Commercially available polysulfone (PSf) membranes with a polypropylene backing are used across a broad range of applications. However, the natural properties of the PSf surface sometimes limit their application. Here we present, how the surface of supported membranes can be heterogeneously activated by lithiation followed by functionalization with acid chlorides at 0°C, permitting modification of commercial PSf membranes without compromising the mechanical integrity of the membrane. Post-functionalization polymer grafting was illustrated through both, a “grafting from” approach by surface initiated atom transfer radical polymerization (SI-ATRP) and by a “grafting to” approach exploiting Cu(I) catalyzed 1,3-cycloaditions of alkynes with azides (CuAAC) introducing hydrophilic polymers onto the membrane surface. Poly(1-vinyl imidazole) (pVim) grafted membranes were exploited as support for immobilization of alcohol dehydrogenase (ADH) in a biocatalytic membrane reactor (BMR) and demonstrated substantial improvements in terms of operational enzyme stability compared to immobilization onto pristine membranes.