INTRODUCTION

There is at present no rapid, reliable commercial method for determining the molecular weight distribution of polyacrylamides, especially for molecular weights exceeding $5 \times 10^6$. Size exclusion chromatography, or SEC, which might be expected to be the method of choice, has molecular weight, polarity, and shear degradation limitations for very high MW polymers. Recently, we reported a new absolute MWD method for high molecular weight water-soluble polymers based upon the combination of band sedimentation and low-angle laser light scattering, termed S/LALLS. The advantages of this new method include applicability for polymers with $M = 10^6$ to $10^8$, automatic sample clarification, minimal adsorption problems, no shear degradation, and the use of commercial components. Two other new methods, hydrodynamic chromatography and field-flow-fractionation, have also been developed recently to meet the need for new separation techniques.

This paper describes the principles and operation of S/LALLS as applied to polyacrylamide and to copolymers of acrylamide and acrylic acid (HPAM). Where appropriate, the results of this new method are compared with SEC/LALLS and supplier's data. The method is also applied to the study of the shear degradation of HPAM polymers in their flow through porous media.
PRINCIPLES OF THE METHOD

Band sedimentation is a technique for separating molecules according to their sedimentation velocity. It was first used in 1951 by Brakke to purify viruses and has since been extensively developed for biochemical applications. Curiously, it has been largely neglected as a separation technique by the polymer science community, even though all the apparatus is commercially available. It is especially well suited to high-molecular-weight, water soluble polymers. The centrifugation can be carried out in either an analytical, or, more commonly, in a preparative centrifuge.

In our use of band sedimentation, the sample was applied as a dilute solution in a thin band onto the top of a centrifuge tube previously filled with a solvent. The tube was then placed in a swinging-bucket rotor and was spun for 2-5h at 20,000-40,000 rpm in a preparative ultracentrifuge. During centrifugation the polymer molecules moved slowly from the starting band toward the bottom of the tube with velocity $dr/dt = s\omega^2r$, where $s$ is the sedimentation coefficient, $\omega$ is the angular velocity of the rotor, and $r$ is the radial distance of the molecule from rotor center. The sedimentation coefficient $s$ reflects the net effects of three forces acting on the molecule: centrifugal force $M\omega^2r$, buoyant force $M\bar{V}_2\rho\omega^2r$, and frictional force $fdr/dt$; here $\bar{V}_2$ is the partial specific volume of the polymer, $\rho$ is the solvent density, and $f$ is the friction factor. The Svedberg equation combines the effect of these three forces:

$$s = M (1-\bar{V}_2\rho)/N_Af$$

and relates $s$ to $M$. Now $f$, of course, also depends upon $M$ and upon the shape of the molecule. For a homologous polymer series, $f \propto M^{0.5} - M^{0.7}$, so that $s = HM^a$ where $0.3 \leq a \leq 0.5$ and $H$ is a constant. Thus a homologous polymer series will have a range of values of $s$ which can be used to achieve a separation. In practice, the values of $\omega$ and $t$ were chosen so that the largest molecules almost reached the bottom of the tube. In our apparatus, this required a radial movement of about 5 cm from original band location near the meniscus. The centrifuge was then gently stopped, and the tubes were analyzed. Because of the density gradient, which prevented convection, the separated polymers were stable in the tube for many hours, allowing ample time for analysis of the separated distribution.