

# Ultracentrifugal Studies of the Degradation of a Fracturing Fluid Polymer: Hydroxypropyl Guar

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## SYNOPSIS

Ultracentrifugal techniques have been employed to investigate the degradation of hydroxypropyl guar (HPG) solutions, and of gels formed with a delayed zirconium cross-linker, by ammonium persulphate at 90°C. Molecular weights,  $M$ , for various samples of degraded polymer were determined by sedimentation/diffusion, and an empirical relationship was established between  $M$  and the sedimentation coefficient at a single, low concentration. This enabled the straightforward determination of  $M$  as functions of persulphate concentration, cross-linker concentration, and time at temperature. It was shown that large decreases in  $M$  occur within the first hour at temperature, but that complete degradation is not achieved. It was further shown that, when a delayed zirconium cross-linker is used, degradation may be less effective when gels are formed and degraded at high shear rates.

## INTRODUCTION

Hydraulic fracturing is employed to increase the flow of crude oil or gas from a reservoir. A fluid containing "proppants," typically sand or ceramic beads, is pumped into the reservoir under high pressure to fracture the rock. The proppants prevent the newly created channels from subsequently closing up. A water-soluble polymer is included in the fluid and cross-linked *in situ* to form a gel. This ensures effective proppant placement and helps control fluid loss. After fracturing, a "breaker" brings about degradation of the polymer to give a low viscosity fluid that can be withdrawn leaving behind the proppants. Both the timing and the efficiency of degradation are crucial; if breakdown of the gel occurs too fast, the proppant may drop out of suspension prematurely, whereas if breakdown is incomplete, residues may remain in the fracture that impede the flow of oil or gas.

Gall and Raible<sup>1,2</sup> have previously used size-exclusion chromatography (SEC) to study the deg-

radation behavior of fracturing fluid polymers. In the present work, ultracentrifugal techniques<sup>3</sup> are employed for the first time in an investigation of hydroxypropyl guar (HPG) as a fracturing fluid polymer. Advantages of ultracentrifugal methods over SEC are that (i) no filtration of solutions is required prior to analysis and (ii) absolute rather than relative molecular weights may be obtained.

HPG is a derivative of guar gum, a polysaccharide obtained from the seed of the guar plant, *Cyamopsis tetragonolobus*. Chemically, guar gum consists of a backbone of D-mannose units joined by  $\beta$ -1,4 linkages, with D-galactose units attached at intervals by  $\alpha$ -1,6 linkages (Fig. 1). In HPG, 40% or less of the sugar hydroxyls are substituted with hydroxypropyl groups.<sup>4</sup> HPG forms a viscous solution at low concentrations in water, which may be converted to a gel by the addition of cross-linking agents such as polyvalent cations. Degradation of the polymer in reservoirs at temperatures of 60–115°C may be brought about with oxidant breakers such as ammonium persulphate.

## EXPERIMENTAL

### Materials

HPG and cross-linker were obtained from an oil field servicing company. The HPG, as received, contained

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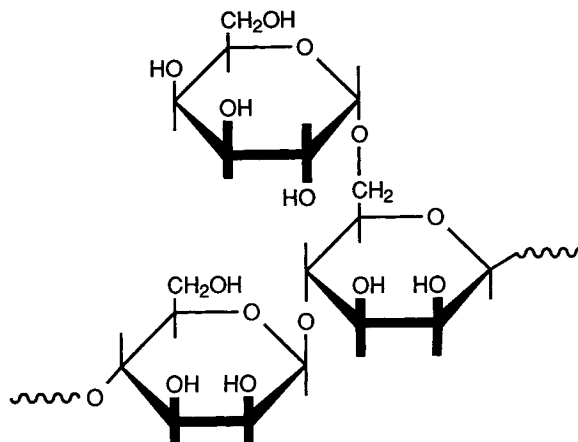


Figure 1 Chemical structure of Guar gum.

about 9% moisture and a similar amount of essentially insoluble material. HPG concentrations quoted in this paper are of the sample as received. The soluble polymer is believed to have a weight-average molecular weight in the region of  $2.5 \times 10^6$ . Thorough characterization of the sample is underway.

Solutions of zirconium cross-linker were prepared in accordance with the supplier's instructions. Ammonium persulphate was employed as breaker.

### Solutions

Solutions of HPG were prepared by weighing out the polymer, adding water, and stirring magnetically. In most cases, 0.5 g HPG were dissolved in 100 cm<sup>3</sup> water. A small volume of ammonium persulphate in water was added by syringe, while stirring vigorously, to give the desired breaker concentration. For cross-linked solutions, the pH of the HPG solution was first adjusted to 9 with aqueous NaOH; then, after adding the breaker, an appropriate quantity of cross-linker solution was added. Gel formation occurred on heating solutions containing HPG and cross-linker.

### Degradation under Static Conditions

Laboratory experiments were undertaken to investigate the extent to which the polymer degraded in the presence of ammonium persulphate breaker at 90°C for different breaker concentrations, cross-linker concentrations, and times at temperature.

Small portions (ca. 7 cm<sup>3</sup>) of solutions prepared as above were transferred to small vials and placed in an oven at 90°C. After a specified time, the vials

were removed from the oven and quenched in ice to stop the reaction. Portions were then taken, diluted with water, and analyzed by sedimentation velocity and, in some cases, by synthetic boundary ultracentrifugal methods.

### Degradation under Shear

In use, fracturing fluids are subjected to shear during both formation and degradation of the gel. This was simulated by heating solutions, prepared as above with 5 g dm<sup>-3</sup> HPG, 0.35% v/v cross-linker solution, and various amounts of breaker in a Physica Viscolab viscometer with shear rates of 100 and 1000 s<sup>-1</sup>. Experiments were also performed in the viscometer with no shear for comparison with the previous static experiments. After degradation, portions of the solutions were taken, diluted with water to one-fifth of the original concentration, and analyzed by sedimentation velocity.

### Ultracentrifugation

Ultracentrifuge experiments were carried out at 20°C using a Beckman model E analytical ultracentrifuge with a Schlieren optical system. For the sedimentation velocity experiments, the rotor speed was 40,000 rev min<sup>-1</sup>. Sedimentation coefficients were evaluated from the rate of movement of the maximum in the Schlieren image.<sup>3</sup>

Table I *S* and *D* for Degraded HPG in Water

Expt No.	HPG Conc (g dm <sup>-3</sup> )	<i>S</i> (10 <sup>-13</sup> s)	<i>D</i> (10 <sup>-7</sup> cm <sup>2</sup> s <sup>-1</sup> )
1	5.0	1.64	
	2.0	2.72	0.425
	1.0	3.86	0.368
2	3.1	2.29	1.00
	2.1	2.44	1.23
	1.0	3.01	1.07
	0.5	3.54	1.28
3	5.0	1.80	
	2.0	2.08	2.87
	1.0	2.31	3.05
4	2.0	2.16	3.78
	1.2	2.07	3.97
	0.6	2.16	
5	3.0	1.90	3.10
	2.0	1.83	3.62
	1.0	2.07	3.76
	0.5		4.66

For the synthetic boundary experiments, a capillary-type synthetic boundary centerpiece was employed, and the rotor speed was 8,000 rev min<sup>-1</sup>. Diffusion coefficients were evaluated by the height-area method.<sup>3</sup>

### Viscosity

For comparative purposes, viscosity measurements were also carried out on degraded solutions. Uncross-linked HPG solutions (5 g dm<sup>-3</sup> in water) were heated for 1 h at 90°C with various amounts of ammonium persulphate. Any residue was allowed to settle, and the viscosity of the supernatant was determined with a couette geometry low shear Contraves LS30 viscometer. The viscosity was not shear-rate dependent.

## RESULTS AND DISCUSSION

### Molecular Weight of Degraded HPG

To establish a molecular weight calibration, five sets of experiments were performed in which HPG was degraded to differing extents. Sedimentation coefficients,  $S$ , and diffusion coefficients,  $D$ , at various concentrations after dilution of the degraded HPG, are given in Table I. Limiting sedimentation coefficients,  $S_0$ , and limiting diffusion coefficients,  $D_0$ , are listed in Table II, together with molecular weights,  $M$ , evaluated using the Svedberg relationship

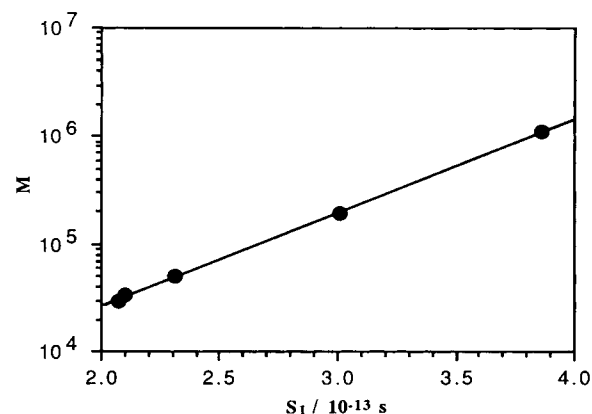
$$M = \frac{RTS_0}{D_0(1 - \bar{v}\rho)} \quad (1)$$

The buoyancy factor  $(1 - \bar{v}\rho)$  at 20°C was determined as 0.377.

In general, a linear relationship between  $\log M$  and  $\log S_0$  is expected. Once such a relationship has been established, molecular weights may be determined from values of  $S_0$ . However, evaluation of  $S_0$

**Table II**  $S_0$ ,  $D_0$ , and  $M$  for Degraded HPG

Expt. No.	$S_0$ (10 <sup>-13</sup> s)	$D_0$ (10 <sup>-7</sup> cm <sup>2</sup> s <sup>-1</sup> )	$M$
1	5.40	0.32	1.09 × 10 <sup>6</sup>
2	3.82	1.27	1.94 × 10 <sup>5</sup>
3	2.50	3.20	5.05 × 10 <sup>4</sup>
4	2.10	4.00	3.39 × 10 <sup>4</sup>
5	2.10	4.67	2.91 × 10 <sup>4</sup>



**Figure 2** Relationship between  $M$  and  $S_1$  for degraded HPG.

is relatively time-consuming, requiring sedimentation velocity measurements at several concentrations, so the possibility was investigated of using an empirical relationship between  $M$  and  $S$  at a single, specific, low concentration. In Figure 2,  $\log M$  is plotted against  $S$  at 1 g dm<sup>-3</sup> concentration, and it can be seen that the plot is linear over the molecular weight range covered (34,000–1,090,000). The data obey the relationship

$$\log_{10} M = 0.8646 \times 10^{13} \times S_1 + 2.696 \quad (2)$$

Using this expression, the molecular weight of degraded HPG may be determined from a single sedimentation velocity experiment at 1 g dm<sup>-3</sup> concentration.

### Degradation under Static Conditions

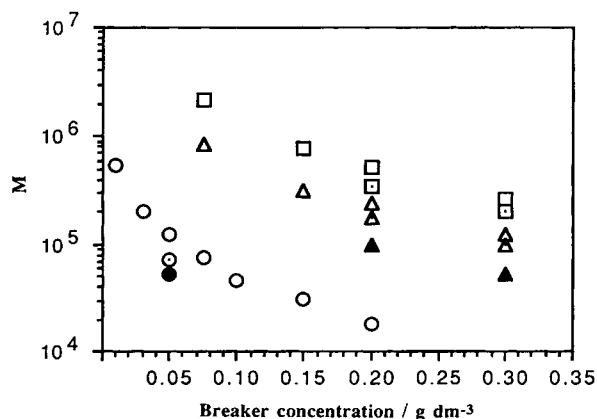
Table III gives values of  $S_1$ , and of molecular weights calculated using eq. (2), for solutions of HPG (initially 5 g dm<sup>-3</sup>) with various concentrations of cross-linker and breaker that had been held at 90°C for various times. For the measurement of  $S_1$ , the degraded HPG solutions were diluted to 1 g dm<sup>-3</sup> prior to sedimentation velocity analysis. The molecular weights (on a logarithmic scale) are plotted against breaker concentration in Figure 3.

It should be noted that the solutions, even after degradation, contained some insoluble residue, which underwent very rapid sedimentation in the ultracentrifuge and did not contribute to the observed sedimentation velocity boundary. The molecular weights quoted are a sedimentation/diffusion-average for the soluble material.

It can be seen in Figure 3 that the molecular

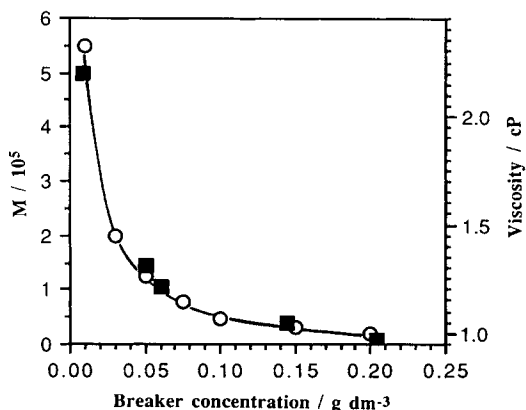
**Table III** Molecular Weights for  $0.5 \text{ g dm}^{-3}$  HPG in Water Degraded with Ammonium Persulphate at  $90^\circ\text{C}$ 

Conc of Cross Linker Solution (% v/v)	Breaker Conc ( $\text{g dm}^{-3}$ )	Time at $90^\circ\text{C}$ (h)	$S_1$ ( $10^{-13} \text{ s}$ )	$M$
0.00	0.010	1	3.52	$5.49 \times 10^5$
	0.030	1	3.01	$1.99 \times 10^5$
	0.050	1	2.78	$1.26 \times 10^6$
	0.050	19	2.49	$7.06 \times 10^4$
	0.050	42	2.35	$5.34 \times 10^4$
	0.075	1	2.53	$7.65 \times 10^4$
	0.100	1	2.27	$4.56 \times 10^4$
	0.150	1	2.07	$3.06 \times 10^4$
	0.200	1	1.80	$1.79 \times 10^4$
0.20	0.075	1	3.73	$8.34 \times 10^5$
	0.150	1	3.25	$3.21 \times 10^5$
	0.200	1	3.10	$2.38 \times 10^5$
	0.200	18	2.96	$1.80 \times 10^5$
	0.200	121	2.65	$9.71 \times 10^4$
	0.300	1	2.78	$1.26 \times 10^5$
	0.300	18	2.65	$9.71 \times 10^4$
	0.300	121	2.35	$5.34 \times 10^4$
0.35	0.075	1	4.22	$2.21 \times 10^6$
	0.150	1	3.70	$7.85 \times 10^5$
	0.200	1	3.48	$5.07 \times 10^5$
	0.200	18	3.29	$3.47 \times 10^5$
	0.300	1	3.16	$2.68 \times 10^5$
	0.300	18	3.02	$2.03 \times 10^5$

**Figure 3** Dependence of  $M$  on ammonium persulphate concentration for uncross-linked HPG solutions after 1 h ( $\circ$ ), 19 h ( $\odot$ ), and 42 h ( $\bullet$ ) at  $90^\circ\text{C}$ , for gels formed with 0.2% v/v cross-linker solution after 1 h ( $\triangle$ ), 18 h ( $\Delta$ ), and 121 h ( $\blacktriangle$ ) at  $90^\circ\text{C}$ , and for gels formed with 0.35% v/v cross-linker solution after 1 h ( $\square$ ) and 18 h ( $\square$ ) at  $90^\circ\text{C}$ . The initial concentration of HPG in all cases was  $5 \text{ g dm}^{-3}$ .

weight of degraded HPG decreases as the breaker concentration increases and increases as the cross-linker concentration increases. Most of the reduction in molecular weight occurs during the first hour at temperature. At longer times, a slow decrease in molecular weight is seen, which may be attributed to thermal hydrolysis. Degraded HPG solutions contain polymer of significant molecular weight, which may restrict the flow of fluids through a reservoir. For example, with 0.35% v/v cross-linker solution and  $0.2 \text{ g dm}^{-3}$  breaker, after 18 h at  $90^\circ\text{C}$ , the molecular weight of soluble material was 350,000.

In Figure 4, molecular weight data (on a linear scale) are compared with viscosity data for uncross-linked HPG solutions after 1 h at  $90^\circ\text{C}$  with ammonium persulphate. A good correlation is achieved. Although breaker concentrations up to  $0.15 \text{ g dm}^{-3}$  bring about massive reductions in molecular weight and in solution viscosity, higher breaker concentrations do not give significantly lower molecular weights.



**Figure 4** Dependence of  $M$  (○) and of viscosity (■) on ammonium persulphate concentration for uncross-linked HPG solutions (initially  $5 \text{ g dm}^{-3}$ ) after 1 h at  $90^\circ\text{C}$ .

### Degradation under Shear

Results from experiments in which gels were formed and degraded in a viscometer are given in Tables IV and V for two series of experiments. Some of the solutions contained significant quantities of gel (effectively infinite molecular weight) after degradation. The gel sedimented rapidly and accumulated at the bottom of the cell, so did not interfere with the sedimentation of the slower moving soluble polymer. However, the concentration of soluble polymer, as determined from the area under the Schlieren peak, was low, so the value of  $S_1$  was estimated with reference to previous data.

In the absence of shear, results similar to those for the previous static experiments were obtained. However, when subjected to shear, differences in

behavior emerge. For the first series of experiments (Table IV), it can be seen that at  $0.06 \text{ g dm}^{-3}$  breaker the sheared solutions contained relatively large amounts of gel after degradation and the soluble material was of relatively low molecular weight. At higher breaker concentrations, the molecular weight of degraded polymer appeared to be higher for sheared solutions than for non-sheared solutions and to increase with increasing rate of shear.

Results from the second series of experiments (Table V) show some differences from the first, illustrating the difficulty in obtaining totally reproducible behavior for cross-linked systems such as these. In general, gel contents are lower and molecular weights of soluble material higher than might be expected on the basis of the first series; a few cross-links may make the crucial difference between high molecular weight polymer and gel. Once again, however, there seems to be a significant effect of shear. It can also be seen that considerable degradation has occurred within 10 min.

These results indicate that shear has an important effect on the formation and degradation of HPG gels; further work is required to elucidate this. No such shear effect was observed for uncross-linked HPG solutions, which indicates that the differences in degradation behavior have their origin in differences in the gel structure (number and distribution of cross-links).

### CONCLUDING REMARKS

The sedimentation velocity technique has proved a particularly useful means of characterizing degraded

**Table IV** Results for  $5 \text{ g dm}^{-3}$  HPG Gels Formed and Degraded in a Viscometer at  $90^\circ\text{C}$  for 1 h: First Series

Shear Rate ( $\text{s}^{-1}$ )	Breaker Conc ( $\text{g dm}^{-3}$ )	HPG Conc after Dilution ( $\text{g dm}^{-3}$ )	$S$ ( $10^{-13} \text{ s}$ )	Estimated $S_1$ ( $10^{-13} \text{ s}$ )	$M$	Approx Gel Content (%)
0	0.06	0.83	4.164	4.0	$1.40 \times 10^6$	—
	0.12	0.86	3.808	3.7	$8.00 \times 10^5$	—
	0.20	1.00	3.475	3.48	$5.00 \times 10^5$	—
	0.30	0.98	3.313	3.31	$3.60 \times 10^5$	—
100	0.06	0.20	3.731	3.2	$3.00 \times 10^5$	80
	0.12	0.78	4.113	3.85	$1.06 \times 10^6$	20
	0.20	0.94	3.680	3.60	$6.40 \times 10^5$	—
	0.30	0.86	3.451	3.35	$4.00 \times 10^5$	—
1000	0.06	0.72	4.111	3.80	$9.60 \times 10^5$	30
	0.12	0.80	4.482	4.10	$1.74 \times 10^6$	20
	0.20	1.17	3.621	3.70	$7.90 \times 10^5$	—

**Table V Results for 5 g dm<sup>-3</sup> HPG Gels Formed and Degraded in a Viscometer at 90°C: Second Series**

Breaker Conc (g dm <sup>-3</sup> )	Shear Rate (s <sup>-1</sup> )	Time at 90°C (min)	HPG Conc after Dilution (g dm <sup>-3</sup> )	S (10 <sup>-13</sup> s)	Estimated S <sub>1</sub> (10 <sup>-13</sup> s)	M	Approx Gel Content (%)
0.04	0	60	0.094	5.511	4	1.4 × 10 <sup>6</sup>	90
	100	60	0.38	5.175	4.1	1.7 × 10 <sup>6</sup>	60
	1000	60	0.89	5.470	5.2	1.5 × 10 <sup>7</sup>	10
0.12	100	10	0.83	5.228	4.9	8.6 × 10 <sup>6</sup>	17
	100	20	1.15	4.638	4.9	8.6 × 10 <sup>6</sup>	—
	100	40	1.00	4.713	4.71	5.86 × 10 <sup>6</sup>	—

fracturing fluids. The present work confirms Gall and Raible's<sup>2,3</sup> observations that relatively low viscosity fluids may still contain partially degraded polymer of sufficient molecular weight to damage and restrict the fracture and that the reduction in viscosity occurs within the first hour. This highlights the need to develop better breakers for fracturing fluids.

This work has further indicated that, when a delayed zirconium cross-linker is used, degradation may be less effective in regions of high shear. This has potentially serious implications, as regions of high shear in an oil well are likely to be those regions where polymeric residues would cause the most damage. The complexity of the degradation reaction under shear could not have been deciphered from either viscometric tests or visual observation of gel degradation, the two methods that are widely used in the fracturing industry to study the break behavior of fracturing fluids.

Although the present contribution has dealt with studies of polymer degradation in the laboratory, the sedimentation velocity technique may also be applied to samples recovered from field trials. There is no need to prefilter such solutions as insoluble

material sediments rapidly in the ultracentrifuge and does not interfere with the observed sedimenting boundary for the polymer. Sedimentation velocity experiments can provide information about both the concentration of the degraded polymer (from the area under the Schlieren peak) and about its molecular weight (from the sedimentation coefficient).

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