Polymer solar cells (plastic solar cells) have seen remarkable improvements in recent years where power conversion efficiencies of up to 6% have been reported for small area devices. However in terms of stability polymer solar cells degrade during illumination and in the dark leading to operational lifetimes that are generally very poor. There has been a recent interest in the operational stability of devices and more importantly on the understanding of why devices and materials break down. This has lead to the discovery of a new class of materials that enable exceptionally long device lifetimes (>20000 hours). This Ph.D. thesis describes the synthesis, characterization and photovoltaic applications of these novel polymer materials. A key feature of these materials is that solubilizing thermocleavable alkyl ester side chains are introduced on the polymer backbone. The side chains make the polymer soluble in organic solvents and allow film formation via solution processing. Subsequently they can be removed by heating in a post-processing step forming a harder insoluble material with enhanced stability. These new thermocleavable materials can potentially offer higher chromophore density, higher level processing and improved stability in a solar cell device.