

Synthetic Rubbers: Polybutadiene

Synthetic elastomers have replaced natural rubber to an astonishing degree, and account for more than 70% of the rubber used today. In the United States alone, 5 million tons of synthetic rubber are produced annually. The principal synthetic rubber elastomer is a copolymer of butadiene and styrene. The latex form of rubber and synthetic elastomers has applications in carpet and gloves, and coagulated latex is used for the production of tires and mechanical goods. It is of critical importance to know the absolute molar mass and its distribution, as well as to gain insight into the conformation of synthetic rubber—which are indicative of the product's end-use performance.

Typically, polystyrene standards are used to estimate the molar masses of these polymers in SEC experiments, but by using a DAWN or miniDAWN multi-angle light scattering (MALS) detector, standards and column calibration are no longer needed. Here, the absolute molar mass and polydispersity, as well as the *rms* radius of two synthetic rubber samples were measured *directly* using SEC combined with a DAWN.

The synthetic rubber samples were analyzed in toluene, and Wyatt Technology's Optilab DSP was used as the refractive index detector for the SEC line. The refractive index increment dn/dc of polybutadiene in toluene is relatively low, and the dn/dc value of the butadiene/styrene copolymer in toluene increases with the ratio of styrene present. In Figure 1, the molar mass and its distribution are determined absolutely—without using any standards or calibration routines.

In addition to the weight-average molar mass and the polydispersity, the DAWN can also determine the *shape* of the polymer by measuring the *rms* radius directly at each elution volume. It is well-known that butadiene forms highly branched polymers and that styrene forms linear polymers—and this is revealed by the DAWN.

Figure 2 shows a logarithmic plot of the molar mass versus the radius of the two synthetic rubber samples. The slope of such a plot is indicative of the *shape* of a polymer. A slope between 0.5 and 0.6 is usually found for linear polymers with a random coil conformation, while spheres have a slope of approximately 0.3. The values obtained for polybutadiene (0.25) and for the butadiene/styrene copolymer (0.38) indicate that this polybutadiene is more branched than the styrene/butadiene copolymer.

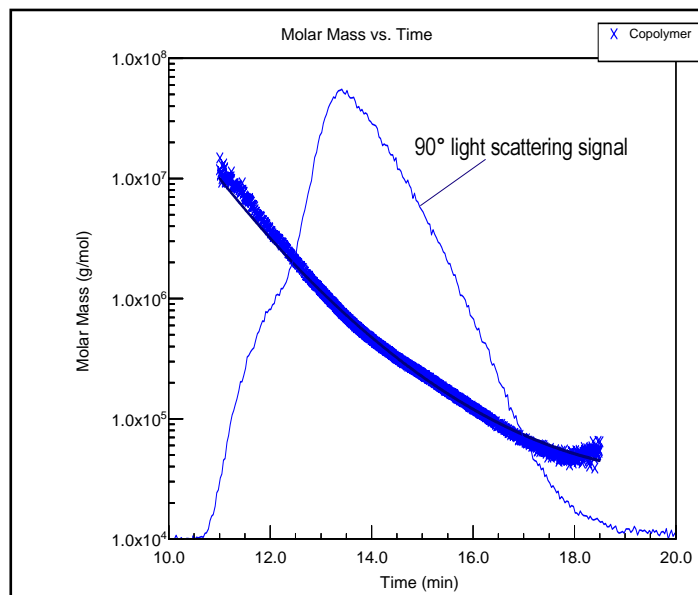


Figure 1. Molar mass versus elution time for the synthetic rubber sample superimposed upon the signal from one of the light scattering detector channels.

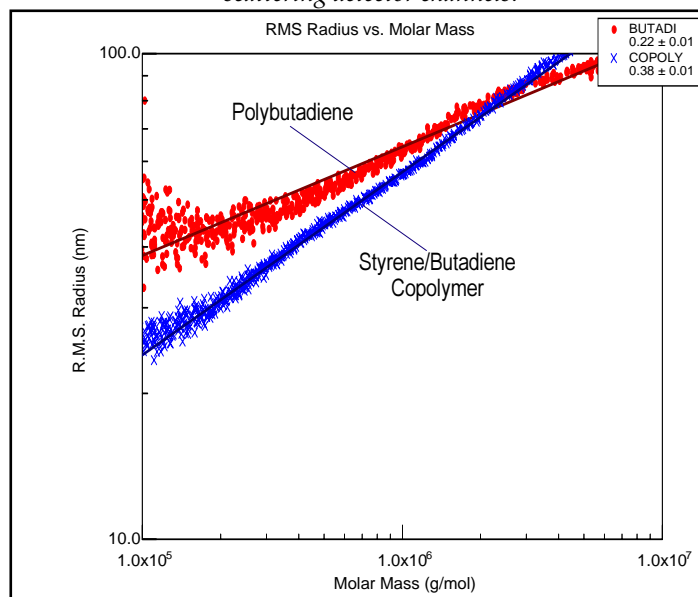
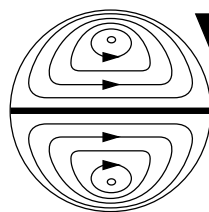


Figure 2. RMS radius versus molar mass ("conformation plot") for the two samples. The slope is indicative of the conformation (rod, coil or sphere) of the molecule.



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