Versatile, Efficient, and Facile Functionalization of Poly(p-phenylene oxide) via Azide-Alkyne "Click" Chemistry

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Functional polymers are currently attracting tremendous attention because of their use in diverse polymer applications, such as fuel cell membranes, gas separation, biomaterials, and polymer semiconductors. Versatile methods for post-polymerization functionalization are needed for the synthesis of these functional polymers with tailored structural and chemical properties. However, most current polymer functionalization methods work only with a limited range of functionalities, require high temperatures, or use expensive transition-metal catalysts. Herein, a wide-scope, facile, and robust method for post-polymerization functionalization of poly(p-phenylene oxide), or PPO, using azide-alkyne “click” chemistry is presented. PPO, a commercially available polymer with high glass transition temperature and excellent chemical stability, was modified with a diverse array of functional groups through a mild, three-step synthesis. PPO was first brominated using NBS. Azide groups were then substituted for bromine onto the PPO backbone by an sn2 reaction. The resulting polymer finally underwent copper-catalyzed azide-alkyne "click" reactions at room temperature, as well as heat-activated cycloadditions, with a variety of alkyne functionalities. This pathway was used to functionalize poly(p-phenylene oxide) with a diverse set of substrates, including alkane, aromatic, and organometallic moieties. Synthesis of these functional polymers was confirmed by IR and H-NMR analysis. Post-polymerization functionalization by azide-alkyne cycloaddition was thus shown to have high functional group tolerance, be high-yielding, and occur rapidly in mild conditions. This functionalization process is therefore a potentially powerful approach for synthesis of new functional polymer materials.

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