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Poly(ε-caprolactone) – a viable scaffold for design of intriguing nanobiomaterials

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The classical medical material workhorse, poly(ε-caprolactone) (PCL), has been employed as a viable scaffold for design of several novel nanomaterials with intriguing, potentially therapeutical and biological properties. The ability to control the living ROP of ε-caprolactone has resulted in various telechelic PCLs. These have been utilized in either ATRP to make amphiphilic block copolymers or by use of various "click" reactions resulting in multi-component materials. Three different examples will be elaborated.

In the first case gold nanoparticles protected with a polymeric shell may combine ablative therapy and site-specific drug delivery in bladder cancer therapy. This may be accomplished by tailoring the surface properties and the size of the gold clusters. The former may be addressed by devising polymeric ligands with desirable features and functional groups. Thus the preparation of the PCL-*b*-PAA corona will be outlined. The synthesis of the effective macro-ligand that allows preparation of the stable gold cluster and provides nanoenvironment for hydrophobic anticancer drugs and mucoadhesive anchoring on mucous membranes is one of the objectives of this study.

The second approach is the ligation of biologically active moieties to the termini of a hydrophobic polymeric chain (PCL) to afford the amphiphilic linear-dendritic macromolecule that comprises rod-like, coil-like, and dendritic fragments. Furthermore this may self-assemble in solid state as well as in aqueous solution. The facile route to linear-dendritic cholesteryl-*b*-PCL-*b*-(L-lysine)$_{G2}$ by thiol-ene and azide-alkyne "click" reactions will be elucidated. Here the driving motivation was to contrive a robust, facile, and effective synthetic strategy.

Finally, the preparation of PCL-based miktoarm core-crosslinked amphiphilic star copolymers with hydrophobic interior, charged hydrophilic surface, and targeting motifs are elaborated. Such nanoscopic core-shell type architectures are envisioned to be excellent candidates as drug delivery devices owing to the enhanced stability in biological fluids. Moreover, they may permit site-specific delivery of their potential cargo due to the presence on the surface of biologically active moieties, such as estradiol and L-lysine dendritic wedges.