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Synthesis of styrene–methyl methacrylate graft and block–graft copolymers *via* combination of atom transfer radical polymerization and stable free radical polymerization

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Abstract—Styrene (St)–methyl methacrylate (MMA) graft and block–graft copolymers were prepared by combination of atom transfer radical polymerization (ATRP) and stable free radical polymerization (SFRP). In the first step, MMA and comonomer 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl methacrylate were polymerized in the presence of ethyl-2-bromo isobutyrate by ATRP in order to give suitable macroinitiator for the following SFRP step of St. Alternatively, first SFRP of St was carried out by using a dual initiator, 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromopropanoate, yielding macroinitiator to be used in ATRP of MMA and the comonomer. The corresponding block copolymer was used as a polyfunctional macroinitiator in SFRP of St to yield final block–graft copolymer. The obtained graft and block–graft copolymers were characterized by ^{1}H-NMR, UV-Vis and GPC measurements.

Keywords: Graft copolymer; atom transfer radical polymerization; stable free radical polymerization.

INTRODUCTION

Recently, controlled/'living' radical polymerization (CRP) has been utilized for the synthesis of polymers with well-defined compositions, architectures and functionalities [1–4]. Among the CRPs, stable free radical polymerization (SFRP) [5] and atom transfer radical polymerization (ATRP) [6] are versatile methods for the controlled radical polymerizations. SFRP is based on the use of stable nitroxide-free radicals, such as 2,2,6,6-tetrametylpiperydinyl-1-oxy (TEMPO). In this system, the reversible termination-dissociation of the growing polymeric chain is the key step for reducing the overall concentration of the propagating radical chain end. In the

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