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Synthesis and characterization of poly(ε-caprolactone) tetra-arm star polymer using tetra terminal alkynyl-substituted phthalocyanine by the combination of ring-opening polymerization and "click" chemistry

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Abstract. The synthesis of poly(ε-caprolactone) (PCL) tetra-arm star polymer was carried out using "click" chemistry and ring-opening polymerization techniques. For this purpose, poly(ε-caprolactone) azido (PCL-N_3) was acquired using ring-opening polymerization of ε-caprolactone and 2-[2-(2-azidoethoxy)ethoxy]ethanol (N_3ol). N_3ol was obtained using sodium azide and 2-[2-(2-chloroethoxy)ethoxy]ethanol. 4-(prop-2-ynyloxy)-phthalonitrile was obtained by using 4-nitrophthalonitrile and propargyl alcohol. 2(3),9(10),16(17),23(24) Tetrakis-[(prop-2-ynyloxy)-phthalocyaninato]zinc(II) (Pc-propargyl) was synthesized by using 4-(prop-2-ynyloxy)-phthalonitrile and a metal salt. By reacting Pc-propargyl and PCL-N_3, PCL tetra-arm star polymer was obtained by "click" chemistry. The products were characterized via scanning electron microscopy, ^{1}H-nuclear magnetic resonance spectroscopy, ultraviolet-visible spectrophotometry, Fourier-transform infrared spectroscopy, and gel permeation chromatography instruments. The spectroscopic analyses of PCL tetra-arm star polymer prove that the star polymer was built through the combination of ROP and "click" chemistry. We provided a protocol for PCL tetra-arm star polymer, and a statement of reproducibility with respect to the properties of this tetra-arm star polymer. This study is an example of a novel type of combination reaction, from ring-opening polymerization to "click" chemistry using phthalocyanine. This can open the door for diverse tetra-arm star polymer synthesis that could potentially cause major advances in synthetic macromolecular chemistry.

***Keywords*:** tetra-arm star polymer; "click" chemistry; ring-opening polymerization; phthalonitrile derivative; metallophthalocyanine.

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