

## Covalently Bonded Multifunctional Polymer Thin Films Based on the Layer-by-Layer Assembly of Activated Esters

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We demonstrate that multifunctional polymer thin films with excellent physicochemical stability can be obtained by the layer-by-layer (LbL) deposition based on the covalent bond formation between adsorbing pairs. The programming of multiple functions into a single covalently bonded multilayer free-standing film by taking advantage of unreacted moieties within the film was also investigated. We introduced two different types of activated ester polymers (P1 and P2) based on pentafluorophenyl (PFP) ester groups, reacting with primary amines in poly(allyl amine) (PAAm) during the LbL deposition, to yield covalently-bonded multilayer films. The difference in the reactivity between P1 and P2 was analyzed in terms of the solubility difference against the solvent for PAAm. Furthermore, simultaneous incorporation of two different functional molecules into a single LbL film by post-treatments as well as the surface patterning with functional groups was also investigated. The film stability in different environmental conditions as well as the facile preparation of free-standing films off the substrate is also addressed.