Multisegmented Block Copolymers by Click Chemistry and ATRP

Click" chemistry is a class of efficient and selective reactions that is characterized by quantitative yields, tolerance to a broad range of functional groups, facile experimental set-up, and minimal synthetic work-up. This class of reactions combines particularly well with controlled radical polymerization methods, such as atom transfer radical polymerization (ATRP), and the two techniques have been prolifically employed for the synthesis of a wide variety of novel polymeric materials, including (multi)block copolymers, stars, brushes, and gels. This note describes the preparation of multisegmented block copolymers by click coupling of block copolymers synthesized by ATRP.

A triblock copolymer consisting of polystyrene (PS) and poly(ethylene oxide) (PEO) was synthesized via ATRP of styrene from a difunctional PEO macroinitiator. The bromine end groups were substituted with azide by reaction with NaN3 in DMF, and the material (N3-PS-PEO-PS-N3) was coupled with propargyl ether to form a multisegmented block copolymer ((PS-PEO-PS)x).

Due to the presence of multiple blocks within a single polymer chain, conventional size-exclusion chromatography (SEC) could not be used to accurately analyze the molecular weight of the starting materials or products. A triple detector system was employed in conjunction with SEC (TD-SEC), utilizing the following detectors: multi-angle laser light scattering (DAWN EOS), differential viscometer (ViscoStar), and differential refractometer (Optilab rEX).

The molecular weight of the starting material was determined by TD-SEC to be 6680 g/mol (Figure 1). Accurate molecular weight analysis is imperative to achieve a significant degree of click coupling, since successful step growth-type reactions require stoichiometric balance among end groups. TD-SEC demonstrated that the click coupling was successful (Figure 2), and a product of higher molecular weight (M_n = 33,100 g/mol) and broader molecular weight distribution was obtained.

A combination of click chemistry with ATRP was utilized to synthesize multisegmented block copolymers. Absolute molecular weight characterization via TD-SEC demonstrated a degree of polymerization of 5 – 7, which includes up to 21 separate blocks in a single polymer chain.

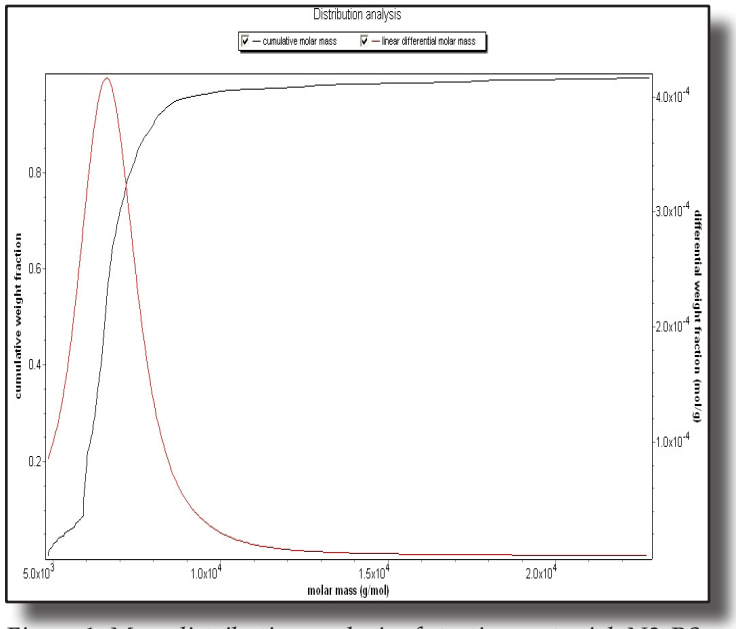

Figure 1. Mass distribution analysis of starting mate rial, N3-PS-PEO-PS-N3

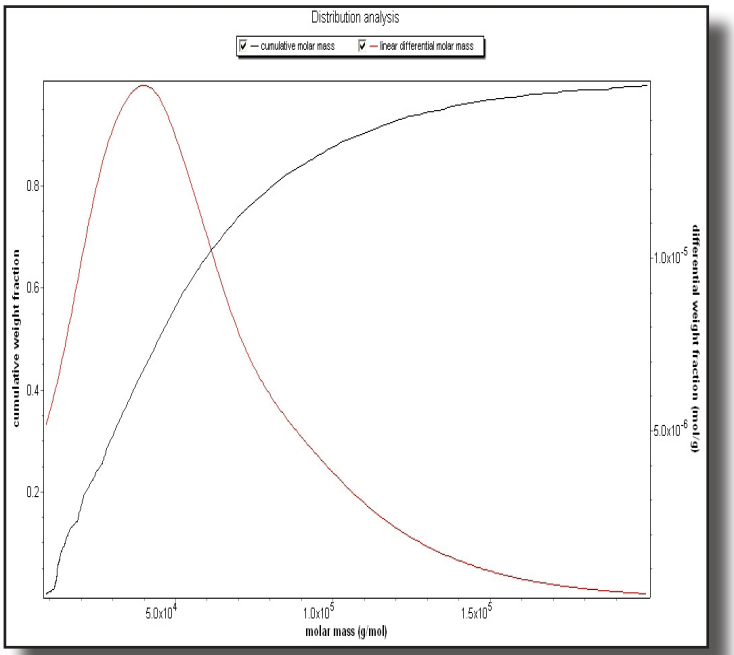

Figure 2. Mass distribution analysis of click coupled product, -(PS-PEO-PS)x-

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