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Synthesis of tri-arm star di-block co-polymer containing poly(tetrahydrofuran-*b*-methyl methacrylate) arms *via* combination of cationic ring-opening polymerization and photosensitized free radical polymerization routes

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Abstract—Trimesic acid trichloride was used as a core to prepare a tri-arm star di-block co-polymer, namely poly(tetrahydrofuran-*b*-methyl methacrylate) ($PTHF_3$-*b*-$PMMA_3$), *via* combination of cationic ring-opening polymerization (CROP) and photo-induced radical polymerization routes. First, a trimesic acid trichloride–$AgSbF_6$ or –$AgCF_3SO_3$ initiation system was utilized for the CROP of THF. The tri-arm star PTHF thus obtained was *in situ* terminated by 2-methyl pyridine *N*-oxide. Second, a sensitized irradiation of PTHF with a 2-methyl pyridinium *N*-oxide photoactive end-group in the presence of anthracene initiated the radical polymerization of MMA in order to give resulting star di-block co-polymer. The obtained polymers were characterized with gel-permeation chromatography (GPC) and ^{1}H-NMR.

Keywords: Star di-block co-polymers; cationic ring-opening polymerization; photo-induced radical polymerization.

1. INTRODUCTION

A star structure is defined as a non-linear polymer, which consists of multiple backbone chains existing from junction points [1]. These polymers show different crystalline, mechanical and viscoelastic properties in comparison with their corresponding linear analogues. The two primary approaches to produce star polymers are known as "arm-first" and "core first". The arm-first approach involves coupling of the preformed linear polymer chains containing functionality at the chain end with a multifunctional coupling agent such as divinyl benzene (DVB). This approach results in a macromolecule with a network-like hub of the coupling agent and preformed linear polymers attached to the hub. The number of arms resulting from the

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