

The Potential of Cu(I)Cl/2,2'-Bipyridine Catalysis in a Triblock Copolymer Preparation by Atom Transfer Radical Polymerization

BOHUMIL MASAR, PETR VLČEK, JAROSLAV KRÍŽ

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

Received 11 April 2000; accepted 21 August 2000

ABSTRACT: The ability of atom transfer radical polymerization (ATRP) in the sequential synthesis of triblock copolymers was examined using Cu(I)Cl/2,2'-bipyridine catalysis at 110°C in toluene, starting from PMMA macroinitiators terminated with the C-Br group. The PMMAs were prepared by living anionic or group transfer polymerization (GTP), followed by bromination of the respective active site with Br₂ or N-bromosuccinimide (NBS). The yield of the terminal bromination in the products of both living polymerizations was 60–64% at best, compared with the yield of the bromination of 1-methoxy-(1-trimethylsilyloxy)prop-1-ene (a model of the GTP active site) with NBS, as found by ¹H-NMR. The PMMA macroinitiators prepared were utilized to start the sequential ATRP, finally affording PMMA-*b*-PBuA-*b*-PSt (*M_n* 69,100), PMMA-*b*-PSt-*b*-PBuA (*M_n* 21,300) and PMMA-*b*-PSt-*b*-PMMA (*M_n* 35,200), which have not yet been synthesized by ATRP. After the second block has been formed, the Br-terminated part of PMMA macroinitiator was removed by extraction or repeated precipitation. In the third (last) sequence polymerization, induction periods were observed. The first two triblock copolymers were free of precursors and have *M_w*/*M_n* values 1.5–1.6 (SEC). In the course of the last step of PMMA-*b*-PSt-*b*-PMMA synthesis, the content of the PMMA-*b*-PSt precursor slowly decreased with increasing MMA conversion. Still, at ≈90% MMA conversion, about 10–15% of the precursor remained in the product. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3514–3522, 2001

Key words: atom transfer radical polymerization; triblock copolymers; sequential synthesis; poly(meth)acrylate; polystyrene

INTRODUCTION

Atom transfer radical polymerization (ATRP) is a very recent method of controlled polymerization of vinyl monomers.^{1,2} Its name is derived from the fact that in this process a halogen atom X (Cl or

Br) of an initiator RX (R is, e.g., a secondary or tertiary alkyl with proper substituents) is transferred to a transition metal complex to generate radicals capable of propagating by addition to a vinyl monomer molecule. The scission of the C—X bond of the initiator or the same bond of the propagating polymer chain is homolytic and an equilibrium reaction.



The equilibrium between C—X and C· radical of the growing chain, mediated by metal complexes

Correspondence to: B. Masar; e-mail: masar@imc.cas.cz.
Contract grant sponsor: European Commission; contract grant number: EU COST P1.10.

Journal of Applied Polymer Science, Vol. 81, 3514–3522 (2001)
© 2001 John Wiley & Sons, Inc.

Mt^{+n}/L and $Mt^{+(n+1)}/L$ (with the metal in oxidation states n and $n + 1$; L denotes a ligand), (Scheme I) is strongly shifted to the left,³ i.e., to the dormant form P_n-X . In this way, radicals are protected from termination, the growth of the chains being almost simultaneous ("controlled"). M_w/M_n values in ATRP are typically in the range of 1.1–1.5 and during the polymerization, the P_n-X functionality is conserved.

A real breakthrough in the ATRP field came out after that Matyjaszewski and coworkers^{4,5} disclosed the controlled polymerization of acrylates with a complex Cu(I)Cl/2,2'-bipyridine (bpy) and Sawamoto et al.⁶ accomplished the same with complex catalysts of rhodium. Any polymer, prepared by ATRP under suitable conditions, is also a macroinitiator. ATRP synthesis of AB diblock and ABA triblock copolymers (in the latter case, B being a starting difunctional block) under Cu(I) salt catalysis with various (meth)acrylates and other vinyl monomers has been described.^{7–9} In the Cu(I) halogenide catalyzed synthesis of block copolymers, ATRP was combined with other polymerization techniques^{10,11} and also various polymers with C—X end groups were used as macroinitiators in ATRP.^{12–15}

The aim of the present work was to explore the synthetic potential of the heterogeneous CuCl/bpy catalyst in the sequential ATRP synthesis of three as yet undescribed triblock copolymers of (meth)acrylates and styrene, namely, PMMA-*b*-PBuA-*b*-PSt, PMMA-*b*-PSt-*b*-PBuA, and PMMA-*b*-PSt-*b*-PMMA. The control of Cu(I)Cl-catalyzed polymerization of MMA is less perfect, and its propagation rate is lower than in analogous polymerizations of acrylates or styrene.^{16,17} Having some experience with other methods of controlled polymerization, we attempted the preparation of the first polymer (macroinitiator) by bromination of the active site of PMMA, prepared by anionic or group transfer polymerization (GTP). From PMMA-Br samples thus prepared, the sequential ATRP synthesis was started.

EXPERIMENTAL

Materials

Methyl methacrylate (99%, Aldrich) was dried with anhydrous $MgSO_4$ and column-distilled with CaH_2 under vacuum (no impurities were present, GLC). BuA (Chemical Works, Sokolov, Czech Re-

public) was purified by washing with aqueous NaOH, drying over anhydrous $CaCl_2$ and CaH_2 and vacuum distilled. Styrene (Fluka, $\geq 99\%$) was passed through a column filled with alumina (Fluka, neutral type 507C, 100–125 mesh). All monomers were stored at $-18^\circ C$ under Ar and freshly distilled with CaH_2 before use. Toluene (puriss., Fluka) was dried in a circulation apparatus over sodium benzophenone ketyl. THF for the use in anionic and GTP polymerization was boiled with sodium and anthracene and distilled. CH_2Cl_2 was shaken with $NaHCO_3$ solution, water, successively dried with anhydrous $MgSO_4$ and CaH_2 , and distilled with CaH_2 . Other solvents were reagent grade.

Methyl 2-lithioisobutyrate (LiiBuMe) was prepared according to the procedure used by Lochmann and Lím.¹⁸ LiCl was dried at $160^\circ C$ for 5 h. 1-Methoxy-1-(trimethylsilyloxy)prop-1-ene (MTS, Aldrich) was vacuum distilled. Tetrabutylammonium fluoride trihydrate (Fluka) was dehydrated by heating at $40^\circ C$ and 0.133 kPa for 3 h to monohydrate (TBAF $\cdot H_2O$).¹⁹ Tris(dimethylamino)sulfonium (trimethylsilyl)difluoride (TASF₂SiMe₃, Aldrich), Cu(I)Cl ($\geq 99\%$, purified, Aldrich), 2,2'-bipyridine ($\geq 99\%$, Aldrich), methyl 2-bromoisobutyrate (BriBuMe, Fluka puriss.), *N*-Bromosuccinimide (NBS, Fluka, 97%), and bromine (Lachema, puriss.) were used as received. Solid compounds were vacuum dried before polymerizations or model reactions.

The Synthesis of Living PMMA and Its C-Br Terminal Functionalization

Anionic polymerization of MMA (0.468 mol/L in THF) at $-70^\circ C$ was performed with LiiBuMe (0.014 mol/L) initiation in the presence of LiCl (0.07 mol/L) for 5 min. GTP of MMA (2 mol/L in THF) was performed with MTS (0.1 mol/L) as an initiator and TBAF monohydrate (0.047 mmol/L) as a catalyst at $-30^\circ C$ for 15–20 min. Conversions of MMA in both anionic and GTP experiments were quantitative (GLC).

Terminal C-Br groups were introduced by the reaction of living PMMA with Br_2 or NBS for 90 min (for details, see Table I). Into the anionic polymerization solution, bromine was introduced directly (sample No. 1). The product of GTP was used either in a polymerization solution (No. 2) or after vacuum evaporation to dryness at subzero temperature and dissolution in CH_2Cl_2 (Nos. 3 and 4). In the former case, a cold PMMA solution was dropped into a solution of brominating agent

Table I Bromination of Living PMMA and Characterization of Br-Terminated Macroinitiators^a

No.	Reagent ^b	Solvent	Temperature (°C)	DF ^c	M_n	M_w/M_n
1	Br ₂ (5 : 1)	Toluene/THF	-70	64	3610	1.09
2	Br ₂ (2 : 1)	THF	-78	60	1930	1.56
3	Br ₂ (2 : 1)	CH ₂ Cl ₂	-78	44	2270	2.12
4	NBS ^d (2 : 1)	CH ₂ Cl ₂	20	60	2220	1.48

^a PMMAs were prepared by anionic polymerization (No. 1) or GTP (Nos. 2–4), initiated by LiBuMe or MTS, respectively.

^b In parentheses, molar ratio of the reagent to initiator.

^c Degree of Br functionalization, relative to terminal groups.

^d *N*-bromosuccinimide.

in THF, precooled to the reaction temperature; in the latter case, the brominating agent solution in CH₂Cl₂ was added into the “living” PMMA solution. The mixture after bromination (if necessary, transferred into CH₂Cl₂ solution) was shaken with 10% Na₂S₂O₃ solution and water, dried with MgSO₄, evaporated, redissolved in CH₂Cl₂, precipitated in heptane, and dried at 45°C *in vacuo*.

Diblock Copolymers (Macroinitiators)

Diblock copolymers were prepared from 1 g of Br-terminated PMMA samples (Table I), 50 mg (0.50 mmol) of CuCl₂, 157 mg (1.00 mmol) of bpy, 5 mL of a monomer (43.5 mmol of St or 35.0 mmol of BuA), and 5 mL of toluene in argon atmosphere. The reaction flask was equipped with a three-way stopcock and a magnetic stirrer and the reaction mixture was degassed with three freeze-pump-thaw cycles. After finishing the reaction under argon at 110°C, the mixture was diluted with 20 mL of THF, filtered through a column filled with 22 mL of alumina and analyzed by GLC. The concentrated filtrate was precipitated into cold MeOH or into a mixture MeOH/H₂O 9 : 1 (v/v); PMMA-*b*-PBuA was precipitated once more. From PMMA-*b*-PSt, the

portion of PMMA not containing Br was extracted with acetonitrile by stirring for 4 h (23°C). Finally, the polymers were vacuum dried at 45°C. For the yield, molecular parameters (SEC) and composition (¹H-NMR) of products, see Table II.

Triblock Copolymers

Triblock copolymers were prepared using 1 g of the respective diblock copolymer (Table II) and 5 mL of a monomer (the same amounts of St or BuA as in the diblock copolymer synthesis, or 47.2 mmol of MMA); the amount of the other components and the reaction temperature were the same as in diblock copolymer synthesis. One-milliliter aliquots were removed from the reaction mixture at suitable time intervals with a syringe and centrifuged; clear solutions were analyzed by GLC and SEC (Table III, Figs 2–4). PMMA-*b*-PBuA-*b*-PSt (No. 1) was isolated from the reaction mixture. The solid after evaporation of the reaction mixture was dissolved in THF, filtered through alumina, precipitated into cold methanol, dried (the overall yield 77.9%), and characterized by NMR (Fig. 6).

Table II Synthesis and Characterization of Diblock Copolymer Macroinitiators

No.	Copolymer ^a	PMMA No. ^b	Time (h)	X ^c (%)	Yield (%)	M_n	M_w/M_n	Mol Fraction ^d	
								MMA	BuA or St
1	PMMA- <i>b</i> -PBuA	4	4.0	45.0	33.3	13,500	1.46	0.27	0.73
2	PMMA- <i>b</i> -PSt	4	23.5	28.3	27.6	11,600	1.23	0.26	0.74
3	PMMA- <i>b</i> -PSt	1	24.0	46.5	42.3	14,200	1.17	0.36	0.64

^a Prepared from 1 g of PMMA macroinitiator and 5 mL of monomer.

^b See Table I.

^c Conversion of BuA or St determined by GLC.

^d Mol fractions of monomers in copolymer determined by ¹H-NMR.

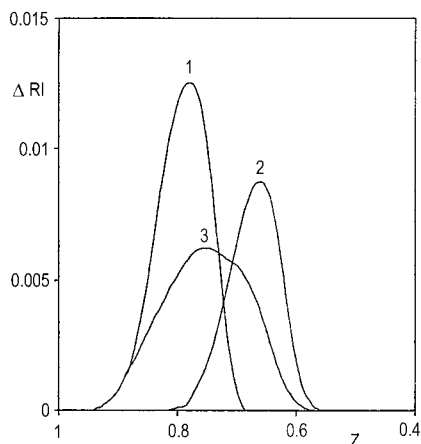


Figure 1 SEC chromatograms of PMMA macroinitiator (**1**, Table I, No. 4), PMMA-*b*-PBuA (**2**, Table II, No. 3), and the residual polymers **3** in the mother liquor after isolation of **2**. *Z* is the relative elution volume ($Z = V_{el}/V_{\text{toluene}}$).

Bromination of MTS

Bromination of the ketone silylacetal group model, MTS, was performed as follows. To a suspension of 154 mg (0.86 mmol) of NBS in 3.8 mL CDCl_3 (dried with Calsit A4), 0.175 mL (0.86 mmol) of MTS was added under dry argon at room temperature. The homogeneous solution was sealed in two cuvettes and reacted at 23°C (240 h) and 50°C (8 h); $^1\text{H-NMR}$ spectra were measured at 23°C. In another experiment, the same amounts of the above compounds were mixed in the presence of $\text{TASF}_2\text{SiMe}_3$ (0.086 mmol). In this case, liquid components were added to solid NBS and $\text{TASF}_2\text{SiMe}_3$ at -78°C and the partly homogeneous mixture was maintained for 96 h at this temperature. After raising the temperature to 23°C, the mixture first became homogeneous; a small amount of a white precipitate separated overnight. The clear solution was also characterized by NMR spectroscopy. In the $^1\text{H-NMR}$ spectra, well-separated signals characteristic of OCH_3 and $(\text{CH}_3)_2\text{C}$ groups of MTS and BrIBuMe were unambiguously assigned by comparison with standards and utilized for quantitative evaluation of the MTS bromination degree (see Results and Discussion). More detailed analysis of the reaction mixture spectra has not been done.

Characterization

The yield of copolymers in Table II was determined gravimetrically. The conversion of monomers was determined by GLC (Hewlett-Packard

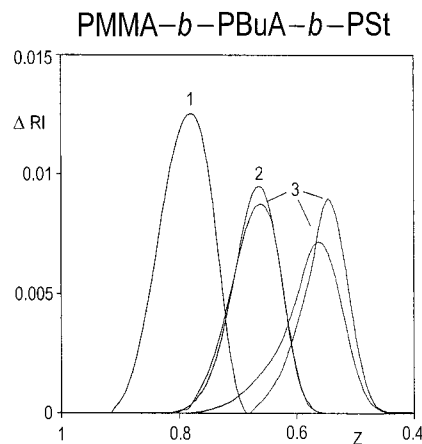


Figure 2 SEC chromatograms of PMMA macroinitiator (**1**, Table I, No. 4), PMMA-*b*-PBuA macroinitiator (**2**, Table II, No. 3), and PMMA-*b*-PBuA-*b*-PSt (**3**, at 2.0, 37.8, and 58.5% St conversions).

8310). M_n and M_w/M_n values were measured by SEC using 10^5 \AA and 10^3 \AA columns in series (PL gel $5 \mu\text{m}$, Polymer Standard Service, Germany) with RI and UV 260 nm detection and calibration with PMMA standards. In eluograms (Figs 1–4), relative elution volumes are given, defined as $Z = V_{el}/V_{\text{tol}}$ (V_{tol} is the elution volume of toluene, added as a standard). $^1\text{H-NMR}$ spectra were measured on a Bruker 300 MHz apparatus in CDCl_3 at 23 or 60°C (polymers) with HMDS standard. The degree of terminal Br-functionalization of PMMA macroinitiators (DF values in Table I) was calculated from the overall terminal group content based on the M_n value and the bromine con-

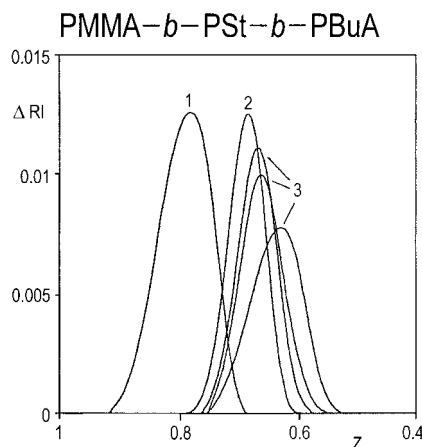


Figure 3 SEC chromatograms of PMMA macroinitiator (**1**, Table I, No. 4), PMMA-*b*-PSt macroinitiator (**2**, Table II, No. 2), and PMMA-*b*-PSt-*b*-PBuA (**3**, at 1.5, 2.5, and 24.0% BuA conversions).

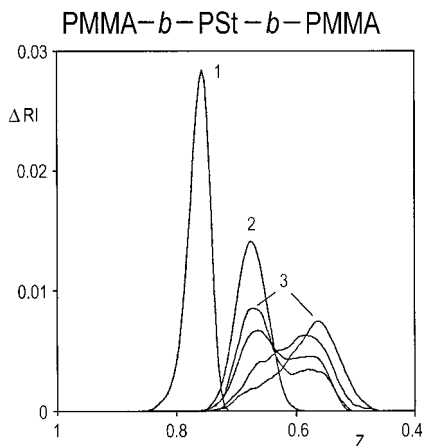


Figure 4 SEC chromatograms of PMMA macroinitiator (**1**, Table I, No. 1), PMMA-*b*-PSt macroinitiator (**2**, Table II, No. 1), and PMMA-*b*-PSt-*b*-PMMA (**3**, at 14.4, 25.3, 65.5, and 89.2% MMA conversions).

tent. The reliability of the available Schöniger bromine analysis^{20,21} was tested by determination in four NBS solutions (containing ~ 0.01 mmol Br, which corresponds to the Br amount in PMMA. The mean error of individual determination was $\pm 15\%$ and the found mean Br content was by 9.5% lower than the theoretical one.

RESULTS AND DISCUSSION

Throughout the following text, terminal halogen atoms (X) in (co)polymers are indicated, for example, PMMA-Br, whenever stress is put on the macroinitiator character. The sequence of blocks in codes corresponds to the actual synthetic sequence.

PMMA Macroinitiator

Characteristics of PMMA, prepared from prepolymers with living nucleophilic end groups (see Experimental) by bromination, are in Table I and Figures 1–3 (SEC traces). The yield of bromination with Br_2 or NBS of the respective carbanion or ketene silylactal end group is 60–64% at best. Because the accuracy of the bromine determination was only ~ 15 rel % (see Experimental), the found values (Table I) are rather a rough estimate. Nonetheless, the incomplete Br termination of PMMA manifests itself in the next synthetic step, i.e., in the synthesis of diblock copolymers. In the mother liquor after precipitation of PMMA-*b*-PBuA (see below, No. 1 in Table II), the

nonbrominated PMMA is present (curve 3 in Fig. 1). Similarly, the presence of PMMA was observed also in acetonitrile extracts of PMMA-*b*-PSt samples No. 2 and 3 (Table II); after purification, the isolated diblock copolymers were free of PMMA (see the following chapter).

An explanation for the incomplete Br-functionalization might be the known tendency of both anionic and ketene silylactal active sites to autotermination. However, we do not prefer this interpretation, at least for the GTP products. The living polymerization procedures used here were recently shown to yield PMMA with theoretical M_n and narrow polydispersities^{22,23} or diblock copolymers free of the first polymer.²⁴ Sogah and Webster postulated²⁵ (but did not prove) an intermediate formation in PMMA of 2-bromoisobutyrate terminal unit from the ketene silylactal end functionality in “self-coupling” of the PMMA chains with $\text{Br}_2\text{-TiCl}_4$ mixture. However, our experiments with a silylactal active site model, MTS, have shown that its quantitative terminal bromination can hardly be achieved. We examined the behavior of MTS in the reaction with a cationic brominating agent, NBS, at 23, 50, and -78°C with and without a desilylation catalyst, $\text{TASF}_2\text{SiMe}_3$, by $^1\text{H-NMR}$ spectroscopy (measured at 23°C , see Experimental). From the ratio of integral intensities of the OCH_3 signals of MTS ($\delta = 3.62$ ppm), and of its bromination product, BriBuMe ($\delta = 3.70$ ppm), and from the same ratios of the $(\text{CH}_3)_2\text{C}$ signal intensities of both compounds ($\delta = 1.36$ and 1.84, respectively), and using the relation $100 \times [\text{BriBuMe}/(\text{BriBuMe} + \text{MTS})]$, the following bromination yields were found: 67% (25°C), 67% (50°C) and 65% (-78°C) from the OCH_3 signals and 68% (25°C), 68% (50°C) and 64% (-78°C) from the $\text{C}(\text{CH}_3)_2$ signals. All the figures are close to each other and to the best result, found by the Schöniger method with brominated PMMA (Table I, Nos. 2–4). Thus, the yield of BriBuMe is far from being quantitative, and the bromination of the silylactal end group seems to be an equilibrium reaction. Indeed, if the equilibration in this reaction mixture is fast enough, the found yield of BriBuMe has to be the same, corresponding to the temperature of NMR spectroscopic measurement (23°C). The difficulties with bromination make the preparation of PMMA-Br by anionic or GTP polymerization less attractive. The direct ATRP synthesis¹⁶ would be easier.

Diblock Copolymers (Macroinitiators)

The reaction times, conversions of monomers, molecular characteristics, and composition of PMMA-*b*-PBuA-X and PMMA-*b*-PSt-X (X = Cl, Br, see below) prepared from PMMA described above are given in Table II. The initial molar ratio of components in the diblock copolymer synthesis, monomer/C-Br/CuCl/bpy (M/I/C/L), was 70 : 0.54 : 1 : 2 (sample No. 1), 87 : 0.54 : 1 : 2 (No. 2) and 87 : 0.35 : 1 : 2 (No. 3). The respective SEC traces are depicted in Figs 2–4. In all cases, under Cu(I)Cl/bpy catalysis at 110°C in toluene, relatively low polydispersity copolymers have been obtained, the M_n and M_w/M_n values being 11,600–14,200 and 1.17–1.46, respectively. As was mentioned above, the nonincorporated part of PMMA was removed from the copolymers by repeated precipitation (No. 1) or by the extraction with acetonitrile (Nos 2 and 3), which is a solvent for PMMA and possibly also for a PMMA-rich fraction and a nonsolvent for PSt. According to Matyjaszewski and coworkers,²⁶ when CuCl is used with a C-Br terminated initiator, halogen exchange occurs during 30–90 min at 90°C, most of the C-halogen groups being transformed into the C–Cl form. In view of that, the C–Cl terminal group in our diblock copolymers predominates over the C–Br group.

The synthesis of PMMA-*b*-PBuA (M_n 19,000 and M_w/M_n 1.15), has been described²⁷ with the initiation system PMMA-Cl/Cu(I)Cl/4,4'-di(nonane-5-yl)-2,2'-bipyridyl (dNbpy) in diphenyl ether at 90°C. An article describing the synthesis of PMMA-*b*-PSt has appeared²⁸ when the present manuscript was prepared for publication. With PMMA-Cl/Cu(I)Br/bpy at 110°C, the copolymer with M_n 43,000 and M_w/M_n 1.40 has been prepared from PMMA with M_n 6300 for 23 h, the macroinitiator being present up to the 40% conversion of styrene.

Triblock Copolymers

In the third sequential polymerization, initiated with diblock copolymer macroinitiators described in the preceding section (Table II, Nos. 1 and 2) and leading to PMMA-*b*-PSt-*b*-PBuA and PMMA-*b*-PSt-*b*-PBuA (Table III, Nos. 1 and 2), the initial molar ratio of reactants, M/I/C/L, was 87 : 0.148 : 1 : 2 (No. 1) and 70.1 : 0.172 : 1 : 2 (No. 2). The well-separated SEC eluograms show an overall shift to a higher molecular weight region (Figs. 2 and 3). The triblock copolymerizates do not contain residues of diblock macroinitiators, which in

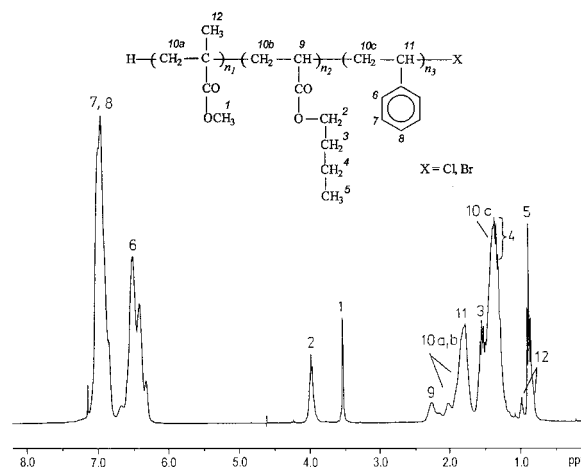


Figure 5 $^1\text{H-NMR}$ spectrum of PMMA-*b*-PBuA-*b*-PSt.

turn, confirms the preservation of all C-X terminal groups and absence of termination. Also, the SEC eluograms of copolymers Nos. 1 and 2 obtained using UV detection at 260 nm (not extra depicted in Figs. 2 and 3) and those using refractometric detection were identical both in shape and positions, confirming a simultaneous growth of all copolymer chains. Thus, sequential ATRP with the simple heterogeneous complex catalyst Cu(I)Cl/bpy turned out to be successful in the sequential synthesis of these two triblock copolymers. The block character of copolymer No. 1 after isolation was confirmed by $^1\text{H-NMR}$ spectroscopy (Fig. 5), the spectrum being a superposition of the spectra of individual blocks.

In contrast to the triblock copolymers just mentioned, the SEC eluogram during the third step of the sequence synthesis of PMMA-*b*-PSt-*b*-PMMA (Table III, No. 3, M/I/C/L = 94.4 : 0.149 : 1 : 2) has a bimodal shape (Fig. 4). With increasing MMA conversion, the triblock copolymer amount increases, whereas the amount of the starting PMMA-*b*-PSt continuously decreases. Still, at ~90% conversion of MMA, some precursor is present. Here the situation is typical of slow initiation.

From SEC eluograms (refractometric data), M_n and M_w/M_n values were obtained using the Mark-Houwink-Sakurada equation for PMMA in THF. M_n data have only an approximative value; nevertheless, when plotted against the monomer conversion in the third step, they show a linear increase (Fig. 6). The M_w/M_n values do not change much, ranging from 1.5 to 1.6 with the exception of PMMA-*b*-PSt-*b*-PMMA, containing a diblock macroinitiator (M_w/M_n 1.7–1.8).

Table III Synthesis and Characterization of Triblock Copolymers

Copolymer ^a	Diblock Macroinitiator ^b No.	Time (h)	X ^{c,d}	M_n^d	M_w/M_n^d
PMMA- <i>b</i> -PBuA- <i>b</i> -PSt	1	27	58.5	69,100	1.59
PMMA- <i>b</i> -PSt- <i>b</i> -PBuA	2	25	24.0	21,300	1.57
PMMA- <i>b</i> -PSt- <i>b</i> -PMMA	3	24	65.5	35,200	1.74

^a Prepared from 1 g of diblock macroinitiator and 5 mL of monomer.

^b See Table II.

^c Conversions of St, BuA, or MMA (GLC) in the last step.

^d After separation of solid particles of the catalyst.

Conversion plots for the third polymerization step (Fig. 7) show induction periods, which are probably caused by slow formation of the heterogeneous catalyst complex in the presence of a polymeric initiator. Clearly, the occurrence of induction periods is a drawback. For a definite block length to be obtained, the corresponding reaction time must be estimated. This is difficult for the induction period region; hence, the control of the multisequential process is somewhat limited.

The following triblock copolymers consisting of primary alkyl (meth)acrylate and styrene blocks, prepared with Cu(I) halogenide catalysis have been described so far, using the B → ABA route: PMMA-*b*-PMA-*b*-PMMA²⁶ (MA = methyl acrylate), PMMA-*b*-PBuA-*b*-PMMA,²⁹ PSt-*b*-PBuA-*b*-PSt,³⁰ and PtBuA-*b*-PSt-*b*-PtBuA²⁹ (tBuA = *tert*-butyl acrylate). Using the A → AB → ABC route, PtBuA-*b*-PSt-*b*-PMA²⁹ was synthesized. In the course of preparation of this manuscript, two articles appeared concerning the diblock copolymer syntheses corresponding to the third (last) steps of our triblock copolymer preparations. Cassebrass et al.³⁰ described the PBuA-*b*-PSt and PSt-

b-PBuA synthesis from Cl-capped first polymers and Cu(I)Cl/bpy in the presence of 10% of dimethylformamide at 130°C. The propagation of BuA on PSt-Cl was significantly slower than that of St on PBuA-Cl, similarly to our experiments No. 1 and 2 (Table III, Fig. 7). The authors observed 1–2-h induction period in the second step of the PBuA-*b*-PSt synthesis. PSt-*b*-PMMA synthesis corresponding to the last step of the triblock copolymer No. 3 formation has been described²⁸ just recently. With PSt-Br (M_n 6400) and Cu(I)Cl/bpy in acetonitrile at 40°C, this copolymer with M_n of 13,500 and M_w/M_n 1.33 was obtained. The benefit of using a more polar solvent or additive seems to consist in acceleration of both the rate of crossinitiation and MMA polymerization. The authors utilized an initiator/catalyst system analogous to that used by Matyjaszewski group²⁶ in PMA-*b*-PMMA synthesis, where the PMA-Br (M_n 5900, M_w/M_n 1.32)/Cu(I)Cl/dNbpy system in diphenyl ether ("mixed halogenide" procedure) enabled a successful initiation of MMA polymerization at 90°C, giving the diblock copolymer with M_n 63,900 and M_w/M_n 1.15. The same experi-

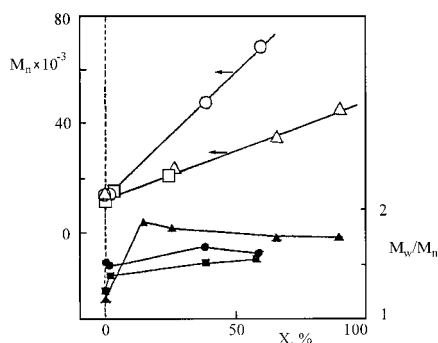


Figure 6 Molecular weight (open symbols) and M_w/M_n (full symbols) of the copolymers in dependence on the conversion (X, %) of the third sequence polymerization. PMMA-*b*-PBuA-*b*-PSt (○), PMMA-*b*-PSt-*b*-PBuA (□), and PMMA-*b*-PSt-*b*-PMMA (△).

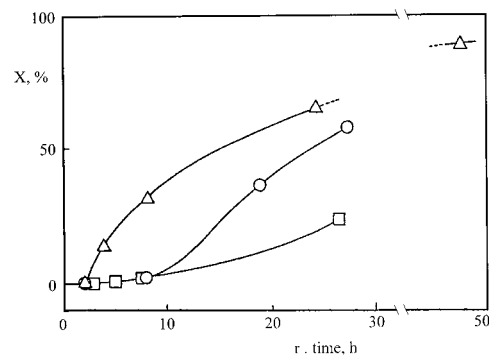
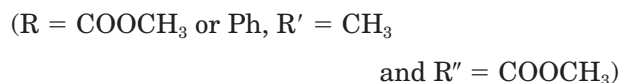


Figure 7 Conversion (X, %) vs. time (h) plots in the third sequence polymerization. PMMA-*b*-PBuA-*b*-PSt (○), PMMA-*b*-PSt-*b*-PBuA (□), and PMMA-*b*-PSt-*b*-PMMA (△).

ment of MMA polymerization, but with the PMA-Cl/Cu(I)Cl initiation ("the same halogenide" procedure) afforded²⁶ only a diblock copolymer (M_n 41,400) with a very high M_w/M_n value (3.63), containing the nonincorporated PMA macroinitiator. Our result on PMMA-*b*-PSt-X (X is predominantly Cl) crossinitiation to MMA (Table III, No. 3) is in the same line. Both results show that under Cu(I)Cl/bpy catalysis, linking of a propagating block with secondary chloride end group (A) to an incoming monomer molecule of the (B) type affording tertiary chlorine-terminated propagating chain (C) (Scheme II)



is slower than further propagation of (B) started by (C). Therefore, (A) persists in the reaction mixture, and its amount decreases only slowly. To obtain PMMA-*b*-PSt-*b*-PMMA (No. 3, Table III) in the third step in pure form, the synthetic way should be somehow adapted in the "mixed halogenide" manner mentioned above. The eluograms in Figures 2–4 document that crossinitiations of the type *sec*-chloride → *sec*-chloride and *tert*-chloride → *sec*-chloride are rapid enough to prevent such a problem.

CONCLUSIONS

The synthetic potential of sequential ATRP using the Cu(I)Cl/bpy complex catalyst in the preparation of triblock copolymers was studied. The first, the PMMA macroinitiator, was prepared either by living anionic polymerization or by GTP with subsequent transformation of the respective active site to the C—Br terminal group by bromination. Terminal bromination of living PMMA, utilized in this work for the preparation of starting macroinitiators, was not quantitative. The non-brominated part of PMMA was separated from diblock copolymers prepared in the next step by extraction or precipitation. [Bromination of the GTP active site model compound, MTS, with *N*-bromosuccinimide also gave only 64–68% yield of 2-bromoisobutyrate (BriBuMe) according to ¹H-NMR spectroscopy having, at the same time, an equilibrium character.] Triblock copolymers, hitherto not synthesized by ATRP, PMMA-*b*-PBuA-*b*-PSt, PMMA-*b*-PSt-*b*-PBuA, and PMMA-*b*-PSt-*b*-PMMA, were obtained in sequential way

and characterized by SEC and ¹H-NMR. In the third sequence of these copolymer syntheses, induction periods were always observed. The first two copolymers prepared were pure, free of precursors. The third product, PMMA-*b*-PSt-*b*-PMMA, contained about 15% of its precursor, PMMA-*b*-PSt-X macroinitiator (X is predominantly Cl), even at 90% MMA conversion. The crossinitiation in the sequence PSt—Cl → MMA is slower than further propagation, similar to that found by Matyjaszewski et al.²⁶ under analogous conditions for the PMA—Cl → PMMA sequence. Combining our present results on the triblock copolymer synthesis with some results of others^{26,28,30} on the diblock copolymer synthesis, and taking into account only primary alkyl (meth)acrylate and styrene monomers and macroinitiators, it can be concluded that the simple Cu(I)Cl/bpy catalysis of ATRP with Cl-terminated macroinitiators in toluene (without further modification of the procedure) is powerful in the polymethacrylate → acrylate, polymethacrylate → styrene, polyacrylate → styrene, and polystyrene → acrylate crossinitiations. In polyacrylate → methacrylate or polystyrene → methacrylate sequences, however, the initiation is slow, and the copolymerization products contain some amounts of the respective macroinitiator as impurity.

The authors express their gratitude to Mrs. E. Jakešová, Mrs. D. Kotíková, and Mrs. M. Plichtová for skillful technical assistance, and GLC and bromine analyses, respectively. Financial support from the European Commission (grant EU COST P 1.10) is also greatly acknowledged.

REFERENCES

1. Patten, T. E.; Matyjaszewski, K. *Adv Mater* 1998, 10, 901.
2. Sawamoto, M.; Kamigaito, M. *Chemtech* 1999, 29, 30.
3. Matyjaszewski, K. In *Controlled Radical Polymerization*, ACS Symp Ser; 685; American Chemical Society: Washington, DC; 1998, p. 258.
4. Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
5. Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
6. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
7. Gaynor, S. G.; Matyjaszewski, K. In *Controlled Radical Polymerization*; ACS Symp Ser 685; American Chemical Society: Washington, DC, 1998, p. 396.

8. Zhang, X.; Matyjaszewski, K. *Polym Prepr (Am Chem Soc, Div Polym Chem)* 1999, 39(2), 560.
9. Zhang, X.; Matyjaszewski, K. *Macromolecules* 1999, 32, 1763.
10. Kajiwara, A.; Matyjaszewski, K. *Macromolecules* 1998, 31, 3489.
11. Acar, M. H.; Matyjaszewski, K. *Macromol Chem Phys* 1999, 200, 1094.
12. Korn, M. R.; Lennon, J. D., III; Glish, G. L.; Gagné, M. R. *Macromolecules* 1999, 32, 5149.
13. Jankova, K.; Kops, J.; Chen, X.; Gao, B.; Batsberg, W. *Polym Bull* 1998, 41, 639.
14. Jankova, K.; Truelsen, J. H.; Chen, X.; Kops, J.; Batsberg, W. *Polym Bull* 1999, 42, 153.
15. Bednarek, M.; Biedron, T.; Kubisa, P. *Macromol Rapid Commun* 1999, 20, 59.
16. Wang, J. L.; Grimaud, T.; Matyjaszewski, K. *Macromolecules* 1997, 30, 6507.
17. Xia, J.; Matyjaszewski, K. *Macromolecules* 1997, 30, 7697.
18. Lochmann, L.; Lím, D. *J Organomet Chem* 1973, 50, 9.
19. Masař, B.; Vlček, P.; Kríž, J.; Kovářová, J. *Macromol Chem Phys* 1994, 195, 289.
20. Schöniger, W. *Microchim Acta* 1955, 123.
21. Schöniger, W. *Microchim Acta* 1956, 869.
22. Fayt, R.; Forte, R.; Jacobs, C.; Jérôme, R.; Ouhadi, T.; Teyssié, Ph.; Varshney, S. K. *Macromolecules* 1987, 20, 1442.
23. Varshney, S. K.; Hautekar, J. P.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *Macromolecules* 1990, 23, 2618.
24. Masař, B.; Vlček, P. *Macromol Chem Phys* 1994, 195, 671.
25. Sogah, D. Y.; Webster, O. W. *Polym Prepr (Am Chem Soc, Div Polym Chem)* 1983, 24(2), 1983.
26. Shipp, D. A.; Wang, J.-L.; Matyjaszewski, K. *Macromolecules* 1998, 31, 8005.
27. Matyjaszewski, K.; Shipp, D. A.; Wang, J. L.; Grimaud, T.; Patten, T. E. *Macromolecules* 1998, 31, 6836.
28. Wang, X.-S.; Luo, N.; Ying, S.-K. *Polymer* 1999, 40, 4157.
29. Matyjaszewski, K.; Acar, M. H.; Beers, K.; Coca, S.; Davis, K. A.; Gaynor, S. G.; Miller, P. J.; Paik, H.-J.; Shipp, D. A.; Teodorescu, M.; Xia, J.; Zhang, X. *Polym Prepr (Am Chem Soc, Div Polym Chem)* 1999, 40(2), 966.
30. Cassebrass, M.; Pascual, S.; Polton, A.; Tardi, M.; Vairon, J.-P. *Macromol Rapid Commun* 1999, 20, 261.