecular structure of the polymer network which constitutes the gel and to illustrate, through observation of the microstructure, the effect shear has on the molecular alignment and configuration of polymers in the semidilute concentration region.

In Figure 3 an AFM image of the polymer network of a HPG gel formed under quiescent conditions is presented. The molecular strands of the HPG molecules are clearly visible in Figure 3, though it is not possible to unequivocally identify cross-linking points of the gel. Importantly, Figure 3 illustrates the random nature of the molecular orientation expected for a gel which has not been sheared.

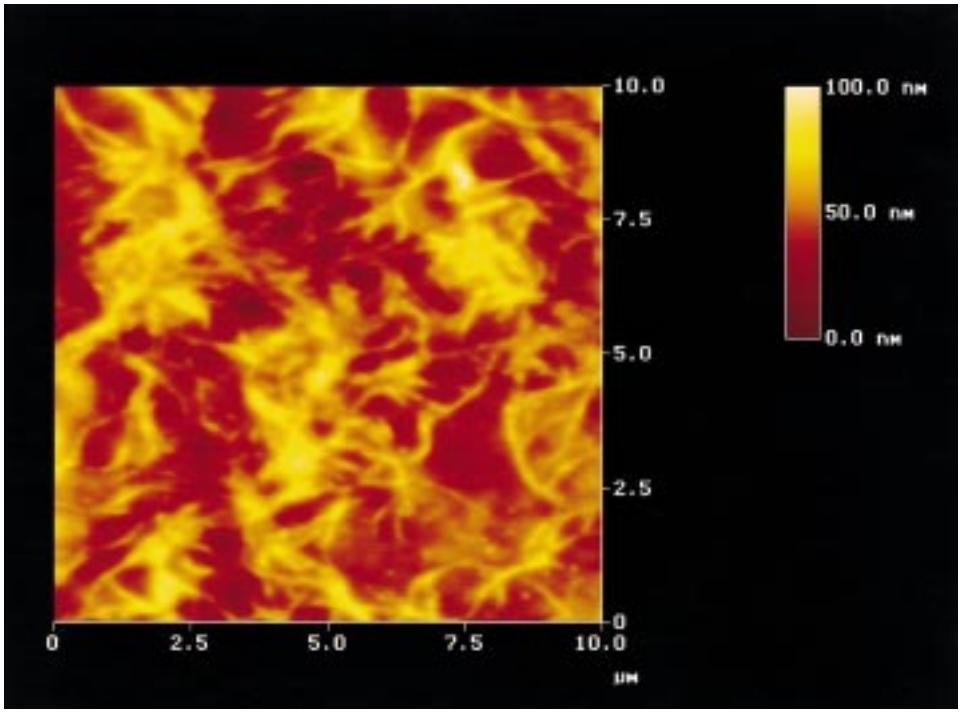

Figure 3. Atomic force microscopy image of borate cross-linked HPG gelled under quiescent conditions. Image size 10 μm × 10 μm.

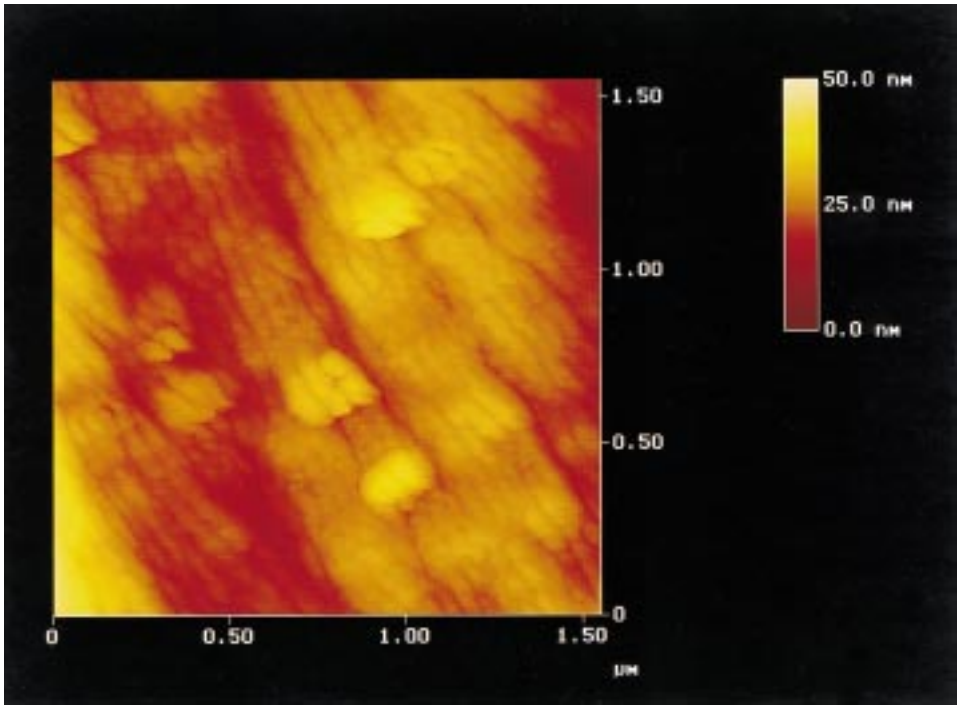

Figure 4. Atomic force microscopy image of borate cross-linked HPG gelled under a shear rate of 200 s^{-1} applied for 10 min. Image size 1.5 μm × 1.5 μm.

It should be noted that the apparent width of the surface features is considerably larger than that expected for individual polymer chains and may reflect tip broadening.

Figure 4 shows an image of an HPG gel formed under a shear rate of 200 s^{-1}, applied for 10 min. A high degree of alignment is evident in the image shown in Figure 4. The contrast in the gel structure relative to the structure illustrated in Figure 3 is quite dramatic. The shear rate of 200 s^{-1} straightens and aligns the polymer molecules in solution, allowing a fiber type molecular structure to be developed. The resultant strength of the gel with an ordered or aligned network structure, due to the applied shear rate of 200 s^{-1}, should be higher than that of the gel with a random network structure which is as observed in the rheological data in the magnitude of G'. Clusters, or bundles, of aligned molecules appear to have formed in the gel structure shown in Figure 4. It is unclear at this stage as to whether the bundle formation evident in Figure 4 is entirely due to the shear alignment or is partially a result of the drying process. It should be noted that the

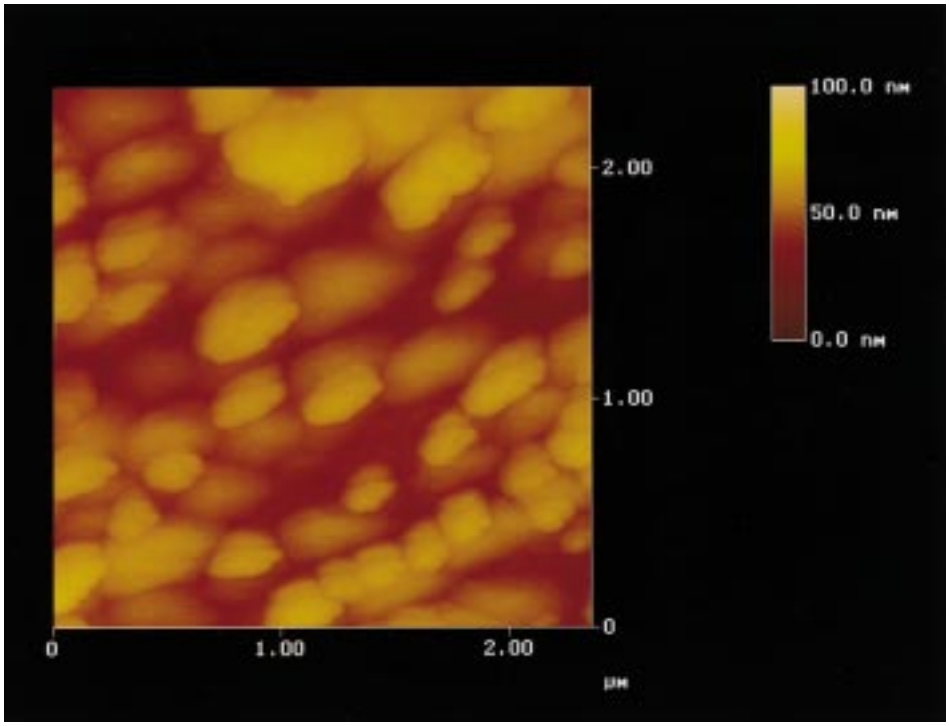

Figure 5. Atomic force microscopy image of borate cross-linked HPG gelled under a shear rate of 1000 s^{-1} applied for 10 min. Image size 2.5 μm × 2.5 μm.

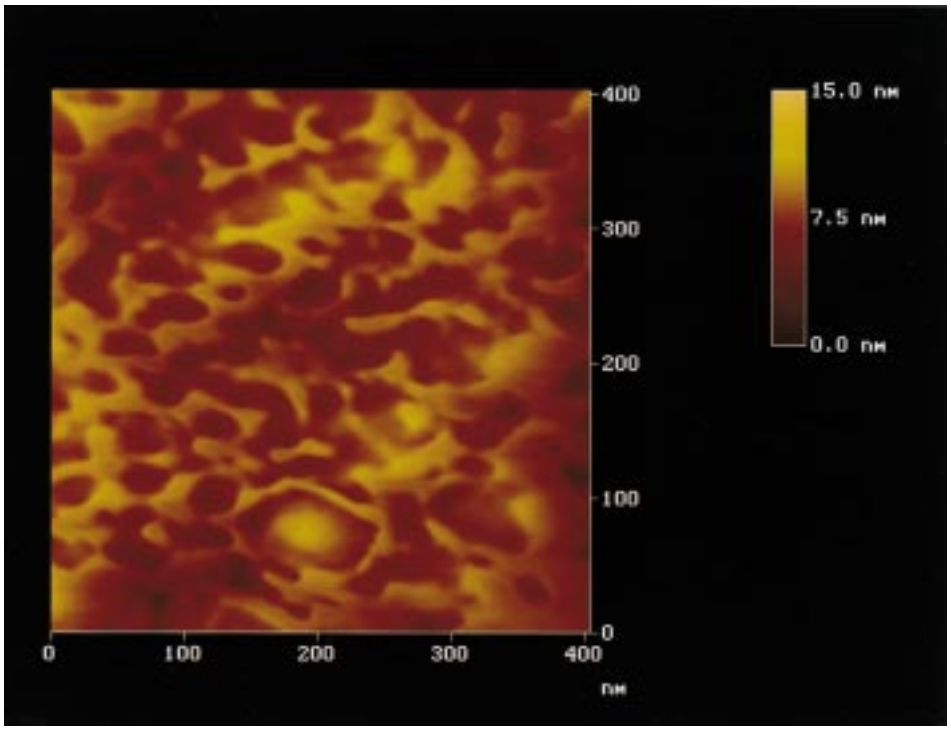

Figure 6. Atomic force microscopy image of borate cross-linked HPG gelled under a shear rate of 1000 s^{-1} applied for 10 min. Image size 400 nm × 400 nm.

effective volume fraction of the polymer observed in Figure 4 is much higher than that observed in Figure 3, presumably a result of the drying process. The dimensions of Figures 3 and 4 are quite different. These images were chosen to best show the microstructural detail observed across the gel.

An image of a gel prepared under a shear rate of 1000 s^{-1} is shown in Figure 5. The gel structure observed is composed of discrete globular entities which are not extensively interconnected. The globular structures are somewhat monodisperse indicating they are formed as a result of a single mechanism or driving force and are not a product of a random process. On closer inspection the polymer structure of the ball-like entities can be observed, Figure 6. The magnification of Figure 6 is substantially higher than that of the other AFM images but does serve to illustrate the apparent highly entangled nature of the globular structure. The globular structures shown in Figure 5 appear to consist of clusters of HPG molecules.

It is expected that the initial size of the polymer clusters would have been larger than is observed and that the size indicated in Figure 5 is reduced due to shrinkage when the sample is dried. It is postulated that the clusters are not formed directly but result from the aligned molecules becoming unstable and collapsing into entangled, ball-like entities of relatively constant dimensions. The dimensions of the clusters are thus expected to be controlled by the forces associated with the shear field. In the initial instance, at a shear rate of 1000 s^{-1}, it is thought that the molecules align in much the same manner as represented in Figure 4 but then become unstable in the shear and tumble to form the globular structures observed.

Conclusion

Atomic force microscopy has been used to observe directly the orientation and conformation of high molecular weight polymers gelled under shear in the semidilute region. At moderate levels of shear (200 s^{-1}) HPG molecules are straightened and aligned, which gives rise to the resultant gel having a higher storage modulus than for a gel formed under quiescent conditions due to the formation of fiber type structures. At high levels of shear (1000 s^{-1}) the aligned structure collapses into clusters of molecules which then have significantly lower gel strength properties as a result of reduced network cross-linking. These observations have the potential to greatly improve the current level of understanding of polymer fluid mechanics and offer a means by which the manufacture of structured materials can be optimized in regard to product strength.

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