

Atom Transfer Radical Polymerization Grafting of Highly Functionalized Polystyrene and Poly(4-Methylstyrene) Macroinitiators with *tert*-Butyl Acrylate

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ABSTRACT: Two monodisperse graft copolymers, poly(4-methylstyrene)-*graft*-poly(*tert*-butyl acrylate) [number-average molecular weight (M_n) = 37,500, weight-average molecular weight/number-average molecular weight (M_w/M_n) = 1.12] and polystyrene-*graft*-poly(*tert*-butyl acrylate) (M_n = 72,800, M_w/M_n = 1.12), were prepared by the atom transfer radical polymerization of *tert*-butyl acrylate catalyzed with Cu(I) halides. As macroinitiators, poly[(4-methylstyrene)-*co*-[(4-bromomethyl)styrene]] and poly[styrene-*co*-[4-(1-(2-bromopropionyloxy)ethyl)styrene]], carrying 40% of the bromoalkyl func-

tionalties along the chain, were used. The dependencies of molecular parameters on monomer conversion fulfilled the criteria for controlled polymerizations. In contrast, the dependencies of monomer conversion versus time were nonideal; possible causes were examined. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2930–2936, 2002

Key words: graft copolymers; polystyrene; *tert*-butyl acrylate; atom transfer radical polymerization (ATRP)

INTRODUCTION

Graft copolymers with defined structures are important goals because of their material properties. Their morphological study is an interesting field for testing phase-separation theories. One new method of controlled polymerization, atom transfer radical polymerization (ATRP),^{1–4} has already been widely used for the synthesis of block, graft, and star (co)polymers as well as polymers with more complex structures based on poly(methacrylate)s, polystyrene, and their copolymers. In ATRP, macroinitiators obtained by various other methods, such as anionic and cationic polymerization with suitably transformed functionalities, have also been used. As initiators, mostly alkyl bromides or chlorides with secondary or tertiary carbon atoms are used, activated in the α position by carbonyl, alkoxy-carbonyl, or phenyl groups, and catalysis is necessary. The proper choice of the initiating system and molar ratio (monomer/initiator/catalyst/complexing ligand or $[M]_0/[I]_0/[C]_0/[L]_0$) is important in any particular synthesis. Cu(I) halides are frequently used as catalysts. A number of monomers have been successfully

polymerized with specific combinations of initiation components under suitable reaction conditions.

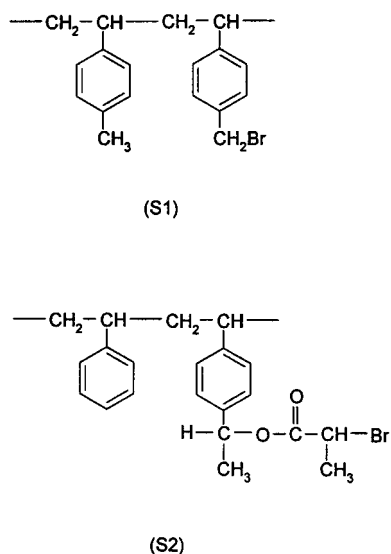
Recently, we prepared well-defined monodisperse polystyrene and poly(4-methylstyrene) macroinitiators carrying bromobenzyl or 1-(2-bromopropionyloxy)ethyl groups in 40% of their repeating units along the backbone.⁵ Here we present some results for *tert*-butyl acrylate (tBuA) grafting of the macroinitiators by grafting-from ATRP mediated by Cu(I) complexes and the characterization of the products.

Perhaps the first example of grafting-from ATRP was for poly(vinyl chloride) with 1 mol % incorporated vinyl chloroacetate structural units.⁶ Poly-{isobutylene-*co*-(4-methylstyrene-*co*-[(4-bromomethyl)styrene])} (EXXPRO, Exxon Chemical Co.) containing 0.4 or 1.3 mol % of CH₂Br groups was grafted with up to 60 wt % poly(methyl methacrylate) (PMMA)^{7,8} or polystyrene.^{7–9} With ATRP, other graft copolymers of polystyrene or styrene copolymers with an alkyl halide function along the backbone have been synthesized just recently. Liu and Sen¹⁰ grafted syndiotactic polystyrene brominated in 1.1–19% structure units with PMMA, poly(methyl acrylate), or atactic polystyrene with Cu(I)Br/*N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) catalysis. The grafting of synthesized (co)polymers^{11,12} and commercial block copolymers^{9,13} with haloalkyl functionalities was performed in the presence of Cu(I) halide and 2,2'-bipyridine (bpy) or its derivatives as ligands. Pan et al.¹³ grafted poly[styrene-*b*-(ethene-*co*-propene)] (Kraton, Shell Co.) after the chloromethylation of about 6% of the ben-

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Scheme 1

zene rings; their characteristics agreed with the criteria for a well-controlled process. Truelsen et al.¹¹ prepared poly(4-methylstyrene)-*b*-polyisobutylene-*b*-poly(4-methylstyrene), and after the bromination of approximately 43% of all 4-methyl groups, block-graft copolymers densely grafted with styrene were synthesized. However, thermal homopolymerization and intermolecular coupling took place during the bulk polymerization, and better results were achieved only at low conversions of styrene.

Beers et al.¹² grafted poly{[2-(2-bromopropionyloxy)-ethyl]methacrylate} with a degree of polymerization of about 200 with styrene and butyl acrylate. Especially with styrene, the formation of the ultimately grafted brush copolymer was studied in detail. This study was extended to the synthesis of double-grafted poly[alkyl methacrylate-*g*-(butyl acrylate-*b*-styrene)] polymeric brushes¹⁴ with interesting behavior at the interface.¹⁵ For crosslinking (gelation) suppression, all reaction parameters had to be carefully optimized, the deactivator [Cu(II) halide, lowering the radical concentration] was added in the proper amount, and the polymerization was stopped at a low conversion. The quoted examples show that coupling and crosslinking by the recombination of terminal radicals are critical when the functionalization of a macroinitiator is high.

EXPERIMENTAL

Materials

Poly(4-methylstyrene) (sample S1) and polystyrene (sample S2) macroinitiators (Scheme 1) were prepared by the modification of the polymers⁵ and were characterized by size exclusion chromatography (SEC); IR, ¹H-NMR, and ¹³C-NMR spectroscopy; and bromine determination. S1 had a number-average molecular weight

(M_n) of 7120 [weight-average molecular weight/number-average molecular weight (M_w/M_n) = 1.08] and 40% Br functionalization in position 4 (2.98 mmol Br/g). S2 had an M_n value of 4100 (M_w/M_n = 1.19) and 40% Br functionalization (2.27 mmol Br/g). tBuA (Fluka; minimum purity 99%) was rectified and distilled with CaH₂ just before polymerization. Cu(I)Cl (Aldrich, Milwaukee, WI; min. 99%) and Cu(I)Br (Fluka; 98%) were extracted with glacial acetic acid, washed with MeOH and Et₂O, and dried. Benzyl bromide (Fluka; min. 98%), methyl-2-bromopropionate (MBP; Fluka; min. 98%), *N,N*-dimethylformamide (DMF; Aldrich; 99.8%), anisole (Fluka; min. 99%), acetone (Fluka; 99.5%), PMDETA (Aldrich; 99%), bpy (Aldrich; min. 99%), aluminum oxide (Fluka; for chromatography, pH 7, Brockmann I grade), Dowex MSC-1 macroporous ion-exchange resin (Aldrich; 20–50 mesh), and solvents (reagent-grade) for purification and isolation of the copolymers were used as received.

Graft copolymerizations

Graft copolymer G1

Solids, that is, the macroinitiator S1 (I, 0.4013 g, 1.08 mmol of C—Br functional groups/g), Cu(I)Cl (C; 0.0269 g, 0.272 mmol), and bpy (L; 0.0847 g, 0.543 mmol), were placed in a round-bottom flask equipped with a three-way stopcock and were evacuated for 30 min. Eight milliliters of tBuA (M; 55.11 mmol) and 0.8 mL of DMF were introduced. After three freeze–draw cycles and filling with dry Ar, the reaction in the stirred mixture was carried out in a dry Ar atmosphere at 110°C. The initial molar ratio of the reactants was $[M]_0/[I]_0/[C]_0/[L]_0 = 50.1:1:0.25:0.5$. Samples of the reaction mixture were taken off after suitable time intervals, solids (catalyst) were separated, and the solution was diluted with tetrahydrofuran (THF) and characterized with gas–liquid chromatography (GLC) and SEC (the results are shown later in Figs. 2–6). The reaction mixture was diluted with 10 mL of THF and 100 mL of acetone, stirred for 1 h with Dowex resin, filtered through a column filled with alumina, and evaporated to dryness in vacuo. The copolymer was repeatedly dissolved in Et₂O and precipitated in 50% MeOH, dried in vacuo, and weighed (Table I and Fig. 1).

Graft copolymer G2

The copolymer was prepared analogously from S2 with the same monomer but with another initiating system, $[M]_0/[I]_0/[C]_0/[L]_0 = 35:1:0.25:0.25$ [I = S2, C = Cu(I)Cl, L = PMDETA], in the presence of 25% acetone (based on the volume of the monomer); the ligand PMDETA was added as the last component. The reaction temperature was 60°C. Isolation and characterization were performed in the same way used for G1.

TABLE I
ATRP Grafting of Bromine-Functionalized Poly(4-methylstyrene) (S1) and Polystyrene (S2) Backbones with PtBuA:
Characteristics of G1 and G2 Reaction-Mixture Final Samples and Products (Copolymers) Isolated From Them

Graft copolymer	Reaction time (min)	p^a	y^b	$M_{n,th}^c$	M_n^d	M_w/M_n^d
G1 ^e	285	0.450	—	63,540	59,720 (72,850)	1.12
G1 ^f	285	—	0.403	63,540	60,190 (75,570)	1.12
G2 ^e	1320	0.813	—	38,060	29,730 (37,500)	1.12
G2 ^f	1320	—	0.615	38,060	34,860 (42,430)	1.14

^a The conversion of tBuA (GLC).

^b The yield of the purified and isolated copolymer.

^c $M_{n,th} = M_{mi}[1 + p(w_a/w_{mi})]$; M_{mi} -molecular weight of the macroinitiator; w_a and w_{mi} -initial weights of tBuA and macroinitiator in the reaction mixture, respectively.

^d Calculated for polystyrene (or PtBuA, in parentheses) from SEC measurements in THF.

^e Data found with the copolymerizate (the reaction mixture after stopping with THF).

^f Data found with the isolated and purified copolymer.

Model homopolymerizations

Poly(*tert*-butyl acrylate) (PtBuA) sample P1 (related to the bromobenzyl-initiated copolymer G1) was prepared with benzyl bromide as an initiator; the other reaction components are the same as those in the G1 experiment ($[M]_0/[I]_0/[C]_0/[L]_0 = 20:1:0.2:0.4$). After 180 min at 110°C, P1 was purified in the same way as

the copolymers described previously, isolated, and characterized [$M_n = 2240$, theoretical number-average molecular weight ($M_{n,th}$) = 2080, $M_w/M_n = 1.97$]. The yield of the isolated polymer was 61.3%. PtBuA sample P2 (related to the graft copolymer G2) was prepared with MBP as an initiator. After reacting for 1350 min at 60°C with an initial ratio of $[M]_0/[I]_0/[C]_0/[L]_0$

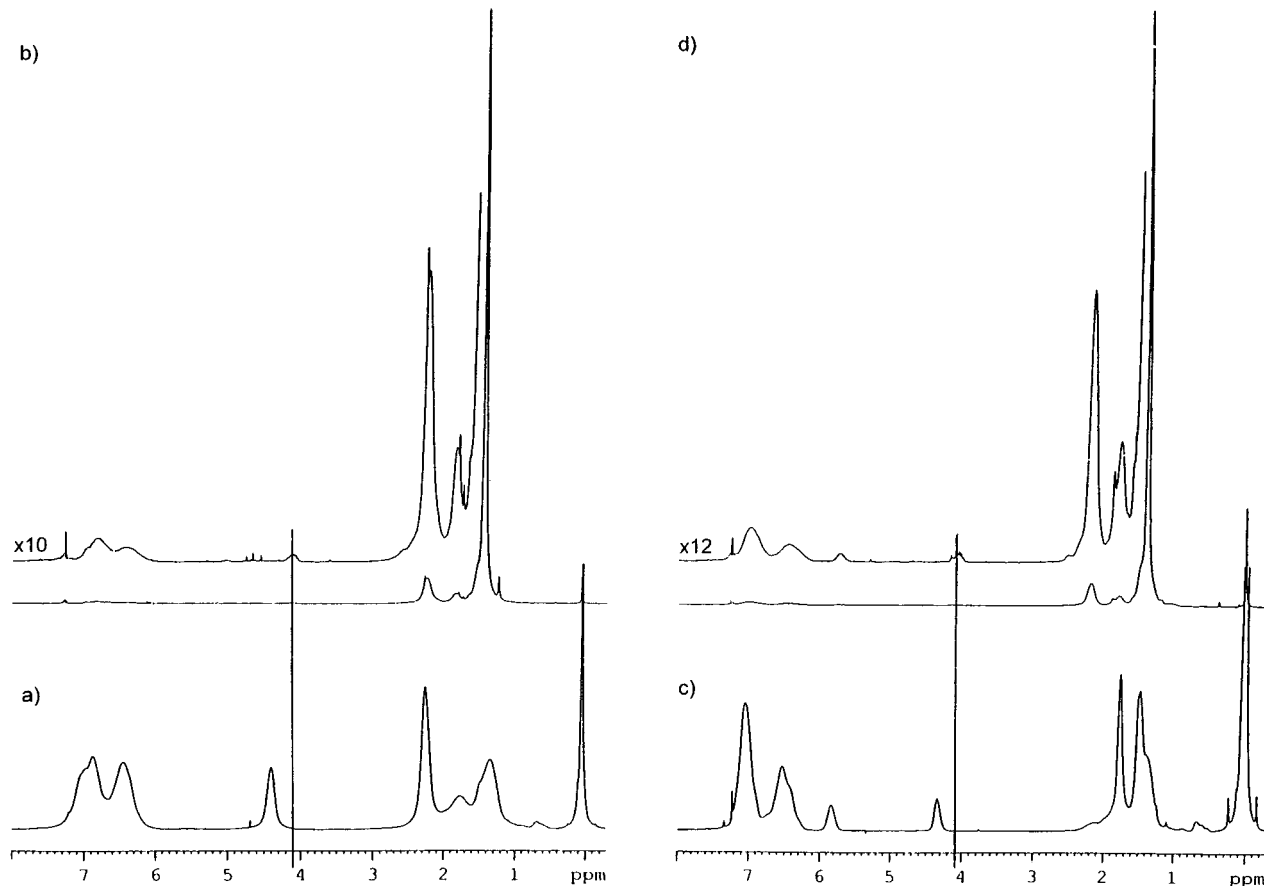


Figure 1 $^1\text{H-NMR}$ spectra of (a) the macroinitiator S1, (b) the corresponding graft copolymer G1, (c) the macroinitiator S2, and (d) the corresponding graft copolymer G2 (see the Experimental section and Table I).

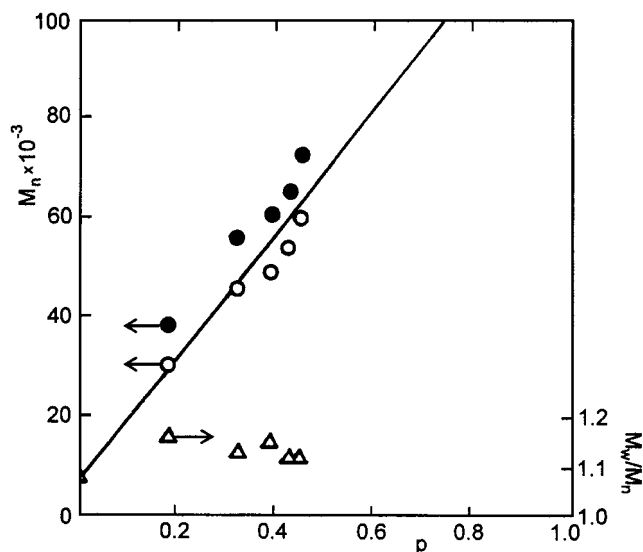


Figure 2 Dependence of M_n and M_w/M_n on tBuA conversion in the synthesis of G1 (see the Experimental section and Table I). M_n values were calculated with Mark–Houwink constants for (●) PtBuA and (○) polystyrene. The straight line denotes the theoretical M_n value course. (△) M_w/M_n values do not depend on the constants used for their calculation from SEC.

= 35:1:0.25:0.25 and in the presence of 25% acetone, P1 was isolated in a 63.1% yield and characterized ($M_n = 4200$, $M_{n,th} = 3740$, $M_w/M_n = 1.19$).

Measurements

The conversion of the monomers was determined with GLC (Hewlett–Packard model 8310, UK). Reaction solvents or anisole (2%) served as internal standards. M_n and M_w/M_n values were measured with SEC with 10^5 - and 10^3 -Å columns in series (5- μ m PL gel, Polymer Standard Service, Mainz, Germany) with refractive-index (RI) and ultraviolet (UV; 260 nm) detection and calibration with PMMA standards. $^1\text{H-NMR}$ spectra of isolated samples were measured on a Bruker Avance DPX 300 apparatus (Karlsruhe, Germany) in CDCl_3 at 60°C with hexamethyldisilyloxane as a standard (Fig. 1).

RESULTS AND DISCUSSION

Poly(4-methylstyrene) carrying pendant bromobenzyl functions (sample S1, Scheme 1) and polystyrene carrying pendant 1-(2-bromopropionyloxy)ethyl functions (sample S2, Scheme 1) were used as macroinitiators for ATRP grafting by tBuA, affording copolymers G1 and G2, respectively.

As the catalyst for G1 synthesis, we chose the Cu(I)Cl (C) and bpy (L) complex. The effect of this catalyst in the benzyl-halide-initiated polymerization of methyl methacrylate was studied by Matyjaszewski et al.¹⁶ Reportedly, the agreement between theoretical

and measured M_n values was not always perfect, the best results being achieved with Cu(I)Cl, bpy, and benzyl bromide. Cu(I)Cl and bpy or substituted bpy ligand were also used in sequential block copolymer synthesis from (meth)acrylates and styrene.^{17–19} Just recently, Davis and coworkers^{20,21} found MBP along with CuBr/PMDETA catalysis to be efficient in the ATRP of tBuA. Therefore, we used this initiating system also for the synthesis of copolymer G2, starting with S2 carrying 2-bromopropionyl groups.

The composition of G1 and G2 was studied with $^1\text{H-NMR}$ spectroscopy (Fig. 1). The formation of graft copolymers was confirmed in both cases by a new peak that appeared at 1.4 ppm and corresponded to the *tert*-butyl group of the tBuA unit. The signals at 6.2–7.2 ppm corresponded to the benzene ring protons of polystyrene or poly(4-methylstyrene) block. The complete disappearance of macroinitiator CHBr signals at 4.4 ppm in S1 [Fig. 1(a)] and 4.35 ppm in S2 [Fig. 1(c)] indicated that all Br functions took part in initiating the tBuA chain growth. At the same time, a new signal at 4.1 ppm appeared that came from CH-(Br)COOC(CH₃)₃ end-group protons [Fig. 1(b,d)]. We verified that in the spectra of model PtBuA homopolymers (P1 and P2; see the Experimental section) prepared under conditions analogous to those used for G1 and G2, the same signal appeared. These findings corroborate the proposed chemical structure of the synthesized graft copolymers G1 and G2.

Figures 2 and 3 show a plot of M_n and M_w/M_n values versus conversion in the course of tBuA grafting on S1 and S2. In both cases, the general drift of M_n reasonably approximates the theoretical straight-line slope characteristic of a controlled process. The M_n values of the graft copolymers were calculated with Mark–Houwink constants for PtBuA and polystyrene.

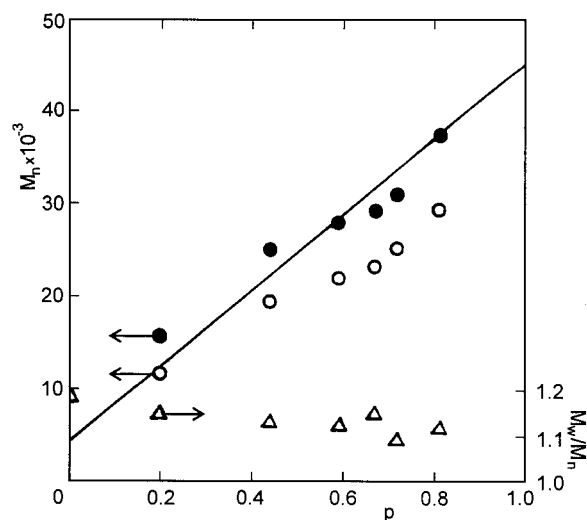


Figure 3 Dependence of M_n and M_w/M_n on tBuA conversion in the synthesis of G2 (see the Experimental section and Table I). See Figure 2 for the meaning of the symbols.

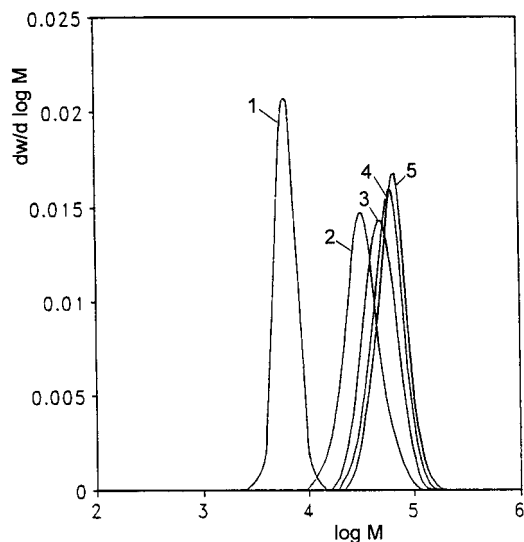


Figure 4 Evolution of the molecular weight distribution (calculated with Mark–Houwink constants for polystyrene) in the course of G1 synthesis. The reaction times were (1) 0, (2) 50, (3) 105, (4) 210, and (5) 285 min.

The data obtained under the assumption that the hydrodynamic behavior of the copolymers is closer to that of PtBuA than that of polystyrene are probably more realistic because all measured graft copolymers contain more PtBuA than poly(methyl)styrene. Anyway, the data cannot be accurate; a graft polymer behaves in solution differently from the corresponding linear polymer. The presented results are based on the refractometric detection of SEC traces. RI and UV traces for both copolymerizations were identical. This is strong evidence that grafting occurred with all macroinitiator molecules simultaneously. The molecular weights of the final graft copolymers were approximately nine times (G1) or eight times (G2) higher than those of the starting macroinitiators.

The remarkable result that can be determined from the data in Figures 2 and 3 is that the copolymerization only slightly altered the narrow polydispersity of the starting macroinitiators. In the course of both grafting procedures, M_w/M_n values ranged from 1.09 to 1.16. This may serve as a further indication of the controlled nature of the grafting. The molecular weight distribution shift with increasing conversion in the course of grafting can be clearly seen in Figures 4 and 5. They provide evidence that no residual macroinitiators remained in the graft copolymers G1 and G2. Therefore, if we take into account the mean number of grafting sites per macroinitiator chain (S1, 19.0; S2, 9.3), the mean length of the grafts can be calculated for the final samples (G1, ca. 27 units; G2, ca. 28 units). According to a comparison of the polydispersities of PtBuA samples P1 and P2, which were prepared under conditions analogous or close to those used in the G1 and G2 experiments (see the Experimental section), the length

of G2 grafts should be much more uniform than that of G1 grafts. The bromopropionate-initiated P2 polymer had a narrow polydispersity ($M_w/M_n = 1.19$), whereas benzyl bromide-initiated P1 was fairly polydisperse ($M_w/M_n = 1.97$), in agreement with published information.^{16,20}

In a typical atom transfer radical homopolymerization process, the kinetics fit to a linear, semilogarithmic, first-order dependence, reflecting the constant concentration of propagating radicals. This concentration is, in turn, directly proportional to the initial concentration of alkyl halide and to the ratio of the catalyst to the deactivator, $[Cu(I)]/[Cu(II)]$.²² It has already been reported^{11,12,14} that in the case of initiation with a highly functionalized macroinitiator backbone, intermolecular coupling or even crosslinking may take place (and actually has taken place). To the best of our knowledge, the kinetics of ATRP grafting have not yet been studied.

In Figure 6, the time course of the graft polymerizations of G1 and G2 is presented. Instead of linearity in the kinetic plots, a negative deviation is observed, that is, a progressive slowdown in comparison with standard ATRP. A first possible cause is a drop in the alkyl halide initiator amount via the termination of radicals. We tried to assess a possible change in alkyl halide function content during grafting by ¹H-NMR spectroscopy, comparing the relative intensities of CHBr signals at the beginning (S1 and S2) and end (G1 and G2) of copolymerizations. For the calculation, the intensity of the CHBr signal has to be related to the intensity of some signal that does not change during the copolymerization. Therefore, the ratio of ¹H-NMR signal intensities of terminal CHBr protons [$I(CHBr)$, $\delta = 4.1$ ppm; see Fig. 1(a,c)] to those of benzene ring protons

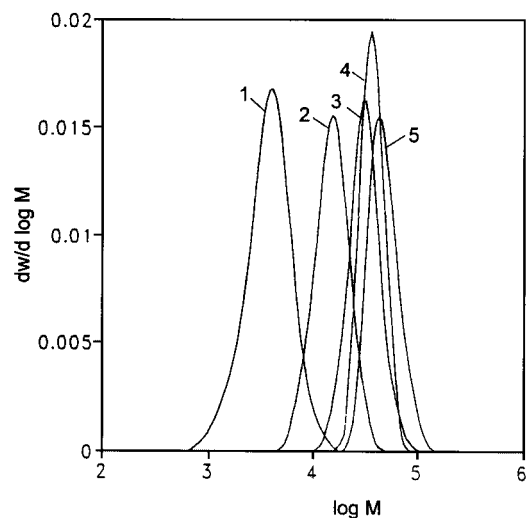


Figure 5 Evolution of the molecular weight distribution (calculated with Mark–Houwink constants for polystyrene) in the course of G2 synthesis. The reaction times were (1) 0, (2) 85, (3) 450, (4) 840, and (5) 1320 min.

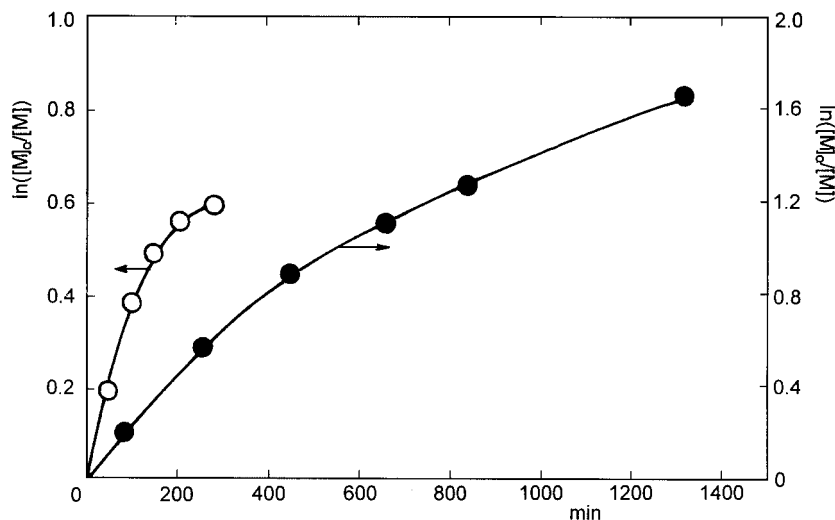


Figure 6 Dependence of $\ln([M]_0/[M])$ versus time for the graft polymerizations of (○) G1 and (●) G2 (see Table I).

[I(PhH), $\delta = 6.2\text{--}7.2$ ppm] in the graft copolymers and analogous values for the respective macroinitiators (calculated with CHBr proton signals of chain-bonded functional groups at 4.35–4.4 ppm) served for assessing the scope of potential termination. The I(CHBr)/I(PhH) ratio for G1 (0.064) is considerably lower than that for the corresponding macroinitiator S1 (0.095). (For S1, one-half of the benzyl bromide CH₂Br signal intensity was taken for the calculation because of two protons.) From this, it follows that during the synthesis of G1, the content of alkyl bromide end groups may have decreased by 30–35%. Termination took place here and retarded the polymerization. The relatively high reaction temperature (110°C) may have supported the termination. As neither a positive deviation of the molecular weight from the theoretical value and a high molecular weight fraction occurrence nor a broadening of the distribution curve was observed (Figs. 2 and 4), this termination could proceed only as disproportionation, not as recombination.

In contrast, the value of I(CHBr)/I(PhH) for G2 (0.075) is only insignificantly lower than that for S2 (0.078), the difference being within the error limit. The negative deviation in G2 kinetics has, therefore, most likely another reason: the drop in the Cu(I)Br/PMDETA concentration in the reaction mixture. The complex catalyst, soluble at the beginning of grafting, precipitated progressively with growing conversion as a dark blue powder, whereas the blue color of the reaction solution became lighter. In G1 synthesis, the precipitation of the respective catalyst might have affected the polymerization kinetics in the same way, but it was not observable; the catalyst was partly solid all the time, and the mixture was turbid.

Further optimization of the grafting under study (e.g., by persistent radical effect) may elucidate and, at the same time, remove the problems with nonstandard kinetics and possible side effects.

CONCLUSIONS

Two monodisperse graft copolymers, one with poly(4-methylstyrene) and the other with polystyrene backbone carrying PtBuA grafts, were synthesized from monodisperse macroinitiators by grafting-from procedures with ATRP. The poly(4-methylstyrene) precursor had 40% of the structural units transformed into benzyl bromide initiating groups (benzyl bromide macroinitiator), whereas the polystyrene precursor carried the same amount of 2-bromopropionyl functions (bromopropionyl macroinitiator) along the chain. All initiating groups were used for grafting. M_n values of the copolymers increased linearly with monomer conversion, being close to theoretical values, and the respective polydispersities ranged from 1.09 to 1.16. Weights of PtBuA eight to nine times greater than those of the macroinitiators were finally built into the copolymers. Taking into account the high macroinitiator functionality and high monomer conversions achieved (45% with the benzyl bromide macroinitiator and 81% with the bromopropionyl macroinitiator), we found the agreement of the copolymer molecular parameters with criteria for controlled polymerization to be exceptionally good. However, semilogarithmic conversion plots displayed negative deviations, indicating the presence of some side effects. These were ascribed either to disproportionation termination (based on ¹H-NMR spectroscopy with the copolymer from the benzyl bromide macroinitiator) or to progressive catalyst precipitation with increasing conversion (with the copolymer from the bromopropionyl macroinitiator).

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