Tailoring of Polymers by Combination of Ionic and Radical Controlled Polymerizations

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Summary: Poly(methyl methacrylate)s with terminal bromine atom, prepared by bromination of anionically polymerized MMA, were used as ATRP macroinitiators giving di- and triblock copolymers with MMA, styrene and butyl acrylate blocks. Multifunctional ATRP macroinitiators were synthesized by introducing bromomethyl or 2-bromoacyloxy groups onto the main chain of polystyrene or poly(4-methyl styrene) and used for ATRP grafting of *tert*-butyl acrylate leading to densely grafted copolymers with more or less uniform grafts.

Introduction

Block and graft copolymers rank among the most interesting tailor-made polymer products and this is why the methods, leading to the copolymers are intensively studied. Atom transfer radical polymerization (ATRP)[1-3] is very recent method of controlled polymerization. Its principle is the existence of an equilibrium between alkyl halide and transition metal salt in the lower oxidation state (dormant form) on one hand and alkyl radical and salt of the metal in the higher oxidation state (active form) on the other, in the presence of a suitable ligand. The equilibrium is strongly shifted to the left-hand side, ie., to the dormant form of initiating (or growing) particle, leading to protection of growing radicals from termination reactions and, consequently, to controlled propagation of polymer chains. During the process, C-halogen bond at the end of the chains is regenerated and hence it can serve as an macroinitiator for polymerization of another monomer, giving a corresponding block copolymer. This has been verified in a number of papers[4-6] dealing with ATRP synthesis of various block copolymers. In principle, any polymer with an appropriate C-halogen functionality can be used as a macroinitiator.

Here, PMMA macroinitiators were prepared by bromination of their "living" chain-ends obtained in either ligated anionic polymerization (LAP) or GTP[7]. Multifunctional macroinitiators were synthesized by functionalization reactions on anionically prepared polystyrene (pSt) or poly(4-methylstyrene) (pMSt)[8]. The prepared macroinitiators were then used in block copolymerization of PMMA chains with butyl acrylate (BuA) or styrene (St) or for grafting of *tert*-butyl acrylate (*t*-BuA) onto the pSt or pMSt backbone[9].

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Experimental

The chemicals used were purified in usual ways, details are given in our recent papers[7-9]. ω-Bromo PMMAs were prepared by bromination of the living polymer formed either by ligated anionic polymerization initiated with methyl 2-lithioisobutyrate in the presence of LiCl[10] at –70°C in THF, or by GTP initiated with 1-methoxy-1-(trimethylsilyloxy)prop-1-ene under catalysis of tetrabutylammonium fluoride monohydrate in THF at -30°C[11]. Bromine or *N*-bromosuccinimide (NBS) were used as bromination agents. The yield of the functionalization was calculated from the molecular weights of the prepared polymers and bromine content[12]. ATRP of St, BuA or MMA initiated using these PMMA macroinitiators or diblock macroinitiators formed in subsequent step was performed in toluene in the presence of CuCl catalyst and 2,2′-bipyridine (bpy) ligand. For details, see ref 7.
PSt and pMSt precursors of multifunctional macroinitiators were prepared by anionic polymerization initiated with *s*-BuLi in THF at -70°C. PSt was acetylated by $AlCl_3$-catalyzed Friedel-Crafts reaction with acetyl chloride in a mixture of chloroform and nitrobenzene[13]. The acetyl groups on benzene rings (degree of substitution 40%) were reduced with $LiAlH_4$ in THF yielding the polymer with 1-hydroxyethyl group in para-positions. Finally, the hydroxy groups were reacted with 2-bromoisobutanoyl bromide or with 2-bromopropanoyl bromide leading to polystyrenes functionalized with 1-[(2-bromo-2-methylpropanoyl)oxy] ethyl- or 1-[(2-bromopropanoyl)oxy]ethyl groups. PMSt was transformed to poly(MSt-*co*-4-(bromomethyl) styrene) by a reaction with NBS. For reaction conditions and details, see ref 8. These multifunctional macroinitiators were used in grafting *t*-BuA by ATRP, catalyzed with CuCl/bpy or CuCl/pentamethyldiethylenetriamine (PMDETA) systems[9].

Results and Discussion

ATRP synthesis of di- and triblock copolymers using PMMA-Br macroinitiators

For initiation, the following Br-terminated PMMAs were used: (1) M_n = 3610, M_w/M_n = 1.09, prepared by LAP, functionalized by Br_2, degree of functionalization 64%; (2) M_n = 2220, M_w/M_n = 1.48, prepared by GTP, functionalized by NBS, degree of functionalization 60%. After finishing the polymerization of the second monomer, a portion of PMMA not containing Br was removed from the product by repeated precipitation or by extraction with acetonitrile. The diblock copolymer macroinitiators prepared in this way are given in Table 1. As the initiating C-Br species was combined with CuCl, it can be reasonably assumed that the terminal chlorine predominates in the copolymers[14]. Using these diblock copolymers with terminal halogen, triblock copolymers were synthesized by CuCl/bpy mediated ATRP; the results are summarized in Table 2. An induction period was observed in all the discussed copolymerizations, the shortest one being observed in the synthesis of PMMA-*b*-pSt-*b*-PMMA triblock. In the PMMA-*b*-pBuA-*b*-pSt and PMMA-*b*-pSt-*b*-pBuA copolymers, no residual diblock macroinitiator was found; moreover, GPC eluograms, obtained using

Table 1: Synthesis and Characterization of Diblock Copolymer Macroinitiators

Run	Copolymer	Time (h)	X_p (%)[c]	M_n	M_w/M_n	m_2[d]
1[a]	PMMA-*b*-pBuA	4.0	45.0	13,500	1.46	0.73
2[a]	PMMA-*b*-pSt	23.5	28.3	11,600	1.23	0.74
3[b]	PMMA-*b*-pSt	24.0	46.5	14,200	1.17	0.64

[a] PMMA macroinitiator 2, see the text; [b] PMMA macroinitiator 1; [c] conversion of the second monomer (GC); [d] mole fraction of the second monomer in copolymer

Table 2: Synthesis and Characterization of Triblock Copolymers

Copolymer	Macroinitiator[a]	Time (h)	X_p (%)[b]	M_n	M_w/M_n
PMMA-*b*-pBuA-*b*-pSt	1	27	58.5	60,100	1.59
PMMA-*b*-pSt-*b*-pBuA	2	25	24.0	21,300	1.57
PMMA-*b*-pSt-*b*-PMMA	3	24	65.5	35,200	1.74

[a] see Table 1; [b] conversion of the third monomer (GC)

both the RI and UV detections do not differ; this indicates that the propagation of the third monomer proceeds simultaneously in all chains of the diblock macroinitiator. Eluograms of the PMMA-*b*-pSt-*b*-pBuA copolymer, and of the corresponding macroinitiators obtained with RI detection are depicted in Figure 1. However, GPC eluograms of PMMA-*b*-pSt-*b*-PMMA in Figure 2 are bimodal and, with increasing MMA conversion, the amount of triblock increases whereas that of the diblock macroinitiator slowly decreases, so that, at ~90% MMA conversion, diblock is still present. This clearly indicates slow initiation in this special case.

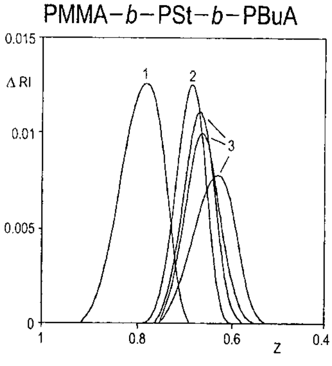


Figure 1. SEC eluograms of PMMA macroinitiator (*1*, No.2, see the text), PMMA-*b*-pSt (*2*, run 2, Table 1) and PMMA-*b*-pSt-*b*-pBuA (*3*, at 1.5, 2.5 and 24.0% BuA conversions)

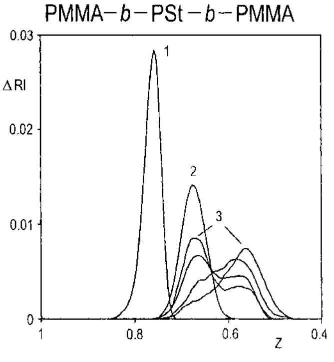
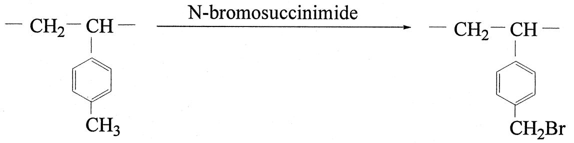


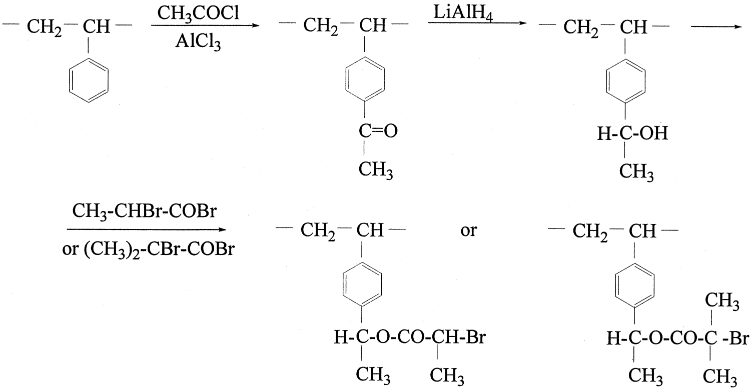
Figure 2. SEC eluograms of PMMA macroinitiator (*1*, No.1, see the text), PMMA-*b*-pSt (*2*, run 3, Table 1) and PMMA-*b*-pSt-*b*-PMMA (*3*, at 14.4, 25.5, 65.5 and 89.2% BuA conversions)

Synthesis of graft copolymers

Multifunctional macroinitiators based on pSt and pMSt were prepared according to Schemes 2 and 3. Compositions and structures of the prepared products were verified by elemental analysis (Br content), NMR and IR spectroscopy, and by GPC. Two of these macroinitiators were used for grafting polymerization of *t*-BuA: S 1, derived from pMSt (Scheme 1), M_n = 7120, M_w/M_n = 1.08, 40% Br-functionalized units, and S 2, based on pSt (Scheme 2), M_n = 4100, M_w/M_n = 1.19, 40% functionalized units with 1-[(2-bromopropanoyl)oxy]ethyl groups. In the polymerization, macroinitiator S 1 was combined with CuCl salt and bpy ligand in the presence of a small amount of dimethylformamide (DMF)[14], whereas S 2 was used in combination with CuCl and PMDETA[15] in the presence of acetone. Results of typical experiments are given in Table 3, the final graft copolymers were analyzed by GPC and NMR. Molecular weights of the copolymers increase proportionally to *t*-BuA conversion and polydispersity indexes of the final products change only slightly in comparison to the corresponding macroinitiators. MWD curves of samples withdrawn from the reaction mixture



Scheme 1 (S 1)



Scheme 2 (S 2)

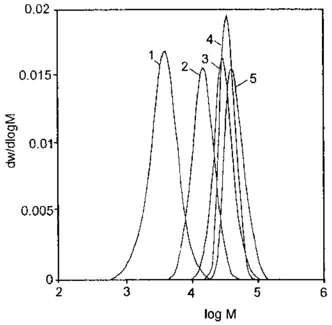


Figure 3. Evolution of MWDs in the course of G 2 copolymerization (Table 3): Reaction time: (*1*) 0, (*2*) 85, (*3*) 450, (*4*) 840 and (*5*) 1320 min

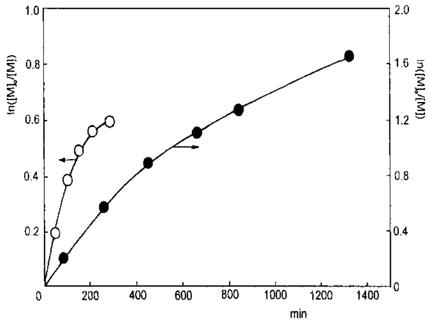


Figure 4. The $\ln[M]_0/[M]$ vs. time plots for graft copolymerizations G 1 (○) and G 2 (●), Table 3

G 2 (see Table 3) at different reaction times are given in Figure 3 (curve *1* represents S 2 macroinitiator). Both the graft copolymerizations (G 1 and G 2) exhibit some features of a "living" process (narrow MWDs, linear dependence of molecular weights on conversion), however, semilogarithmic conversion plots show negative deviations, as can be seen in Figure 4. The problem was studied by NMR, comparing the intensities of protons of C$\underline{H}$Br at 4.1 ppm and protons in benzene rings Ph$\underline{H}$ at 6.2-7.2 ppm for both graft copolymers and the corresponding macroinitiators. For G 1 copolymer, lowering of the CHBr content during polymerization was found indicating spontaneous termination, probably by disproportionation. In contrast, for G 2 copolymer and for S 2 macroinitiator the C$\underline{H}$Br/Ph$\underline{H}$ intensity ratios are virtually the same so that the negative deviation in kinetics is likely caused by a decrease in concentration of the catalyst complex which progressively precipitates during polymerization.

Table 3: Grafting *t*-BuA from macroinitiators S 1 (copolymer G 1) and S 2 (copolymer G 2)

Copolymer	Time (min)	X_p (%)[a]	$M_{n,\,th}$	M_n[b]	M_w/M_n
G 1	285	45.0	63,540	60,190 (72,850)	1.12
G 2	1320	81.3	38,060	34,860 (42,430	1.14

[a] *t*-BuA conversion from GC; [b] calculated for pSt or for p*t*-BuA (in parentheses)

Conclusions

Br-terminated PMMAs, prepared by anionic polymerization initiate ATRP block copolymerization of St or BuA giving diblock copolymers which are more suitable macroinitiators for synthesis of triblock copolymers with narrow MWDs. The only exception is the triblock PMMA-*b*-pSt-*b*-PMMA with bimodal MWD caused by a slow initiation in the third step. By polymer reactions, pSt and pMSt can be converted to multifunctional ATRP macroinitiators with 2-bromoacyl groups (the former) or bromomethyl groups (the latter) which, under optimized conditions, can be used in grafting of *t*-BuA leading to densely grafted copolymers with uniform grafts.

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