A series of poly(γ-chloropropyl-L-glutamate) (PCPLG) with controlled polymer molecular weight (MW=5-28 kg·mol⁻¹) and molecular weight distribution (PDI=1.16-1.26) have been prepared from hexamethyldisilazane (HMDS)-mediated ring-opening polymerization of γ-chloropropyl-L-glutamic acid based N-carboxyanhydride (CP-NCA). CD, FTIR and WAXS analysis reveal that the polymers adopt α-helical conformations both in solution and the solid state. Their helical surfaces can be readily decorated with functional moieties to confer desired properties, as demonstrated by the quantitative derivatization of the PCPLG side chains with azido functional groups that are amendable to “click” chemistry. Subsequent side-chain conjugation with mannose moieties via copper-mediated [2+3] alkyne-azide 1,3-dipolar cycloaddition affords water-soluble mannose-polypeptide conjugates with quantitative grafting efficiency occurring under mild conditions. CD analysis reveals that the mannose-polypeptide conjugates also retain α-helical conformations in aqueous solution.