

**New Telechelic Polymers by Ring-Opening Polymerization and  
New Linear and 4-arm Star Block Copolymers by Combination of  
ROP and ATRP**

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**Abstract**

A great deal of research activity has been devoted towards the preparation of telechelic polymers due to their applications as cross-linkers, chain extenders, and important building blocks for various macromolecular structures, including block, graft copolymers, star polymers etc. Ring opening polymerization (ROP) of  $\epsilon$ -caprolactone, D, L-lactide is initiated by a bio based functional initiator, namely 4-(hydroxymethyl)-1, 3-dioxolan-2-one (glycerol 1, 2-carbonate) in the presence of various catalysts to yield  $\alpha$ -(cyclic carbonate),  $\omega$ -hydroxyl telechelic PCL, PDLLA respectively with controlled molecular weights, relatively narrow PDI and with good end group fidelity is demonstrated. The end-capping reaction of  $\alpha$ -(cyclic carbonate),  $\omega$ -hydroxyl telechelic PCL and PDLLA with itaconic anhydride is also demonstrated to yield  $\alpha$ -(cyclic carbonate),  $\omega$ -(carboxylic acid) telechelic PCL and PDLLA respectively. The end group's structure derived from the initiator (glycerol carbonate) is confirmed by NMR, FT-IR and MALDI TOF MS.

New linear and 4-arm star PCL-b-PCCMA copolymers were synthesized by using bromopolyesters, initially synthesized by ROP of PCL, as macroinitiators for the ATRP of cyclic carbonate methacrylate (CCMA). Combination of these two controlled processes affords well-defined block copolymers of a wide array of compositions and with relatively narrow PDI. Side chains cyclic carbonate group reaction with amine such as 2-phenylethylamine enabled the block having hydroxy urethanes pendant groups without the use of the relatively more hazardous isocyanates and without any by-product. Both these linear and 4-arm star PCL-b-PCCMA copolymers find applications in the fields of lithium ion conductivity, controlled drug delivery, as compatibilizers etc.