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Comb copolymers of polystyrene-poly(*tert*-butyl (meth)acrylate) prepared by combination of nitroxide mediated polymerization and photoinduced *iniferter* technique

Daniel Gromadzki [a,b,*], Ričardas Makuška [b], Miloš Netopilík [a], Petr Holler [a], Jan Lokaj [a], Miroslav Janata [a], Petr Štěpánek [a]

[a] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Square 2, 162 06 Prague, Czech Republic*
[b] *Department of Polymer Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania*

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Abstract

Comb copolymers consisting of polystyrene backbone and poly(*tert*-butyl (meth)acrylate) side chains were synthesized by combination of nitroxide (TEMPO)-mediated polymerization (NMP) and photoinduced grafting from *macro-iniferter*s. First, poly(chloromethylstyrene), PCMS, with the degree of polymerization $\overline{DP_n} \approx 200$ and two random poly(styrene-*co*-chloromethylstyrene) copolymers, P(S-*co*-CMS), with similar $\overline{DP_n} \approx 75$ but different content (8 and 14 mol%) of CMS units, were synthesized by NMP. In the second step the CMS units both in the homopolymer and the copolymers were converted to *N*,*N*-diethyldithiocarbamyl groups (DC) yielding photosensitive multifunctional *macro-iniferters*. Finally, *tert*-butyl methacrylate *t*BuMA was grafted from the synthesized polymer backbones by *iniferter* technique under UV-irradiation yielding copolymers polystyrene-*graft*-poly(*tert*-butyl methacrylate) PS-*g*-P(*t*BuMA). Grafting initiated by the *macro-iniferters* containing ~6–11 DC initiating sites per macromolecule proceeded by pseudo-living polymerization mechanism, i.e., the number-average molecular weight increased with conversion and the SEC traces were unimodal. In contrast, photo-polymerization initiated by highly functionalized polystyrene backbone was poorly controlled. Hydrolysis of loosely grafted copolymers PS-*g*-P(*t*BuMA) afforded amphiphilic copolymers polystyrene-*graft*-poly(methacrylic acid). Molecular parameters of the synthesized graft copolymers in dilute THF solutions were determined by scattering (DLS, SLS, SAXS) and viscometric measurements.

Keywords: Controlled radical polymerization; TEMPO; *Macro-iniferter*; Polystyrene-*graft*-poly(*tert*-butyl methacrylate); Amphiphilic graft copolymer

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1. Introduction

Synthesis, theoretical and experimental investigations of graft copolymers have received remarkable research interest over the past years [1]. Properties

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[*] Corresponding author. Address: Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Square 2, 162 06 Prague, Czech Republic. Tel.: +420 296 809 262; fax: +420 296 809 410.
E-mail address: d_grom@interia.pl (D. Gromadzki).

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of graft copolymers depend on molecular parameters such as nature and degree of polymerization of the backbone, length and density of the side chains [2]. Strategies employed for the preparation of graft copolymers include "grafting through" also known as the macromonomer approach, i.e., radical copolymerization of a macromonomer with a low molecular weight comonomer [3,4]. Graft copolymers prepared this way are rather ill-defined having low $\overline{DP_n}$ and are contaminated with residual macromonomers and side products. Another strategy involves "grafting onto" in which preformed polymers or oligomers are attached to the polymer main chain bearing reactive groups [5,6]. An advantage of this method is that both the polymer backbone and attachable chains (branches) can be prepared by different "living" polymerization techniques leading to the products of well-defined molecular weights and narrow polydispersities. However, the common problems are low grafting efficiency originating from limited diffusion of attachable chains to reactive centers of the backbone, and complicated purification of the products. The "grafting from" approach seems to overcome the limitations of the above methods; this pathway proved to be successful for the synthesis of well-defined cylindrical brushes under properly chosen conditions [7].

Recent innovations in the chemistry of free-radical polymerization led to the development of various techniques providing access to functional (co)polymers of low polydispersity and desired architecture tailored for specific applications. The most extensively investigated techniques include nitroxide mediated polymerization (NMP) [8], atom transfer radical polymerization (ATRP) [9], reversible addition fragmentation chain transfer (RAFT) [10] and macromolecular design via interchange of xanthates (MADIX) [11].

Otsu in 1982 pioneered "living" radical polymerization that can be initiated via photochemical or thermal route using dithiocarbamate compounds [12,13]. Dithiocarbamates act as *iniferters* in radical photopolymerization; the latter process involves initiation, chain transfer and termination. Decomposition of dithiocarbamates generates carbon radicals initiating polymerization of vinyl monomers and less-reactive dithiocarbamyl (DC) radicals acting as reversible terminators. This is, however, an idealized mechanistic picture of *iniferter* polymerization. Recent studies revealed more complex behaviour of the terminating groups: DC can dimerize to form dithiuram, initiate polymerization by adding to alkenes, or can eliminate CS_2 by side reactions resulting in complete loss of "livingness" [14–17].

Nevertheless, there are several important advantages of *iniferter* radical polymerization compared to other controlled radical polymerization techniques. First, *iniferter* polymerization can be initiated photo-chemically which is a faster process than thermal initiation. Second, *iniferter* polymerization can be carried out at room temperature and might be useful considering some functional monomers that are thermally unstable. Moreover, the dithiocarbamate end group is easily convertible to the thiol (–SH) functionality that could be used for further transformations [18].

It was demonstrated recently that *iniferter* dithiocarbamate chemistry can be used to construct complex macromolecular architectures, such as block [19–25] and graft copolymers [26–28], polymer stars [29–31], hyperbranched [32–34] and other polymeric materials [35–38] as well as for modification of surfaces by surface-initiated graft polymerization [39].

Although direct *photo-iniferter* controlled radical polymerization of methacrylic acid leading to its homopolymer and block copolymer with styrene was recently achieved [40], the protection/deprotection chemistry route is more common strategy because of possible interference of free acid functionality with polymerization mediators [41]. Employing protected monomer of methacrylic acid, ABA type triblock copolymers with outer *t*BuMA segments were prepared by *photo-iniferter* technique [42].

Synthetic route for graft copolymers presented in the current work is in some way similar to that of Ishizu who used photoinduced "grafting from" ATRP to grow *t*BuMA and styrene side chains from the multifunctional polystyrene *macro-iniferter* [43]. It resulted in densely grafted brushes with diblock copolymer side chains of low PDI. However, the *macro-iniferter* backbone was prepared by thermal free-radical polymerization of *N*,*N*-vinylbenzyl diethyldithiocarbamate (VBDC) yielding branched backbone with limited $\overline{DP_n}$.

On the other hand, nitroxide (TEMPO)-mediated polymerization yields both linear homopolymer of CMS and copolymers P(S-*co*-CMS) of low PDI with variable content of CMS functionality [44,45]; after installation of dithiocarbamate groups, they are suitable *macro-iniferters* for the "grafting from" polymerization of various monomers.