Detection of Microgels in Polyacrylamide Solutions Using Microcapillary Flow Analysis

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Synopsis

A new technique for quantifying the amount of multimolecular microgel material in water-soluble polymers is described. The enhanced velocity of the large microgels during flow through a 25 μm capillary is the basis for a separation between the microgels and dissolved polymer. With the use of laser-excited fluorescence detection, the arrival of fluorescently-tagged polyacrylamide samples at a downstream location is recorded. The presence of small amounts of microgel has a deleterious effect on the ability to filter polymer solutions. Analysis of samples before and after filtration suggests that a significant amount of microgel material above 8 μm in diameter is present in samples that exhibit poor filterability characteristics. Treatment of a sample with base is found to improve filterability and to decrease the amount of microgel in the sample.

INTRODUCTION

Polyacrylamide is a water-soluble polymer that has been extensively used as a mobility control agent in enhanced oil recovery operations.[1] The effectiveness of a polymer for this purpose is determined by several factors, one of which is the ability of the polymer solution to flow through the porous rock medium without plugging the rock pores. This property is generically called "filterability."[2] If a polymer solution plugs a laboratory filter, it is likely that plugging of the reservoir will occur as well. Therefore, filtration is often the basis for laboratory screening tests for the presence of microgels. Poor filterability has been attributed to the presence of trace amounts of microgel (multimolecular aggregates or crosslinked polymer) in the polymer solution.[2] It has been proposed that a source of these microgels is the thermally or chemically induced formation of imide bridges between polyacrylamide molecules.[3,4]

The amount of microgel in a polyacrylamide sample varies according to how the polymer was prepared. Polymerizations carried out under conditions which favor high production capacity, for instance, can result in increased amounts of microgel. Since removal of these gels on a commercial scale without degrading the high molecular weight polymer is difficult, it is important that reaction products have acceptably small amounts of microgel material.

Determination of the microgel content of a polymer sample has, to date, been rather qualitative. One notable exception is the use of centrifugation,

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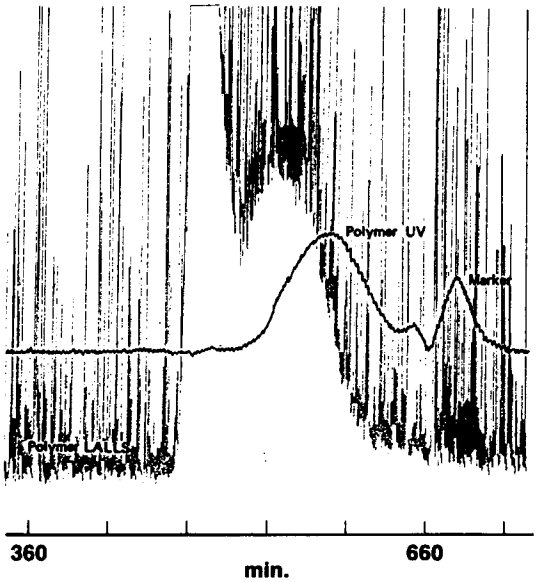

Fig. 1. Detection of microgels in HDC/LALLS experiments. The UV and LALLS detectors' outputs show the presence of a very high molecular weight species in low concentration. This peak can be attributed to microgels, which convect through the packed column faster than other species.

ultrafiltration, and gravimetric analysis to quantitatively determine the microgel fraction in synthetic rubber samples.[5,6] This technique is most applicable to samples with large microgel fractions, and is not suitable for analyzing trace amounts of microgels in dilute polymer solutions. Conventional chromatographic techniques for analyzing polymers (size exclusion chromatography and hydrodynamic chromatography) are not appropriate for quantitative microgel analysis because the microgels are too large (> 10 μm) to emerge from a packed column. Therefore, for polymer samples with trace amounts of microgel, filterability tests alone are often used to determine the sample quality.

During our previous determination of the absolute molecular weight distribution of polyacrylamides using low-angle laser light scattering (LALLS) and hydrodynamic chromatography (HDC),[7] microgels manifested themselves as a peak preceeding the polymer peak in the output from the LALLS detector. Figure 1 shows the raw data from such an analysis. Note that, because of the small amount of microgels, a corresponding peak on the UV detector trace does not appear. Figure 2 shows the data from the analysis of a polymer in which microgels do not appear.

It is important to note that HDC/LALLS analysis is not an appropriate technique for quantifying microgels since the column acts as a filter and removes some of the microgel material. This paper describes a new chromatographic technique for quantifying the microgel content in water-soluble polymer samples. The technique is based on separating the microgels from dissolved polymer by flowing a small amount of solution through a 25 μm i.d. capillary tube. The capillary is large enough that filtering of the sample does not occur.

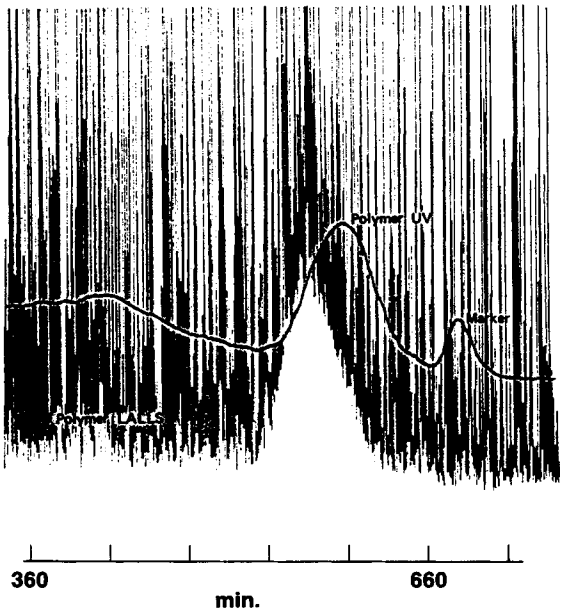

Fig. 2. HDC/LALLS data showing the absence of microgels. The chromatogram of this sample displays no peak preceding the polymer peak. The HDC/LALLS analysis gives a qualitative assessment of the amount of microgel contamination.

THE SEPARATION MECHANISM

The enhanced velocity of particles during laminar flow through tubes is a phenomenon that has been noted by several investigators. Two notable examples are the transport of red blood cells through capillaries[8] and the separation of various sized colloidal particles by flow through small diameter chromatography tubing.[9,10] There are two fundamental mechanisms which cause particles to move through a tube faster than their suspending fluid.

The first of these mechanisms is steric exclusion of particles from the tube walls because of the particles' finite size.[11] Since the particles cannot occupy radial positions where the fluid velocity is slowest, the average particle velocity is faster than the average fluid velocity. The difference between the two velocities is a function of the ratio of the tube radius and the particle size. This mechanism is the basis for hydrodynamic chromatography, a technique for sizing colloidal particles and high molecular weight polymers.[7,12]

The second mechanism of enhanced velocity is the radial migration of particles from the wall regions to regions where the velocity is higher. This phenomenon has been observed for rigid particles[13] as well as for deformable particles such as red blood cells[14] and fluid droplets.[15] This migration is observed even at extremely low Reynolds numbers. The radial migration velocity is dependent on the fluid velocity and the particle size. Whereas deformable particles migrate inward and concentrate at the tube axis,[16] solid spheres, rods, and disks migrate away from the tube axis as well as from the tube wall and concentrate at a radial position 0.6 of the distance from the axis to the wall (the "tubular pinch" effect[17]). The time required for solid spherical

particles to reach equilibrium transverse positions in plane Poiseuille flow was derived by Ho and Leal.[18]

In our experiments, a pulse of dilute fluorescently tagged polymer solution is convected through a 25 μm i.d. capillary. The microgels which contaminate the sample are of comparable size (10 μm) to the capillary. For these conditions, radial migration of particles from the wall is complete after 20 s, and diffusion of particles back to the walls is insignificant (the diffusion coefficient of a 10 μm particle is approximately 10^{-10} cm^2/s). The migration takes place sufficiently early in the experiment for most particles to overtake dissolved polymer molecules before arriving at the downstream fluorescence detector. A crude separation of the microgels from the soluble polymer is thus achieved. The chromatogram of such an experiment contains a main polymer peak preceded by sharp spikes due to the passage of individual microgel particles through the detector cell. Although there is no unique correlation between the microgel particle sizes and the spikes' locations (no size separation within the microgel fraction), the intensity and frequency of these spikes indicates the number of microgels in the sample. This data, coupled with filtration experiments, yields information on the size of the microgels.

EXPERIMENTAL

Microcapillary Flow System and Fluorescence Detector

The microcapillary flow system used is similar to one configured by Jorgenson and Guthrie[19] for capillary open-tubular liquid chromatography. Although this system is designed for HPLC applications, it lends itself nicely to the polymer flow system that we require. A schematic of the flow system is shown in Figure 3. Solvent (0.002M NaN_3) is held in a reservoir and is forced through the capillary with compressed air. The solvent is filtered through a 0.22-μm filter (Millipore, Bedford, MA), before flowing through the injection valve (Valco, Houston, TX), splitting tee and the capillary itself, which is a 60-cm length of 25 μm i.d. vitreous silica tubing (SGE Inc., Austin, TX).

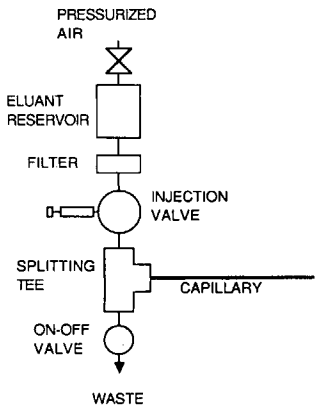

Fig. 3. Microcapillary flow system. Pressurized air forces fluid in the tee through the capillary. The flow rate can be controlled by adjusting the air pressure.

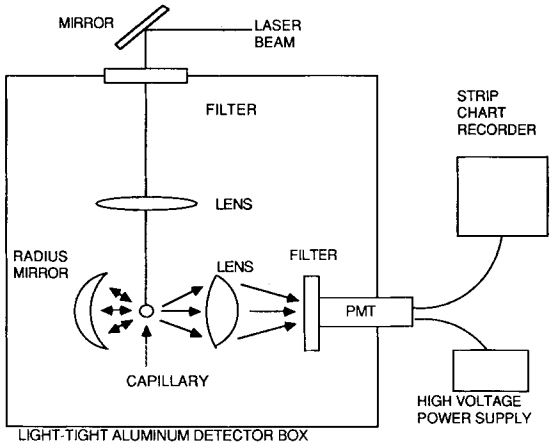

Fig. 4. On-column laser-excited fluorescence detector. The laser beam (488 nm) is focused onto the capillary and the emitted fluorescent light measured by a photomultiplier tube. The detector elements are enclosed in a light-tight aluminum box.

For use with this microcapillary system, Guthrie et al.[20] designed a laser-excited fluorescence detector which uses a small section of the capillary itself as the detector cell. Such an "on-column" detector is needed because the entire capillary volume (300 nL) is small compared to the detector cell volumes of conventional chromatography detectors ($\sim \mu$L). In addition, this configuration completely eliminates the band broadening associated with a capillary-detector connection. A similar detector was constructed for this work and is shown in Figure 4. Fifty mW of the blue line (488 nm wavelength) of a 2-W Ar-ion laser (Model 85, Lexel, Palo Alto, CA) is used to excite the fluorescein tags on the polymer. The emitted fluorescent light is directed with a radius mirror and an aspheric condenser lens into a photomultiplier tube operated at -1500 V. The amplified output is collected on a strip chart recorder. A detailed analysis of the flow rate dependence of the response of the detector (associated with fluorescence photobleaching) is described elsewhere.[21]

Preparation of Polyacrylamide Samples

Polyacrylamide emulsion samples (concentrated polyacrylamide solution droplets suspended in an organic oil phase) were inverted using 3% NaCl and 0.1% Triton X100 surfactant. Dry samples were dissolved in 3% NaCl. The resulting polymer solutions (3000 ppm polymer) were fluorescently tagged in the following manner. First, 200 mL of the polymer solution was adjusted to pH 6 with HCl. Next, 8 mL DMSO in 12 mL water, 50 μL acetaldehyde, 50 μL cyclohexyl isocyanide (Aldrich, Milwaukee, WI), and 3 mL of a solution of fluoresceinamine isomer I (Aldrich) in DMSO (1 mg/mL) were sequentially added with stirring. The reaction was allowed to proceed without stirring at room temperature for 16 h. To isolate the tagged polymer, 1 mL of the reaction mixture was precipitated with 20 mL acetone. After the acetone was decanted (along with precipitated and suspended emulsion oil and salt), the polymer precipitate was dissolved in 20 mL 0.002M aqueous NaN_3. Dissolution was allowed to occur without stirring and usually took 24 h. The tagged

polymer (approximately 130 ppm) was then diluted to 65 ppm for analysis. Since the microgel and soluble polymer have essentially identical chemical structure, the tagging reaction is assumed to proceed indiscriminately in the two phases.

Six polyacrylamide samples were prepared in this manner for the microcapillary analysis. The samples are: S1, a commercial, low carboxyl content, dry polyacrylamide; S2, a commercial, medium carboxyl content, emulsion polyacrylamide; S3, a commercial medium carboxyl content, emulsion polyacrylamide with poor filterability; S4, a laboratory-prepared emulsion sample with a significant microgel fraction. Sample S5 is the same as S4, except it is brought to pH 11 (with NaOH) for 16 h before tagging. This treatment was found to improve sample filterability. The improved filterability due to basic treatment suggests that microgels are formed by imide crosslinks between polymer chains. The imide bond would be broken in basic conditions. Sample S6 is a commercial 30% carboxyl content polyacrylamide supplied by Marathon Oil Company. This polymer is reported to be free of microgels.[22]

These samples were analyzed as prepared. Additional analyses were performed on S4 after this sample had been filtered through 8- or 3-μm pore size Millipore filters in order to determine, at least approximately, the size of the microgel particles.

Polymer Injections

Injection of small amounts ($\sim$ nL) of polymer into the column is accomplished using a static splitting technique[19] shown schematically in Figure 5. First, with valve 2 open, the tee is filled with polymer solution [Fig. 5(2)]. During this filling process, little sample will flow into the column because of its large resistance. Next, valve 2 is closed, and polymer solution is forced into the column at a specified driving pressure for a known interval of time [Fig. 5(3)]. Then, valve 2 is opened again in order to flush the tee clear of polymer solution [Fig. 5(4)]. Valve 2 is finally closed, and the sample is forced through the column at the desired driving pressure [Fig. 5(5)].

With this injection technique, approximately 20 nL of the polymer solution were injected into the capillary at 15 psig. The volume of injected sample was calculated using the equation relating flow rate to pressure drop, solvent

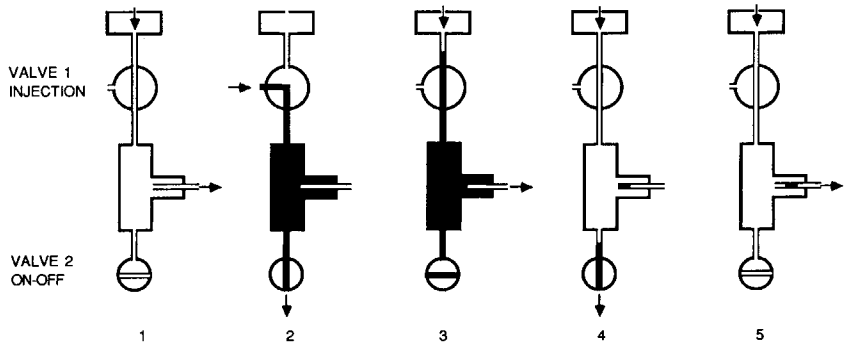

Fig. 5. Capillary injection sequence: (1) normal flow; (2) filling the tee; (3) injecting into the capillary; (4) purging the tee of excess sample; (5) elution of the polymer.

viscosity, and the column dimensions. The driving pressure used for the flow in these experiments was 5 psig. The arrival of the microgels at the detector cell began approximately 3 min after the injection, and the main polymer peak occurred at approximately 5 min.

The driving pressure of the experiment corresponds to a flow rate of approximately 750 pL/s. Mechanical degradation during shear of these high molecular weight polyacrylamides is known to occur at sufficiently high shear stress (about 10^4 dyne/cm^2).[23] In the present study, the maximum wall shear stress is on the order of 10 dyn/cm^2. We thus assume that degradation is not important in these experiments.

Filterability Tests

A common qualitative assessment of the purity (microgel content) of commercial polyacrylamide products is the filterability test. One such test was used on the polymers studied by microcapillary flow. A 0.05% polymer solution in 4% NaCl was allowed to filter (under the pressure of 4 in. of solution) through a 25-mm diameter Millipore membrane (pore size: 5 μm). The time required to filter 10 mL of polymer solution was recorded. If this volume was not filtered after 1320 s (22 min), the test was halted and the volume of filtered solution recorded. This test yields information on the relative amount of large insoluble microgel material in a sample. Note that the low polymer concentration (0.05%) and large pore size (5 μm) ensure that the membrane will not be plugged if large microgels are not present.[24]

RESULTS

The detector responses of the microcapillary flow analysis for the six polyacrylamide samples are shown in Figure 6. Samples S1 and S6 appear as broad but clean peaks, indicating the absence of a microgel fraction. Sample

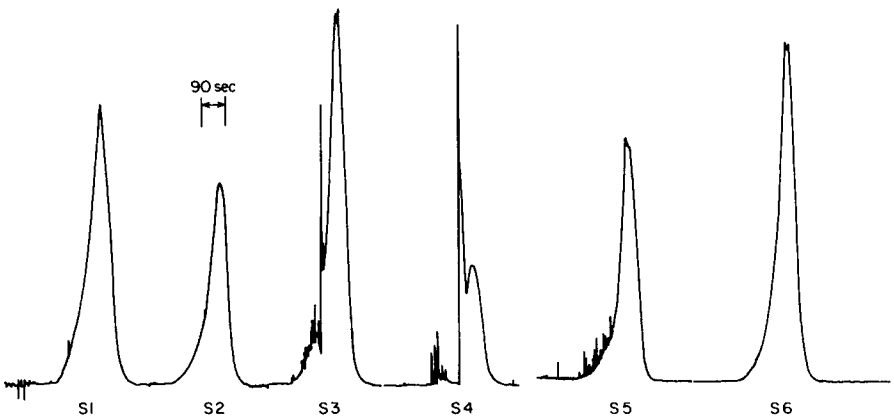

Fig. 6. Chromatograms of microcapillary flow analysis experiments. Capillary: 25 μm i.d., 60 cm length. Flow rate: 750 pL/s. (S1) Commercial, low carboxyl content, dry polyacrylamide; (S2) commercial, medium carboxyl content, emulsion polyacrylamide; (S3) commercial, medium carboxyl content, emulsion polyacrylamide with poor filterability; (S4) laboratory-prepared emulsion polyacrylamide; (S5) S4 after treatment with base; (S6) commercial, 30% carboxyl content polyacrylamide.

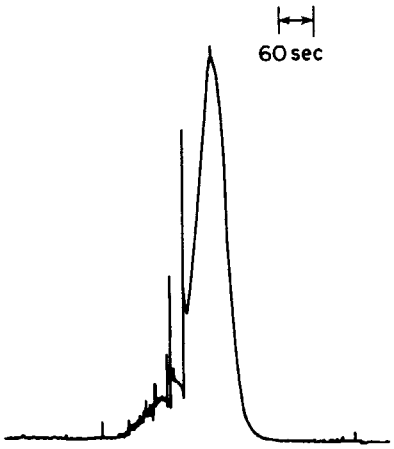

Fig. 7. Chromatogram of analysis of sample S3 after 1 month. Note that the sample is essentially unchanged during this time period.

S2 also appears to be clean, which is in agreement with the filterability test (10 mL filtered in 280 s). The next sample, S3, displays poor filterability characteristics (7.8 mL filtered in 1320 s), and its chromatogram clearly shows a significant amount of microgel.

The laboratory-prepared polymer, S4, is shown to have a significant amount of microgel—more, in fact, than any of the other samples. The filterability test on S4 yielded only 0.5 mL in 1320 s. When this sample was treated with base to reduce the microgel fraction, its filterability improved dramatically (7 mL in 1320 s). By comparing the chromatograms of S4 and S5 (the treated

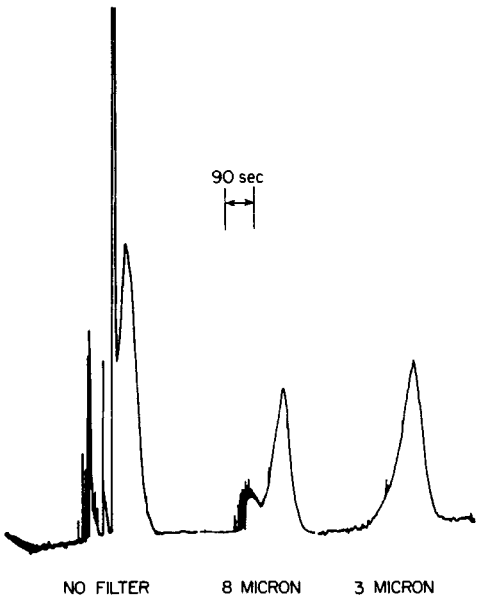

Fig. 8. Filter study of sample S4. The 8-μm pore size Millipore filter removes most of the microgel material. The 3-μm filter removes essentially all of the detectable microgels.

sample) in Figure 6, it is evident that the treated sample displays a decrease in (but not an elimination of) the microgel fraction.

To show that the microgels are not the result of temporary physical entanglements arising during sample preparation, sample S3 was analyzed both immediately after sample preparation and one month later. A comparison of Figure 7 and the chromatogram of S3 in Figure 6 suggests that there is no significant change in the amount of microgel during this period. This result, coupled with the fact that chemical treatment reduces the amount of microgel, suggests that the microgels are formed by chemical crosslinking.

In order to determine the approximate size of the microgels, the S4 sample was filtered through Millipore filters (8 and 3 μm) before injection into the capillary. Figure 8 shows that much of the microgel is removed by the 8-μm filter, indicating that the majority of the microgel particles are at least this size. In addition, the 3-μm filter removes essentially all of the detectable microgel material.

CONCLUSIONS

We have demonstrated the usefulness of the microcapillary chromatography system to applications in the analysis of water-soluble polymers. Reaction conditions for the preparation of polyacrylamide are shown to be important parameters to the quality of the resulting polymer. The microgel material, which causes poor sample filterability, can be easily seen by the laser fluorescence detector. Microcapillary flow analysis, coupled with filtration through filters of known pore size, can provide information on both the absolute size and relative abundance of the microgel material in a polymer sample.

Further experiments on the analysis of microgels in water-soluble polymer samples are underway in our laboratory. Multimolecular aggregates formed by polymer associations, for instance, should be observable using the method described in this paper. Recent results indicate that the microcapillary system can be modified for use in sizing polymer molecules and in determining the particle size and concentration of dilute latex suspensions. These analyses are achieved by flow through a 10-μm capillary, where the hydrodynamic chromatography (HDC) mechanism is operative. Although packed bed HDC analysis of water-soluble polymers has been successfully used in this laboratory and elsewhere,[7,25] single capillary HDC of polymer molecules, which offers the advantages of low dispersion and the absence of polymer-deforming elongational stresses, has not previously been reported.

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