

Degradation of High Molar Mass Polymers

The degradation of high molar mass polymers is known to occur in an extensional flow field, in which polymer chains elongate and become susceptible to mid-point scission. A transient extensional flow can be obtained by using high pressure to push polymer solutions through an orifice or capillary tube. In order to analyze the polymers after a pass through a capillary, it is important to get the molar mass (M_w) and polydispersity index (PDI) in a *direct* and *accurate* way.

Instead of using size-exclusion chromatography (SEC) alone to characterize the polymers, which requires tedious column calibration and the use of polymer standards, one can utilize SEC coupled with a DAWN or miniDAWN multi-angle light scattering (MALS) detector to analyze the polymer molar mass distribution and obtain the absolute M_w and PDI.

In our experiments, high M_w polydisperse polymers (PDI > 1.4) in aqueous solution were injected under high pressure through a transient extensional flow field at the entrance of a capillary tube (i.d. 250 μ m). Using the DAWN to characterize the polymer solutions, we observed that the chain scission events occurring during multiple passes through the capillary entrance cause a marked *decrease* in PDI, along with a decrease of the average M_w .

The phenomena was observed for various kinds of water-soluble polymers, including linear polyacrylamide (LPA), polydimethylacrylamide (pDMA), poly(ethylene-oxide) (PEO), and LPA nanogels.

Plots of differential weight fraction vs. polymer molar mass show how the M_w and PDI change systematically with each pass of the polymer solution through the capillary. Strikingly, the PDI is seen to *decrease* to values as low as 1.12 for polymer samples that were initially much *more* polydisperse.

The application of a transient elongational flow field to polymers suggests a novel, physical method for the generation of diverse classes of monodisperse polymers of relatively high molar mass.

Reference: B.A. Buchholz, J.M. Zahn, M. Kenward, G.W. Slater, A.E. Barron, "Flow-induced chain scission as a physical route to narrowly distributed, high molar mass polymers," *Polymer* (2004) **45**, 1223-1234.

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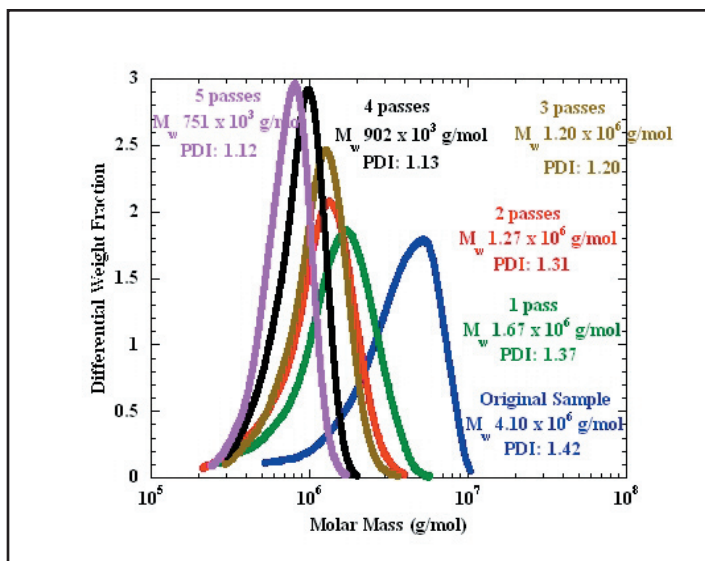


Figure 1. Tandem GPC-MALS characterization results obtained for linear polyacrylamide in aqueous solutions. The applied pressure was 1000 psi with a polymer solution concentration of $c = 0.1\%$ (w/v) in a 15 cm long capillary with an inner diameter of 250 μ m.

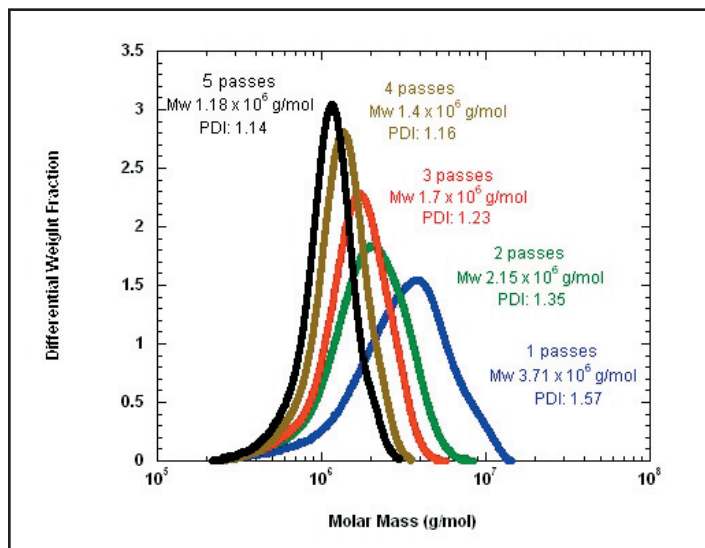
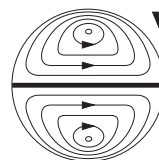


Figure 2. Tandem GPC-MALS characterization results obtained for polyacrylamide nanogels in aqueous solution. The applied pressure was 500 psi with a polymer solution concentration of $c = 0.1\%$ (w/v) in a 15 cm long capillary with an inner diameter of 250 μ m.



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