IPRIME—3M Industrial Fellow
Research Summary
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Selective Fluorination of Commodity Diene-containing Block Copolymers
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Initial Objectives
Examine the effect of fluorine-incorporation on the properties of styrene-isoprene-styrene (SIS) or styrene-butadiene-styrene (SBS) triblock copolymers (i.e. Kraton™, Vector™), as a visiting IPRIME Industrial Fellow in the Department of Chemistry with Prof. Marc Hillmyer. This collaboration will serve as an educational experience for a member of 3M's Controlled Architecture Materials program (Jim Nelson, sponsored by the Corporate Process Technology Center). Emphasis will be placed on gaining a fundamental understanding of the fluorination routes and (time permitting) on block copolymer characterization tools, such as two-dimensional small-angle X-ray scattering (SAXS), which are unavailable at 3M.

Executive Summary:
1. Demonstrated the feasibility of perfluoroalkyl iodide (R_fI) chemical modification on commercially available styrene-butadiene-styrene (SBS) triblock copolymers. Use of a triethylborane-mediated synthetic process in trifluorotoluene/hexanes mixtures produced a range of polymers with varying fluorochemical incorporation. A Vector^{Tm} 2518 SBS material (M_n = Ca. 1.1 x 10^5, 31 wt % PS, 1% diblock SB impurity, predominantly 1,4 PB) was used exclusively in this study.
2. A variety of $C_nF_{2n+1}I$ (n= 4,6,8,10) moieties were examined as synthons in this study. Experimentally, the most robust system was the perfluorobutyliodide-modified SBS material, which remained soluble in trifluorotoluene (TFT), THF and chloroform solutions. Unfortunately, the longer perfluorinated chains presented challenging solubilities once incorporated on the butadiene segments of these high molecular weight SBS polymers.
3. Attempts to examine the R_fI chemical modification of isoprene containing SIS materials were abandoned after encountering difficulty in achieving partial or complete modification. The increase in steric congestion that is encountered upon switching from butadiene to isoprene resulted in incomplete substitution (<50%) and significant broadening of the molecular weight distribution.
4. Established hydrogenation techniques are costly and time consuming, thus a variety of experimental techniques aimed at the removal/replacement of the polymeric alkyl iodide were examined. These methods included:
   i. treatment with Mg in THF/TFT;
   ii. reduction with $NiCl_2x6H_20$/Zn in wet THF/TFT; and
   iii. idehydrohalogenation via treatment with NaOH.

The Ni/Zn mixed-metal catalyst system was the most promising of these methods. However, drastic changes in solubility of the C_4F_9-I-modified SBS materials were observed upon treatment with the Ni/ZN system.

5. Other Functionalized alkyl Halides. Me_3SiI and ICH_2CN were obtained to explore as extensions of the triethylborane-mediated synthetic route. Use of the iodoacetonitrile material in these grafting experiments is thought to provide a convenient route to side-chain or end-functional polymers via reduction of the nitrile after grafting.