

Graft Copolymers and High-Molecular-Weight Star-Like Polymers by Atom Transfer Radical Polymerization

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ABSTRACT: Grafting of *tert*-butyl acrylate (*t*BuA), methyl methacrylate (MMA), and styrene (St) monomers (M) by Cu(I)-mediated ATRP from polystyrene (PSt) macroinitiator ($M_n = 5620$, polydispersity index, PDI = 1.12), containing initiating 2-bromopropionyloxy groups (I) (bound to 34% of aromatic cores; 11 groups per backbone), was performed using conditions suitable for the respective homopolymerizations. The preparation of PSt-*g*-*t*BuA in bulk using an initial molar ratio $[M]_0/[I]_0 = 140$ had a controlled character up to $M_n = (132\text{--}148) \times 10^3$ (PDI = 1.08–1.16). With MMA and St and using the same $[M]_0/[I]_0$, preliminary experiments were made; the higher the monomer conversion, the broader was the distribution of molecular weight of the products. Graft copolymerizations of all these monomers at $[M]_0/[I]_0 = 840$ or 1680 were successfully conducted up to

high conversions. Low-polydispersity copolymers, with very long side chains, in fact star-like copolymers, were obtained mainly by tuning the deactivator amount in the reaction mixture. (PSt-*g*-*t*BuA, $DP_{n,sc}$ (DP of side chain) = 665, PDI = 1.24; PSt-*g*-PMMA, $DP_{n,sc} = 670$, PDI = 1.43; PSt-*g*-PSt, $DP_{n,sc} = 324$, PDI = 1.11). Total suppression of intermolecular coupling was achieved here. However, the low concentrations of initiator required long reaction times, leading sometimes to formation of a small amount (~5%) of low-molecular-weight polymer fraction. This concomitant process is discussed, and some measures for its prevention are proposed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3662–3672, 2006

Key words: graft copolymers; star polymers; ATRP

INTRODUCTION

Atom transfer radical polymerization (ATRP) is the most robust and versatile method of controlled radical polymerization, particularly useful for synthesis of graft and star copolymers.^{1–4} The “grafting from” and “core first” procedures proved to be more attractive and viable than “grafting onto,” “grafting through,” or “arm first” methodologies.

In ATRP, the growing polymer radical is protected for the greater part of polymerization time by reversible capping with halogen or another suitable group. Nevertheless, ATRP still remains a branch of radical polymerization, and as such it suffers from possible slow initiation, chain transfer, and termination side effects, although to a much lower extent than classical radical polymerization.

The application of “grafting from” ATRP procedure greatly improved uniformity of graft copolymers and enabled the synthesis of new products. One of the new

developments is the synthesis of densely grafted, uniform “bottle brush copolymers.”^{5–16} The products were visualized on molecular level by atomic force microscopy, which confirmed their unique structure.

In addition to Cu(I) halides, other transition metal compounds (Ru, Ni, Fe) were also successfully employed in the “grafting from” ATRP.^{17–21} The experience with “grafting from” ATRP, catalyzed by Cu(I) salts, was utilized in the synthesis of polymer brushes bound to micro- and nanoparticles and flat surfaces. The results were also reviewed recently.²²

For the “grafting from” methodology applied to star copolymer synthesis,⁴ i.e., the “core first” approach, the same is valid as was said earlier for the “grafting from”. Molecular weight of most prepared stars ranged from several thousands to 20,000–50,000. Molecular weight higher than 200×10^3 was attained only in a few studies.^{23,24}

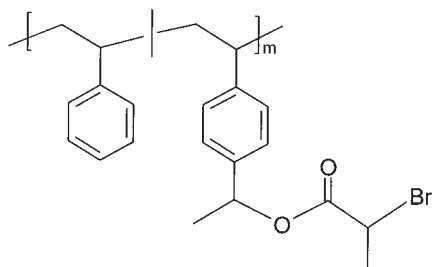
There is a common factor for both the “grafting from” and “core first” ATRP methodology: recombination termination of propagating side chains (arms). Polyfunctional growing moieties may be taken as polyradicals prone to crosslinking.

In the present study, we continued the work in copper-mediated ATRP grafting from functionalized polystyrene (PSt) macroinitiator (MI, Scheme 1), carrying 2-bromopropionyloxy initiating groups.^{25–27}

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Scheme 1. Multifunctional MI.

This work had two aims. First, we tried to improve the control of ATRP grafting from MI up to $M_n \sim 10^5$, because our previous study²⁶ has shown a nonideal first-order kinetics in experiments with a current concentration of initiating groups in the reaction mixture containing acetone. Second, it was interesting to examine whether it is possible to prepare graft copolymers with considerably longer side chains, than so far attained. We tried to reach up to limits of control of the grafting from MI as macroinitiator, using high $[M]_0/[I]_0$ ratios and monomer conversions higher than ~ 15 –25%, so far taken as the upper limit, when termination is to be excluded.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (99%, Aldrich, Milwaukee, WI), *t*BuA ($\sim 99\%$, Fluka purum), and styrene (St) ($\geq 99.5\%$, Fluka puriss.) were distilled with CaH_2 and stored at -18°C . CuCl ($>99\%$, Aldrich) and CuBr ($\geq 99\%$, Fluka, Buchs, Switzerland) were purified by extraction with glacial acetic acid, washed with ethanol, and dried. CuCl_2 (97%, Aldrich), CuBr_2 ($\geq 99\%$, Fluka), N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), 4,4'-dinonyl-2,2'-bipyridyl (dNbpy, 97%, Aldrich), N,N,N',N'',N''',N'''' -hexamethyltriethylenetetramine (HMTETA, 97%, Aldrich), toluene (puriss. $>99.5\%$, Fluka), *m*-xylene (puriss. $>99\%$, Fluka), methanol (r.g., Lachema, Czech Republic), and butyl acetate (puriss. $\geq 99\%$, Fluka) were used as received.

Characterization methods

Monomer conversions were determined using GLC (Clarus model 500, Perkin–Elmer, UK). The reaction solvents or anisole served as internal standards. SEC eluograms were measured and evaluated using two devices. Device 1 (SEC-1/RI measurement): HP 6000 pump (Labora, Czech Republic), 10^5 and 10^3 \AA columns in series (PL gel, $5 \mu\text{m}$, Polymer Standard Service, Germany), RI-detector; calibration in the M_n range 3×10^2 to 1.8×10^6 , with linear monodisperse

PSt standards (Polymer Standard Service, Mainz, Germany). The data were evaluated using professional software Caliber (Polymer Laboratories, Czech Republic). Device 2 (SEC-2 measurement): Deltachrom pump (Watrex Comp.), autosampler Midas (Spark Instruments, The Netherlands), two columns with PL gel MIXED-B LS ($10 \mu\text{m}$), separating in the M_n range 4×10^2 to 10×10^6 . Dawn-DSP-F laser light scattering (MALLS) photometer (Wyatt Technology Corp., USA) and Shodex RI-71 refractive index detector (Japan) were used as detectors. SEC data were evaluated in two ways: (1) Using a calibration dependence obtained for several PSt standards in the M_n range 400 – 1.6×10^6 , and the values were recalculated to those of linear-chain polymers, using Mark–Houwink constants for PSt, *Pt*BuA or PMMA (depending on the major component) (SEC-1/RI measurement) (2) Dual LS/RI data were evaluated using Astra Software 4.70.07 (SEC-2/LS measurements). The injection-loop volume was 0.1 mL. The data were accumulated and processed using Astra Software 4.70.07.

For all copolymers prepared, the total consumption of initiating functions at the very beginning of all polymerizations was verified by SEC. For example, evolution of SEC traces with reaction time (synthesis 3, Table I, Fig. 1) shows that MI disappeared from the mixture quickly. In the experiments, in which we followed the grafting up to very high molecular weights, ^1H NMR spectrometric monitoring of M_n was not sensitive enough, owing to a very low content of MI in the products. We used SEC as the only characterization method.

The calculated M_n values for graft copolymers, $M_{n,\text{calc}} = M_{n,\text{mi}} \times [1 + (p/100)(w_m/w_{\text{mi}})]$, where $M_{n,\text{mi}}$ is the M_n of PSt macroinitiator MI, w_m and w_{mi} values correspond to initial weights of monomer and MI in the reaction mixture, and p is the monomer conversion, following from GLC data (%).

Macroinitiator

The starting monodisperse PSt macroinitiator MI, $M_{n,\text{mi}}$ (number-average molecular weight of MI) = 5260 (V.P.O., K-7000, Knauer, Germany), $\text{DPI} = 1.12$ (SEC-1/RI) (Scheme 1), was synthesized according to the literature.²⁵ Its content of bromine, calculated approximately from ^1H NMR spectra, is 2.40 mmol/g. A more accurate value, derived from bromine content determination (16.57%, Schöniger method), corresponds to 2.07 mmol Br/g. The Br content together with a mass balance calculation gives the mean number of initiating sites per MI chain (11) and the degree of functionalization of the backbone (34% of benzene rings).

TABLE I
ATRP Grafting of *tert*-Butyl Acrylate, Methyl Methacrylate, and Styrene from Multifunctional Macroinitiator MI at Its Current Concentration ($[M]_0/[I]_0/[Cu(I) \text{ halide}]_0 = 140 : 1 : 1$)

Sample	Catalyst ^a	Toluene % (v/v)	<i>T</i> (°C)	<i>t</i> (min)	<i>p</i> (%)	$M_{n,calc} \times 10^{-3b}$	$M_n \times 10^{-3}$		M_w/M_n	
							LS ^c	RI ^d	LS ^c	RI ^d
<i>tert</i> -Butyl acrylate										
1	E	0	50	305	64.9	132.2	146.5	71.9	1.13	1.10
2	E	0	60	210	70.4	143.0	–	79.3	–	1.10
3	E	0	70	310	73.4	148.7	–	94.9	–	1.16
4	F	0	80	250	67.1	136.7	–	84.2	–	1.08
Methyl methacrylate										
5	G	50	80	270	35.1	58.9	–	42.2	–	1.34
6	G	50	25	4800	97.4	154.1	461	168.2	1.84	1.84
Styrene										
7	H	20	110	195	48.0	81.7	–	112.7	–	3.58

^a E = [CuBr(PMDETA)], F = [CuBr(dNbpy)₂], G = [CuCl(dNbpy)₂], H = [CuBr(HMTETA)].

^b $M_{n,calc} = M_{n,mi} \times [1 + (p/100)(w_m/w_{mi})]$, see Experimental part.

^c Based on SEC-2/LS measurement.

^d Based on SEC-1/RI measurement.

Polymerization

MI, catalyst, deactivator, and a solid complexing ligand (dNbpy) were evacuated at 133 Pa for 30 min and filled with argon in a cylindrical glass reaction flask, equipped with a T-shaped stopcock and a magnetic stirrer. The monomer and solvent, bubbled with argon for 30 min in advance, were transferred into the flask, with deoxygenated injection syringe. After three freeze–pump–thaw cycles, addition of a liquid ligand, and homogenization, the reaction was carried out under dry argon. Samples were taken at appropriate time intervals and analyzed by GLC and SEC-1/RI (Fig. 2), after aeration, dilution with THF, and filtration (PTFE microfilters, Whatman, 0.2 micrometer pores). The polymerizate in the flask was diluted with THF, filtered, and precipitated twice, in excess of MeOH (St copolymers), 80:20 v/v MeOH/H₂O (MMA copolymers), or 60:40 v/v MeOH:H₂O (*t*BuA copolymers), and the copolymer was separated, washed, and

dried in vacuo (40°C, three times, for 10 h), and the monomer conversion was determined gravimetrically. The conversion did not differ from GLC data (*p*, %) by more than 2–3%. SEC of the isolated samples was performed with SEC-2/LS (see earlier).

RESULTS AND DISCUSSION

Grafting from MI at currently used initial initiator concentration ($[M]_0/[I]_0 = 140 : 1$)

The MI is quite a low-molecular-weight polymer ($M_n = 5260$). It can be taken as a backbone for the “grafting from” as well as a core for the “core first” star synthesis. The *p*-chloromethyl or bromomethyl groups bound to the aromatic core of commercial PSt were already utilized in ATRP.^{28–31} As initiating groups, they were also introduced into the PSt chain or copolymer segment by halomethylation,^{32,33} by transformation of 4-OMe or 4-OCOCH₃ group in PSt copolymer,³⁴ or by copolymerization of St with 4-(halo-

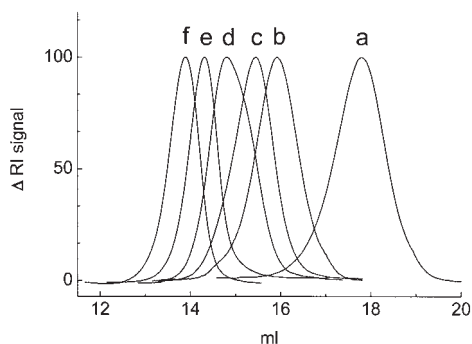


Figure 1 SEC traces (SEC-1/RI) in the course of PSt-*g*-PtBuA synthesis (sample 3, Table III) with [CuBr(PMDETA)] catalyst. $[M]_0/[I]_0/[CuBr(PMDETA)]_0 = 140 : 1 : 1$, 70°C. Reaction times (min): 0 (a ≡ MI), 25 (b), 40 (c), 85 (d), 130 (e), 210 (f).

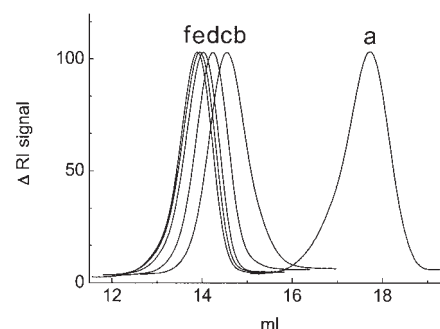


Figure 2 SEC traces (SEC-1/RI) in the course of PSt-*g*-*t*BuA synthesis (sample 4, Table I) with [CuBr(dNbpy)₂] catalyst. $[M]_0/[I]_0/[CuBr(dNbpy)_2]_0 = 140 : 1 : 1$, 80°C. Reaction times (min): 0 (a), 40 (b), 70 (c), 120 (d), 160 (e), 250 (f).

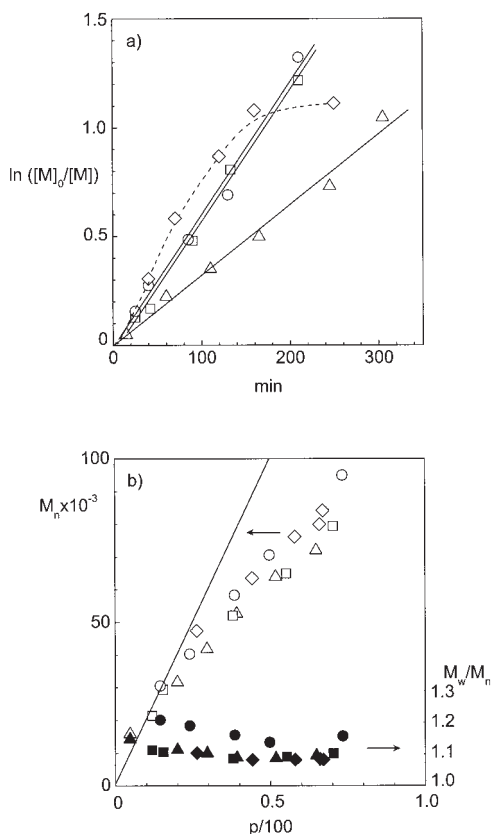


Figure 3 PSt-*g*-PtBuA synthesis (Table I). $[M]_0/[I]_0/[C]_0 = 140 : 1 : 1$. C = [CuBr(PMDETA)]: 50°C (sample 1, Δ); 60°C (2, \square); 70°C (3, \circ). C = [CuBr(dNbpy)₂]: 80°C (4, \bullet). (a) First order kinetics. (b) M_n (empty symbols) and PDI (M_w/M_n) (full symbols) versus monomer conversion (SEC-1/RI).

methyl)styrene or other monomer with benzyl halide function.^{35–39}

The ratio of $[M]_0/[I]_0 = 140 : 1$ corresponds to “currently used” initiator concentration, $[I]_0 \approx 30\text{--}60\text{ mM}$. Using this ratio usually means that ATRP is still a controlled process, i.e., M_n is equal to $M_{n,calc}$ or not much different from it up to high conversions.

The kinetics of the synthesis of PSt-*g*-PtBuA from MI reported previously²⁶ was now reexamined in bulk. Linear first-order kinetics of *t*BuA bulk polymerization was observed in a temperature range of 50–70°C, with [CuBr(PMDETA)] catalysis in the conversion range up to 60–70% (Table I, samples 1–3, Fig. 3(a,b)). The copolymer samples have low values of PDI, 1.10–1.16, and symmetric SEC traces, as is shown in Figure 1 for sample 3. M_n values, obtained by SEC-1/RI (device 1, see Experimental part), correspond to $M_{n,calc}$ only up to $\sim 15\%$ conversion, and then deviate from theory. M_n obtained by SEC, calibrated with linear standards, gives always lower values for branched polymers. This is a consequence of different hydrodynamic volumes of linear and branched particles with the same M_n . The M_n found by multiangle laser scattering detection SEC-2/LS (device 2, Experi-

mental part) for sample 1 is more than twofold than determined by SEC-1/RI and close to the theory.

In spite of the linearity of the kinetics, the process is still not ideal. First, although the rate at 60°C under CuBr(PMDETA) catalysis is markedly higher than at 50°C, there is practically no difference between the rates at 60 and 70°C [Fig. 3(a)]. Second, the reaction mixtures of samples 1–3 are clear, light green solutions, only at the beginning of the polymerization, and they gradually turn blue with fine dark blue precipitate formation. The reason for the visual change may be a change of complex catalyst structure or a change of activator or deactivator solubility when polymer conversion increases.

The first-order kinetics of *t*BuA grafting under [CuBr(dNbpy)₂] catalysis at 80°C [Table I, sample 4, Fig. 3(a)] is linear only up to $\sim 40\%$ conversion; however, the polydispersity is low, decreasing to PDI = 1.08 at 67% conversion, and SEC traces are narrow.

Copolymerization of MMA (Table I, samples 5 and 6) or St (Table I, 7) was attempted at the same molar ratio $[M]_0/[I]_0 = 140 : 1$, in the presence of toluene with the same stoichiometry of other components, as in the grafting of *t*BuA mentioned earlier. The halogen exchange⁴⁰ (Br-functionalized MI/[CuCl(dNbpy)₂] catalyst) was applied (samples 5 and 6). The grafting at 80°C was stopped at 35% conversion. PSt-*g*-PMMA 5 with $M_n(\text{SEC-1/RI}) = 42 \times 10^3$, PDI = 1.34 and symmetrical main SEC peak, with a hint of lower-molecular-weight fraction, was obtained (Fig. 4). When the copolymerization was performed at 25°C for a much longer time and stopped at almost total conversion, a shoulder could be detected on the high-

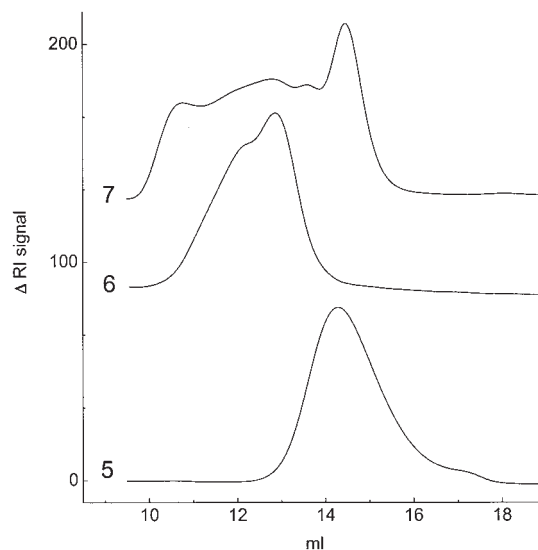


Figure 4 SEC traces (SEC-1/RI) of copolymers prepared at the ratio $[M]_0/[I]_0/[C]_0 = 140 : 1 : 1$ (Table I). PSt-*g*-PMMA, sample 5, 80°C, C = [CuCl(dNbpy)₂], $p = 35.1\%$; 6, 25°C, C = [CuCl(dNbpy)₂], $p = 97.4\%$. PSt-*g*-PSt sample 7, 110°C, C = [CuBr(HMTETA)], $p = 48.0\%$.

molecular-weight side of SEC trace of sample 6 (Fig. 4). $M_n(\text{SEC-2/LS})$ is much higher than the calculated value and $\text{PDI} = 1.84$. Accordingly, coupling by termination took place here.

A considerable extent of coupling is evident also from the higher than calculated M_n value, and a very broad SEC trace of PSt-*g*-PSt 7 ($\text{PDI} = 3.58$), prepared in 48% yield, under [CuBr(HMTETA)] catalysis at 110°C (Table I).

These experiments indicate that the application of reaction conditions similar to those utilized in 1–4 synthesis led to side reactions in grafting of MMA and St.

A comparison of the earlier results with the published data should be made with caution. Various parameters of multifunctional MIs or star cores, such as composition, theoretical molecular weight, character of initiating groups, their number, and density of backbone functionalization, the respective addition of a deactivator, etc., differ in published experiments.

The accuracy of the calculation of the number-average degree of polymerization of side chains ($\text{DP}_{n,\text{sc}} = (M_n - M_{n,\text{mi}})/(M_{\text{mon}} \times \text{number of initiating groups per backbone})$ where M_{mon} = molecular weight of monomer) depends on the accuracy of determination of M_n and on the actual number of function groups per backbone that virtually initiated the polymerization. This number was only scarcely mentioned among graft polymer characteristics. The $\text{DP}_{n,\text{sc}}$ values are absolutely reliable only if the concentration of radicals is close to the initial concentration of initiating groups during the respective polymerization, and M_n of the copolymer is close to $M_{n,\text{calc}}$, or if side chains have been cleaved and their M_n properly characterized. In this article, $\text{DP}_{n,\text{sc}}$ values were calculated according to the aforementioned formula also in evaluation of literature data.

Comparison might probably best serve a study on the “grafting from” synthesis by Gnanou and coworkers.²⁴ When *t*BuA was copolymerized from 2-bromopropionyloxy groups bonded to octafunctional 4-*tert*-butylcalixarene core at very high values of $[M]_0/[I]_0$, $[t\text{BuA}]_0/[I]_0/[CuBr]_0/[bpy]_0/[\text{solvent}] = 800$ or $2400 : 1 : 1 : 2 : 10\%$ ethylene carbonate at 100°C to 20–40% conversion, the copolymer with $M_n = 28\text{--}77 \times 10^3$, $\text{PDI} \sim 1.1$, $\text{DP}_{n,\text{sc}} \sim 15\text{--}40$ was prepared. Neither shoulders nor side peaks were observed on SEC traces of the prepared star copolymers. This corresponds to our results for PSt-*g*-*t*BuA (samples 1–4), displaying $\text{PDI} \sim 1.1$ and $\text{DP}_{n,\text{sc}}$ about 60. However, we were able to use a “common” (i.e., much higher) initial concentration of initiator, and ATRP was controlled up to a high conversion (63–75%).

Hovestad et al.⁴¹ utilized a 12-functional carbosilane dendrimer of $M_n = 4600$ for the synthesis of star polymer with MMA arms. Using the ratio $[\text{MMA}]_0/[2\text{-bromoisobutyryloxy-}]_0/[CuBr]_0/[OPMI]_0 = 100 :$

$1 : 1 : 2$ (OPMI = *N*-octyl-(2-pyridyl)methanimine) and reaction temperature 90°C, the copolymer formed with $\text{PD}_{n,\text{sc}} \sim 45$, $M_n = 33 \times 10^3$ and $\text{PDI} = 1.29$ (MMA conversion = 46%). Higher molecular weight species were formed continuously during reaction (tailing SEC traces), and a shoulder of higher molecular weight appeared above 25% conversion similar to our sample 6 (Table I).

In St grafting (sample 7), complete loss of control of molecular weight distribution was observed (Fig. 4). The clear occurrence of coupling is consistent with the results of authors, utilizing $-\text{C}_6\text{H}_4\text{CH}_2\text{Br}$ initiating groups. The same was observed in the synthesis of PSt-*g*-PSt by “grafting from” method, using $[\text{St}]_0/[-\text{C}_6\text{H}_4\text{CH}_2\text{Br}]_0 = (36\text{--}56) : 1^{34}$ or $1260 : 1^{35}$.

On the whole, the copolymers 1–7 show that using MI and a low value of the ratio $[M]_0/[I]_0 = 140$, the tendency of growing side chains to intermolecular coupling manifested itself as high-molecular-weight fraction formation, decreasing in the order $\text{St} > \text{MMA} >> \text{BuA}$. The control of grafting with *t*BuA was perfect up to unusually high conversions under the conditions used for samples 1–3 (Table I).

Grafting of *t*BuA, MMA and St from MI at low initiator concentrations ($[M]_0/[I]_0 = 840$ or $1680 : 1$)

Owing to termination of propagating radicals by recombination, the maximum attainable $\text{DP}_{n,\text{sc}}$ can show an upper limit. The propagating multifunctional macromolecules of graft and star polymers may also couple. The coupling can go on, resulting in the formation of a network. The probability of termination increases with graft length and increasing concentration of radicals in the reaction mixture. For suppressing termination, short reaction times (or stopping the reaction at a low monomer conversion) and a low amount of radicals in the reaction mixture is needed. For lowering the concentration of growing radicals, initial concentration of both initiator (initiating groups) and catalyst has to be lowered and a deactivator, CuBr_2 or CuCl_2 , was added for enhancing the protection of growing radicals by halogen capping. Such precautions and stopping ATRP at a low conversion have been applied in “grafting from” and “core first” Cu-mediated synthesis many times. Their simultaneous application enabled Matyjaszewski et al.⁴² and Müller and coworkers⁹ to synthesize the aforementioned precisely defined “cylindrical (bottle)brushes” and “star brushes” with original architecture, based on densely functionalized poly[2-(2-bromopropionyloxy)ethyl methacrylate] backbone (each backbone unit being an initiating site), with M_n up to $\sim 150 \times 10^3$. At reaction temperatures 70–80°C with the ratio $[M]_0/[I]_0 \sim 400\text{--}600$ ($[I]_0 \approx 8\text{--}16$ mM), up to 5% CuBr_2 (relative to CuBr) was added to the mixture. The copolymers were isolated at low monomer conversions, 2–6%. The isolated prod-

TABLE II
ATRP Grafting of *tert*-Butyl Acrylate from the Multifunctional Macroinitiator MI at Its Low Concentration
($[M]_0/[I]_0 = 840$)

Sample	Catalyst (deactivator) ^a	Stoichiometry ^b	Solvent % (v/v)	T (°C)	t (h)	p (%)	$M_{n,calc} \times 10^{-3}$ ^c	$M_n \times 10^{-3}$		M_w/M_n	
								LS ^d	RI ^e	LS ^d	RI ^e
8	E	840 : 1 : 2 : 0.1	butyl acetate 15%	90	52	51	600	– ^f	131	– ^f	2.36
9	F	840 : 1 : 1 : 0	toluene 15%	70	9	80	930	– ^f	514	1.24 ^g	1.38
10a	G	840 : 1 : 6 : 0	<i>m</i> -xylene 20%	40	31	23	270	– ^f	193	– ^f	1.10
10b	G	"	"	"	77	47	610	674 ^g	402	1.18 ^g	1.40
blank ^h	G	840 : 0 : 6 : 0	"	70	9	2	– ^f	– ^f	43	– ^f	1.40

^a E = [CuCl/dNbpy], [CuCl₂/dNbpy], F = [CuCl/PMDETA], G = [CuBr/PMDETA]. Ligand concentration, $[L]_0 = n([CuX]_0 + [CuX_2]_0)$; $n = 1$ (PMDETA) or 2(dNbpy).

^b $[M]_0/[I]_0/[C]_0/[D]_0$ (C = Cu(I) catalyst, D = deactivator, i.e., Cu(II) halide).

^c $M_{n,calc} = M_{n,mi} \times [1 + (p/100)(w_m/w_{mi})]$, see Experimental part.

^d Based on SEC-2/LS measurement.

^e Based on SEC-1/RI measurement.

^f Not determined.

^g Unimodal SEC—peak without any shoulders.

^h Experiments in absence of MI.

ucts ($M_n \sim 1\text{--}4 \times 10^6$) had low polydispersity index, PDI = 1.22–1.38. However, the individual grafts, PBuA, PSt, PBuA-*b*-PSt, and PSt-*b*-PBuA side chains, were rather short ($DP_{n,sc} = 9\text{--}50$, only exceptional up to 90).

To suppress the termination (observed in the polymerizations of MMA (6) and St (7)), and to prepare copolymers with long side chains, we have made some experiments, hereinafter "low-initiator experiments" (Tables II and III), using 6 and 12 times higher ratios of $[M]_0/[I]$ than mentioned earlier, thus lowering the concentration of initiating groups in reaction mixtures to 6–8 mM (840 : 1) or 3–4.5 mM (1680 : 1).

In the preparation of high-molecular-weight graft (co)polymers by ATRP, the limits of control and of attainable length of side chains depend on several factors. When suitable reaction components and suitable reaction conditions are chosen, the process control and $DP_{n,sc}$ depend on monomer and on the propensity of the respective propagating radical to bimolecular termination or on other side reactions (slow initiation, chain transfer). For achieving high $DP_{n,sc}$ low (macro)initiator concentrations are needed, causing in turn prolongation of the reaction time and a higher sensitivity of the system to impurities. In the following experiments, well-tried catalysts, ligands,

TABLE III
ATRP Grafting of Methyl Methacrylate and Styrene from the Multifunctional Macroinitiator MI at Its Low Concentration in the Presence of *m*-Xylene (20% v/v)

Sample	Catalyst (deactivator) ^a	Stoichiometry ^b	T (°C)	t (h)	p (%)	$M_{n,calc} \times 10^{-3}$ ^c	$M_n \times 10^{-3}$		M_w/M_n	
							LS ^d	RI ^e	LS ^d	RI ^e
Methyl methacrylate										
11	E	840 : 1 : 1 : 0	90	3	45	410	1648	435	1.72	1.92
12a	E	1680 : 1 : 6 : 0.6	90	6.5	25	460	– ^f	268	– ^f	1.41
12b	E	"	"	13	49	900	745 ^g	378	1.43 ^g	1.62
13	F	1680 : 1 : 1 : 0.1	90	18	46	850	822	781	1.27	1.43
14	F	1680 : 1 : 3 : 0.3	30	24	41	820	1253	893	1.82	1.28
15a	F	1680 : 1 : 3 : 0.9	30	31	18	340	– ^f	392	– ^f	1.23
15b	F	"	"	74	61	1124	1354	781	1.27	1.43
Styrene										
16	F	1680 : 1 : 3 : 0.3	120	40	21	400	140	50	2.77	4.52
16G ^h	F	"	"	"	19	382	377 ^g	241	1.11 ^g	1.08

^a E = [CuCl/dNbpy], [CuCl₂/dNbpy], F = [CuBr/dNbpy], [CuBr₂/dNbpy]; $[dNbpy]_0 = 2([CuX]_0 + [CuX_2]_0)$.

^b $[M]_0/[I]_0/[C]_0/[D]_0$ (C = Cu(I) catalyst, D = deactivator, i.e., Cu(II) halide).

^c $M_{n,calc} = M_{n,mi} \times [1 + (p/100)(w_m/w_{mi})]$, see Experimental part.

^d Based on SEC-2/LS measurement.

^e Based on SEC-1/RI measurement.

^f Not determined.

^g Unimodal SEC—peak without any shoulders.

^h Sample 16 after extraction with cyclohexane.

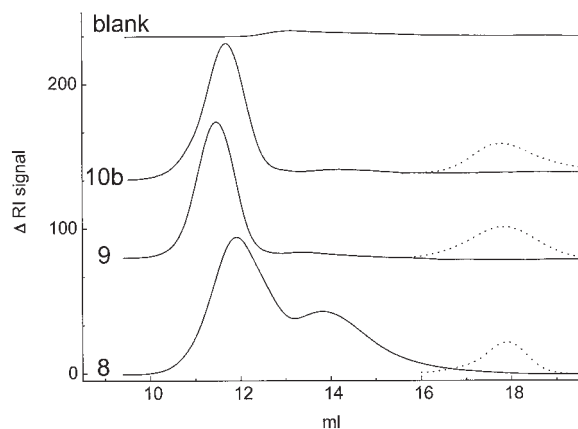


Figure 5 SEC traces (SEC-1/RI) of PSt-*g*-*t*BuA samples (Table II) synthesized at the ratio $[M]_0/[I]_0 = 840:1$. Dotted traces: initial reaction mixtures (MI). Sample **8**, 90°C, $[I]_0/[CuCl]_0/[CuCl_2]_0/[dNbpy]_0 = 1:2:0.1:4.2$, 15% v/v butyl acetate, $p = 51\%$; **9**, 70°C, $[I]_0/[CuCl]_0/[PMDETA]_0 = 1:1:1$, 15% v/v toluene, $p = 80\%$; **10b**, 40°C, $[I]_0/[C]_0/[PMDETA]_0 = 1:6:6$, 20% v/v *m*-xylene, $p = 47\%$; “blank” experiment, $[I]_0/[C]_0/[PMDETA]_0 = 0:6:6$, 20% v/v *m*-xylene, $p = 1.5\%$.

and solvents (toluene or *m*-xylene) were used with individual monomers.

The probability of coupling and crosslinking of growing polymer radicals by bimolecular termination increases with increasing chain length. Tailing or shoulders on the high-molecular-weight side of SEC traces of graft or star copolymers with side chains, formed by St and MMA monomer units, were observed many times,^{5,11,23,33,34,41} especially when monomer conversion value was higher than $p = 0.12$ – 0.25 .

Grafting with *t*BuA

The distribution of the copolymers with *t*BuA side chains (Table II, Fig. 5(9,10)) is unimodal, with symmetrical peaks, but the main product peak is accompanied by a side peak of lower molecular weight (20 – 40×10^3 , Fig. 5). (The origin of the low-molecular-weight fraction will be discussed separately in the last paragraph.) This side peak was rather large when butyl acetate was added as a solvent to the reaction mixture catalyzed by $[CuCl(dNbpy)_2]$, in the presence of deactivator $[CuCl_2(dNbpy)_2]$, at 90°C (sample **8**). In this experiment, the reaction was slow, M_n (SEC-1/RI) values were very low and PDI was high (2.36). The samples prepared in the presence of *m*-xylene, without Cu(II) halide added, and catalyzed by $[CuCl(PMDETA)]$ (**9**) or $[CuBr(PMDETA)]$ (**10b**) at 70°C ($p = 84\%$) or 40°C ($p = 47\%$) contained the lower-molecular-weight fraction only in a small amount ($\sim 5\%$).

The main peak of copolymers **9** and **10b** has unimodal shape according to SEC, with LS detector, in con-

trast to low-molecular-weight polymer side peak, in SEC traces recorded with RI detector. This is well documented by comparison of SEC-2/LS and SEC-1/RI eluograms for **10b** in Figure 6. (At the same time, $PDI(SEC-2/LS) = 1.18$ is distinctly lower than $PDI(SEC-1s/RI) = 1.40$; Table II). This difference stems from the fact that the signal of the LS detector is proportional to $M_n^{abs} \times C$ (where M_n^{abs} is absolute molecular weight and C is the concentration of the eluted population), while the data of the RI detector are proportional only to C . This explains a lower sensitivity of LS detector in the low-molecular-weight region.

Anyway, M_n values, calculated for samples **9** and **10b** from SEC-2/LS data, are in reasonable agreement with $M_{n,calc}$ values. In addition, there are no shoulders or side peaks in the high-molecular-weight region of SEC traces of samples **8**, **9**, **10a**, and **10b**. Therefore, ATRP grafting of *t*BuA from MI at low $[I]_0$ is also fairly resistant to chain coupling (Fig. 5).

Grafting with MMA

MMA grafting from MI at a low concentration of initiating functions (Table III, samples **11**–**15**) has been examined in the presence of 20% of *m*-xylene and using dNbpy as the ligand. In these experiments, the syntheses differed in the following reaction parameters (1) Cu(I) chloride/bromide, (2) concentration of Cu(I) and Cu(II) halides and their ratio, (3) reaction temperature. In spite of this diversity, some conclusions can be drawn (see later). Both SEC devices (Experimental part) were used for characterization.

PSt-*g*-PMMA **11** ($[M]_0/[I]_0/[CuCl]_0 = 840:1:1$, 90°C/3 h, $p = 45\%$) was obtained with too high M_n and PDI values, $M_n(SEC-2/LS) = 1648 \times 10^3$ versus $M_{n,calc} = 410 \times 10^3$, $PDI(SEC-2/LS) = 1.72$, possessing a high-molecular-weight shoulder in SEC [Fig. 7(a, b)].

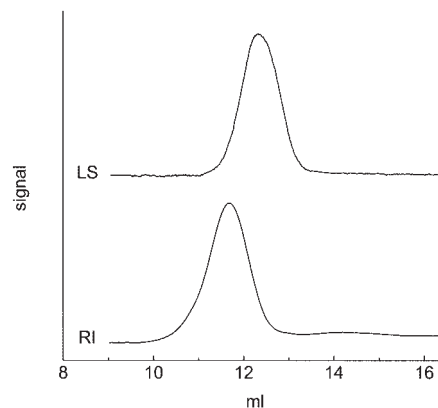


Figure 6 The influence of detection system on the shape of a SEC trace of PSt-*g*-*t*BuA **10b** (Table II). RI detector (SEC-1), LS detector (SEC-2).

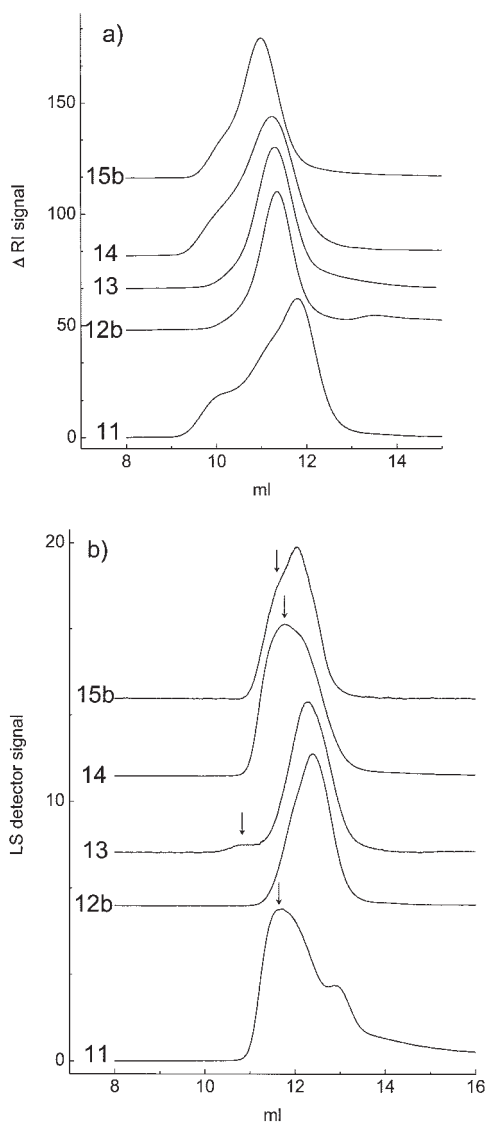


Figure 7 SEC traces of PSt-g-MMA copolymers prepared with low initial initiator concentration (Table III), $[M]_0/[I]_0 = 840:1$ (sample **11**) or $1680:1$ (samples **12b**, **13**, **14**, and **15b**). (a) Detection by refractometry (SEC-1/RI); (b) Detection by laser light scattering (SEC-2/LS). The arrows point to fractions (shoulders) formed by coupling.

Obviously, in the absence of deactivator, the tendency to termination is considerable. Even sample **5** (Table I, $[M]_0/[I]_0 = 140$) prepared at a lower reaction temperature, with lower p value and in a shorter reaction time, had not such broad distribution. In other MMA copolymerizations, a higher $[M]_0/[I]_0$ ratio, $1680:1$ was used and Cu(II) halide was added. Monomer conversions reached up to 41–56% (**12**, **13**, **14**, **15a**, and **15b**). When CuBr in the presence of added CuBr₂ was applied, with $[CuBr_2]_0$ increasing from **13** ($[I]_0/[CuBr]_0/[CuBr_2]_0 = 1:1:0.1$) through **14** ($1:3:0.3$) to **15** ($1:3:0.9$), shoulders were present in the respective SEC traces in high-molecular-weight region and were significant when LS detection was applied [Fig. 7(b)].

Distribution of molecular weight of sample **13**, as monitored with the SEC-1/RI (device/detector) seems narrower, but the LS detector trace shows clearly the occurrence of termination. M_n (SEC-2/LS) values of **14** and **15b** are markedly higher than theoretical values (Table III).

Only sample **12b**, prepared by halogen exchange⁴¹ at a shorter reaction time and with the highest activator and deactivator concentration ($[I]_0/[CuCl]_0/[CuCl_2]_0 = 1:6:0.9$), had a uniform and symmetric SEC peak (by both SEC-1/RI and SEC-2/LS detector), without a hint of coupling [Fig. 7(a,b)]. Its M_n (SEC-2/LS) value was not far from $M_{n,calc}$.

The copolymerization **12b** proceeded without any termination, but the product contains a small low-molecular-weight fraction [SEC-1/RI, Fig. 6(a)], but not on the SEC-2/LS trace [Fig. 7(b)].

Grafting with St

An attempt to prepare high-molecular-weight PSt-g-PSt from MI at a ratio of $[M]_0/[I]_0/[CuBr]_0/[CuBr_2]_0/[dNbp]_0/solvent = 1680:1:3:0.3:6.6:20\%$ *m*-xylene and 120°C (sample **16**, Table III) proceeded without gelation for 40 h to final conversion $p = 21\%$. The cyclohexane-extracted sample **16G** has M_n (SEC-2/LS) = 377×10^3 ($M_{n,calc} = 400 \times 10^3$) and a narrow-molecular-weight distribution (PDI(SEC-2/LS) = 1.11), without any trace of side fraction (Fig. 8). The unextracted sample **16** possesses a very broad distribution with a low-molecular-weight fraction. The occurrence of the low M_n homopolymer is due to thermal polymerization.^{6,33}

Graft length achieved in grafting from MI

From the results in Tables II and III, it follows that some of the synthesized high-molecular-weight copolymers possessed symmetrical SEC peaks (LS detection), and the polymer had low polydispersity, displaying no termination. This concerns the following

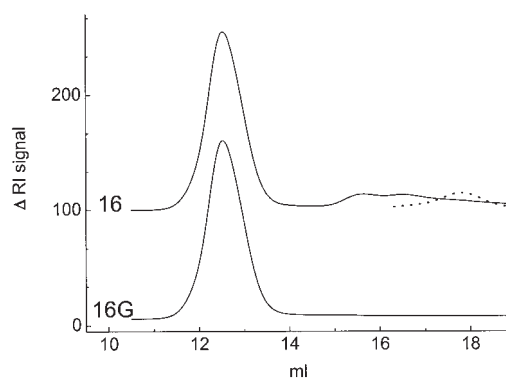


Figure 8 SEC traces (SEC-1/RI) of PSt-g-PSt (Table III). Sample **16** and **16G** (after cyclohexane extraction). The dotted line: initial reaction mixture.

samples ($DP_{n,sc}$ calculated from $M_n(\text{SEC-2/LS})$): PSt-*g*-PtBuA **9** ($DP_{n,sc} = 665$), **10b** ($DP_{n,sc} = 470$), PSt-*g*-PMMA **12b** ($DP_{n,sc} = 670$), and PSt-*g*-PSt **16/E** ($DP_{n,sc} = 325$). The length of these side chains ranks among the highest calculated values for polyacrylate, polymethacrylate, and PSt chains, synthesized by the "grafting from" ATRP methodology.

Matyjaszewski et al.²³ used a cyclotriphosphazene core derivatized with six 4-(bromomethyl)phenoxy groups, as initiator, for grafting with methyl acrylate in bulk, under $[\text{CuBr}(\text{dNbpy})_2]$ catalysis at 90°C. Using a ratio of $[\text{M}]_0/[\text{I}]_0/[\text{C}]_0 = 11,100 : 1 : 12$ at monomer conversion $p = 57\%$, they obtained a star copolymer of $M_n(\text{LS}) = 557 \times 10^3$, $M_w/M_n = 1.19$, $DP_{n,sc} = 1070$. Gnanou and coworkers²⁴ used eight-functional 4-*tert*-butylcalix[8]arene core as initiator for St grafting in bulk, catalyzed by $[\text{CuBr}(\text{bpy})_2]$ at 100°C. Using the ratio $[\text{M}]_0/[\text{I}]_0/[\text{C}]_0 = 20,000 : 1 : 1$, they isolated ($p = 22\%$) a star copolymer of $M_n(\text{LS}) = 580 \times 10^3$ (after cyclohexane extraction of low-molecular-weight PSt impurity), $DP_{n,sc} = 693$ (M_w/M_n not reported). In the same article, 4-*tert*-butylcalix[8]arene, carrying eight 2-bromoisobutyryloxy groups, served for MMA grafting in diphenyl ether at 90°C, with $[\text{CuBr}(\text{bpy})_2]$ catalyst at the reactant ratio $[\text{M}]_0/[\text{I}]_0/[\text{C}]_0 = 16,000 : 1 : 1$. The star copolymer of $M_n(\text{LS}) = 232 \times 10^3$, $M_w/M_n = 1.08$ and $DP_{n,sc} = 287$ was isolated ($P = 14\%$). However, when the experiment was repeated²⁴ with higher $[\text{I}]_0$ ($[\text{M}]_0/[\text{I}]_0 = 5600 : 1$ and $4000 : 1$), shoulders were present in SEC traces of the products in the high-molecular-weight region.

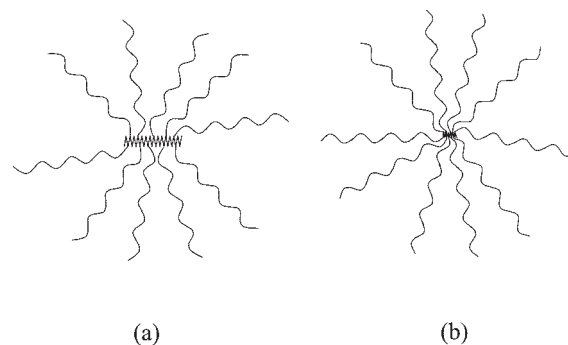
To our knowledge, the cited results^{23,24} present the synthesis of star copolymers carrying longest side chains. Interestingly, in the literature describing Cu-mediated "grafting from" ATRP, only copolymers, carrying poly(*t*BuA) side chains not longer than $DP_{n,sc} \sim 80$, have been described. In a vast majority of other communications, $DP_{n,sc}$ values of (meth)acrylate and St side chains were in the range of 20–100.¹⁶

Copolymers **9**, **10b**, **12b**, and **16** are star polymers with highest molecular weights prepared and their side chains are 6–11 times longer than the MI backbone (Scheme 2). The coupling of macromolecules was fully suppressed here.

Low-molecular-weight fraction occurrence

Low-molecular-weight tails, shoulders, or side peaks present in SEC traces of graft or star copolymers prepared by ATRP with St side chains were repeatedly ascribed to thermal polymerization,^{43–45} and the explanation might be used as well for our copolymer samples **7** and **16**.

Low-molecular-weight polymer fractions analogous to those present in SEC traces of our samples with (meth)acrylate side chains (arms) **9**, **10a**, **10b**, **12a**, and **12b** (Figs. 5, 7(a) and 8) have also been recently ob-



Scheme 2. Approximative depiction of graft copolymers prepared by grafting from MI. (a) Copolymers prepared with the ratio of $[\text{M}]_0/[\text{I}]_0$, equal to 140 : 1 (Table I; $DP_{\text{arm}}/DP_{\text{MI}} \sim 1 : 1$). (b) Copolymers prepared with the $[\text{M}]_0/[\text{I}]_0 = 840 : 1$ or $1680 : 1$. $DP_{\text{arm}}/DP_{\text{MI}} \sim 7\text{--}15 : 1$ ("star-like" structure).

served.^{15,16,31,42} Their origin is different. The cause consists in initiation efficiency of oxygen (air) residues in the presence of Cu(I) complex catalyst.⁴⁶ Recently, this was observed and studied⁴⁷ for the system MMA + CuCl or CuCl₂ complexes at 90°C. The oxygen initiation promotes formation of homopolymers, sometimes also of narrow polydispersity. When oxygen was strictly removed from such a mixture, a very low extent of MMA homopolymerization ($p = 1\%$) was observed in the presence of CuCl (90°C, 32 h). In the same communication,⁴⁷ a commercial block copolymer of isobutylene and 4-methylstyrene, EXXPRO 3035, containing 4-bromomethyl functions ($M_n = 2 \times 10^5$, 16 Br atoms per polymer chain), was grafted with MMA at 90°C for 24 h in chlorobenzene in the presence of $[\text{CuCl}(\text{dNbpy})_2]$, under common experimental conditions (Schlenk flask with rubber septum). Owing to very low concentration of bromide, the proportion of MMA homopolymer in the product was remarkable ($\sim 20\%$ of chains were initiated by air residues) and its low-molecular-weight side peak appeared in SEC eluograms. The occurrence of low-molecular-weight fraction in SEC-1/RI eluograms of our samples prepared with low $[\text{I}]_0$ (Tables II and III) can be ascribed to the same cause, since our experimental methodology did not differ from that described many times. The aforementioned low-molecular-weight side peak in eluograms shifts in the course of reaction to higher molecular weights (Fig. 9 (sample **10** and **12**)). This homopolymer fraction obviously takes part in ATRP process.

In the PSt-*g*-PSt synthesis (sample **16**, Fig. 8), the polymodality extended to the oligomer region indicates the occurrence of both oxygen initiation and thermal initiation.

In the copolymer synthesis utilizing much higher "common" initial concentration of initiating functions ($[\text{M}]_0/[\text{I}]_0 = 140 : 1$, Table I, samples 1–7 discussed

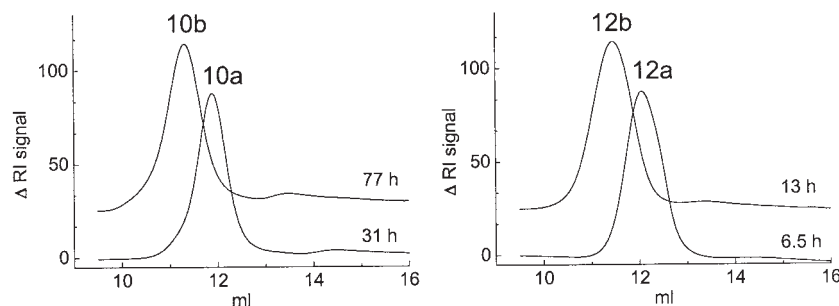


Figure 9 Shift of peaks in SEC eluograms (SEC-1/RI) in the course of the synthesis of PSt-*g*-*t*BuA (Table II, **10a** and **10b**) and PSt-*g*-MMA (Table III, **12a** and **12b**).

earlier), the ratio of $[O_2]_0/[I]_0$ is much lower. Therefore, low M_n side peaks are very small, owing to short reaction times and partly hidden in SEC traces of regular products (Fig. 1). We verified the occurrence of the concurrent initiation by a blank experiment, with the reaction mixture consisting of *t*BuA and Cu(PMDTA) (Table II, “blank” sample, Fig. 5).

PSt-*g*-PMMA’s **14** and **15** (Table III, Fig. 7), prepared at 30°C, display only a very slight hint of tailing of SEC traces at low molecular weights. Nanda et al.⁴⁷ also found only a negligible extent of initiation, with oxygen at room temperature. PSt-*g*-PMMA **12b** displays a small, but clearly separated low-molecular-weight peak in SEC-1/RI trace, not observed in eluograms of other high-molecular-weight PSt-*g*-PMMA samples. The probable explanation of this effect consists in the highest concentration of both Cu(I) and Cu(II) in this case. The increase in the catalytic effect of copper halides in oxygen initiation, with their increasing concentration, is known.^{46,47}

The undesirable low-molecular-weight homopolymer fractions can be occasionally removed, for example from PSt-*g*-PSt **17**, by extraction with cyclohexane. Isolation of the high-molecular-weight copolymers PSt-*g*-PMMA **11–15**, by precipitation with a mixture MeOH/H₂O 80 : 20, possibly narrowed their molecular weight distribution. (More perfect removal of PMMA fraction of $M_n \sim 20\text{--}30 \times 10^3$ from **12b** could be probably achieved by further exhaustive solvent extraction. For PMMA of that M_n , a solubility window was found to exist at the 6–30% H₂O (v/v) content in ethanol.⁴⁸) In contrast, we were not able to achieve purification by extraction/fractionation of PSt-*g*-*t*BuA copolymers **9** and **10b**.

To prevent the low-molecular-weight fraction formation, either subsequent purification of products should be applied or total absence of O₂ guaranteed. As an alternative, removal of oxygen residues from the ATRP reaction mixture could be achieved by simply adding phenolic antioxidants. Such compounds do not interfere with ATRP of MMA and even enhance the polymerization rate.⁴⁹ However, these suggestions need further study.

CONCLUSIONS

The Cu-mediated ATRP “grafting from” method utilizing a low-molecular-weight ($M_n = 5260$) monodisperse PSt macroinitiator (carrying an average eleven 2-bromopropionyloxy initiating groups along the backbone) was performed with *t*BuA, MMA, and St monomers either at a “current” initial concentration of initiator, $[I]_0 = 30\text{--}60$ mM (corresponding to the ratio $[M]_0/[I]_0 = 140 : 1$) or at its “low” concentration, $[I]_0 = 3\text{--}8$ mM ($[M]_0/[I]_0 = 840\text{--}1680 : 1$).

The products of *t*BuA “grafting from” in the bulk at “current” value of $[I]_0$, in the absence of deactivator, were copolymers of narrow polydispersity, and first-order kinetics of their formation was linear up to high conversions. The increase in M_n (SEC, RI detection) during polymerization has the expected shape. Analogous preliminary experiments performed for MMA and St at the same $[M]_0/[I]_0$ displayed a pronounced broadening of the copolymer distribution, at monomer conversions 97% (MMA) and 48% (St), and shoulders on SEC traces occurred.

In another series of experiments, $[M]_0/[I]_0 = 840$ or 1680 was maintained. In *t*BuA copolymerizations, both in the presence and absence of deactivator, coupling by termination was absent even at conversions 50–80%. The coupling was prevented in St copolymerization in the presence of $[CuBr_2(dNbpy)_2]$. In MMA grafting, only a high concentration of CuCl₂ prevented the occurrence of high-molecular-weight shoulders. The synthesis of copolymers, with low polydispersity and M_n values ranging from $\sim 300 \times 10^3$ to $\sim 1300 \times 10^3$, was shown, possessing M_n values close to $M_{n,calc}$ according to SEC eluograms, with LS detection. The maximum $DP_{n,sc}$ values were 320–670.

However, another adverse effect with serious implication for purity of these copolymers, consisting most probably in concurrent initiation with oxygen residues, became evident when the initiator concentration was low ($[M]_0/[I]_0 = 840$ or 1680). A low-molecular-weight fraction detected by SEC with refractometry sensor appeared and could be easily overlooked if LS

detection alone were applied [cf. **12b**, Table III, Fig. 7(a,b)]. (In “grafting from” with St, the thermal initiation also contributes to the low-molecular-weight fraction formation.) Comparing our results with the observations of others,^{46,47} it seems that the usually used procedure of oxygen removal from ATRP reaction mixtures is not satisfactory for the “grafting from” synthesis of polyfunctional high-molecular-weight graft copolymers or stars. A simple method of preventing the formation of undesirable low-molecular-weight polymer fraction was proposed.

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