

Rigid-rod Type Polymers: poly(*n*-hexyl isocyanate)

Polyisocyanates are of considerable interest due to their applications in various fields such as optical switches, liquid crystals, degradable materials, composites, and chiral recognition. For many of these applications it is desirable that the molecular weight (M_w) and the molecular weight distribution (MWD) of the polymers be controlled and defined. So it is very important to know accurately the M_w using reliable instrumental techniques.

We synthesized polyisocyanates by living anionic polymerization of *n*-hexyl isocyanate (HIC) using sodium benzamide (NaBA) initiator. This is a novel initiator because it leads to PHIC with a perfect control over the molecular weight. The polymers were characterized by SEC-LS, which furnished reliable and absolute MW data.

SEC-LS samples were prepared from 0.01g of the polymer in 10 mL THF. Molecular weights of the polymers were calculated from the response of a DAWN EOS multi-angle light scattering detector that was connected to a size exclusion chromatograph (MALS/SEC). THF was used as the mobile phase at a flow rate of 1.0 mL/min. The dn/dc value for PHIC in THF at 40°C was measured with an Optilab RI. After dn/dc was measured for 5 different concentrations for one polymer sample, SEC-LS data were acquired with refractive index detection at 40°C.

To examine the living nature, the polymerization of HIC was carried out using various molar ratios of the monomer and the initiator, to yield PHIC samples in the M_w range of 10,000 - 40,000 gmol^{-1} . A good linear relationship between $[\text{monomer}]/[\text{initiator}]$ and M_w was observed as shown in Figure 1, which supported the living character of PHIC in the anionic polymerization.

Block copolymerization is the most reliable method to confirm living polymerization. We carried out block copolymerization between HIC and (3-triethoxysilyl)propyl isocyanate (TESPI) using NaBA, P(HIC-*b*-TESPI) which was quantitatively produced with narrow MWD and the SEC-LS spectrum clearly shifted towards the higher molecular weights without tailing (Figure 2).

The molecular weight of the polyisocyanates can be accurately determined by multi-angle laser light scattering-size exclusion chromatography.

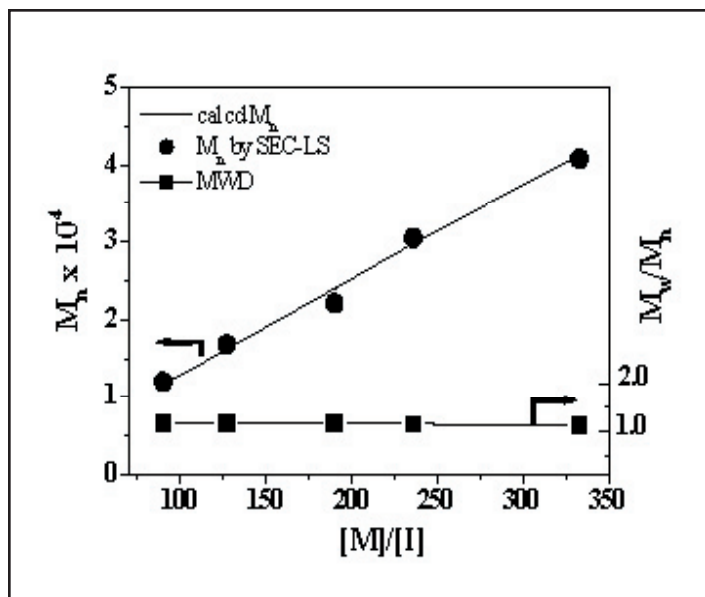


Figure 1. Molecular weight and molecular weight distribution vs. the feed ratio of HIC to NaBA. (Adapted from J.-S. Lee et al. JACS, 2005, 127, 4132. Copyright from ACS)

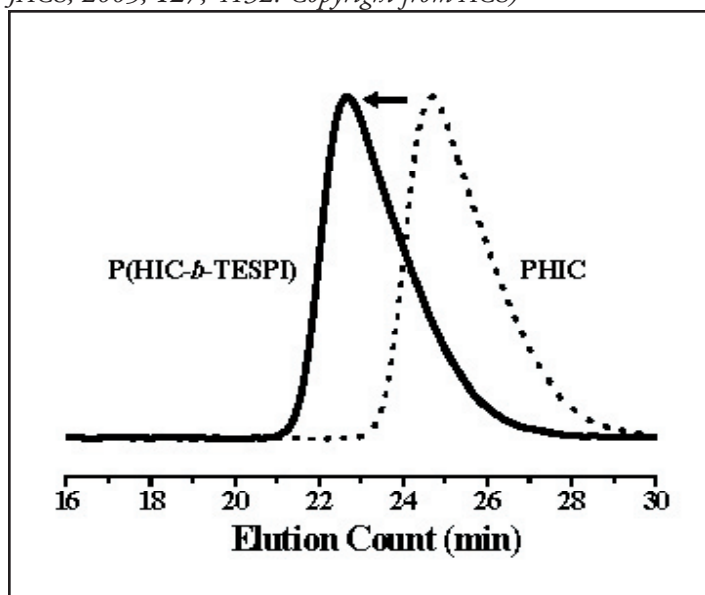


Figure 2. SEC curves of PHIC and P(HIC-*b*-TESPI) obtained by homopolymerization and block copolymerization using NaBA, respectively: PHIC, M_n : 13,600, M_w/M_n = 1.09, P(HIC-*b*-TESPI), M_n : 21,300, M_w/M_n = 1.09. .