

Block Copolymers by Transformation of "Living" Carbocationic into "Living" Radical Polymerization. II. ABA-Type Block Copolymers Comprising Rubbery Polyisobutene Middle Segment

SIMION COCA, KRZYSZTOF MATYJASZEWSKI

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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ABSTRACT: A general method for the transformation of "living" carbocationic into "living" radical polymerization, without any modification of chain ends, is reported for the preparation of ABA block copolymers. For example, α,ω -difunctional polyisobutene, capped with several units of styrene, Cl-St-PIB-St-Cl, prepared cationically ($M_n = 7800$, $M_w/M_n = 1.31$) was used as an efficient difunctional macroinitiator for homogeneous "living" atom transfer radical polymerization to prepare triblock copolymers with styrene, PSt-PIB-PSt ($M_n = 28,800$, $M_w/M_n = 1.14$), methyl acrylate, PMA-PIB-PMA ($M_n = 31,810$, $M_w/M_n = 1.42$), isobornyl acrylate, PIBA-PIB-PIBA ($M_n = 33,500$, $M_w/M_n = 1.21$), and methyl methacrylate, PMMA-PIB-PMMA ($M_n = 33,500$, $M_w/M_n = 1.47$).

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INTRODUCTION

Controlled/"living" polymerization methods offer an efficient way to control the primary structure of polymer chain (molecular weight, polydispersities, and terminal functionalities) and is a powerful tool for the synthesis of polymers with precise molecular architecture.^{1,2} The synthesis of block copolymers usually requires efficient controlled/"living" polymerization.³

Tailored ABA block copolymers with polyisobutene (PIB) as a middle segment can be prepared by several methods. The most frequently used of these methods include, "living" carbocationic sequential monomer addition, and "living" carbocationic site transformation techniques.^{2,4} The synthesis of triblock copolymers by "living" carbocationic sequential monomer addition involves the poly-

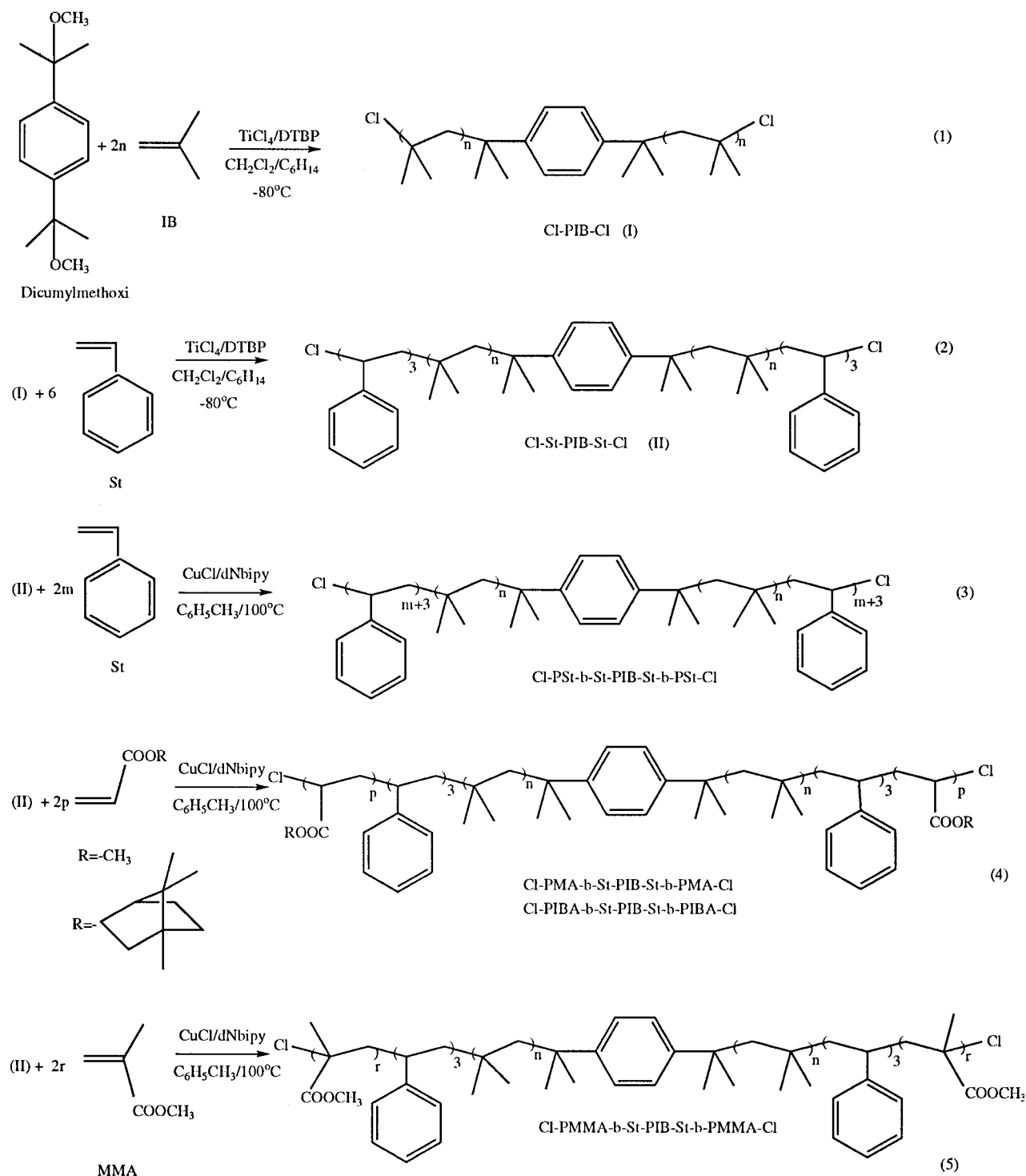
merization of isobutene induced by difunctional initiator, followed by the addition of the second monomer: styrene,^{5,6} derivatives of styrene,^{7–9} or indene.¹⁰ There are two specific features of these sequential monomer addition methods. First, only cationically polymerizable monomer can be used. Second, to increase the crossover efficiency when the second monomer is more reactive than isobutene (*p*-methylstyrene or α -methylstyrene) a reaction of "living" PIB chain ends with nonpolymerizable monomer (1,1-diphenylethylene) is necessary before addition of the second monomers.^{8,9} Another approach to block copolymers is based on site transformation technique. For example, a thermoplastic elastomer with PIB mid block and poly(methyl methacrylate) (PMMA) hard block^{11,12} was prepared by using cationic to anionic site transformation. Thus, Cl-PIB-Cl was first prepared by "living" carbocationic polymerization of isobutene. The polymer was dehydrochlorinated and subsequent hydroboration-oxidation of the corresponding α,ω -diisopropenyl-PIB yielded HO-PIB-OH.¹² α,ω -Hy-

Correspondence to: K. Matyjaszewski

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droxyl telechelic PIB was then esterefied, resulting in PIB diisobutyrate. Subsequent lithiation with an equimolar amount of lithium diisopropylamide produced an α,ω -dianion that was used to initiate anionic polymerization of MMA. The same block

copolymer has been synthesized by combining "living" carbocationic polymerization with group transfer polymerization (GTP).¹³ α,ω -Hydroxyl telechelic PIB, prepared using a method similar to the above, was converted in two steps to a difunc-



Scheme 1.

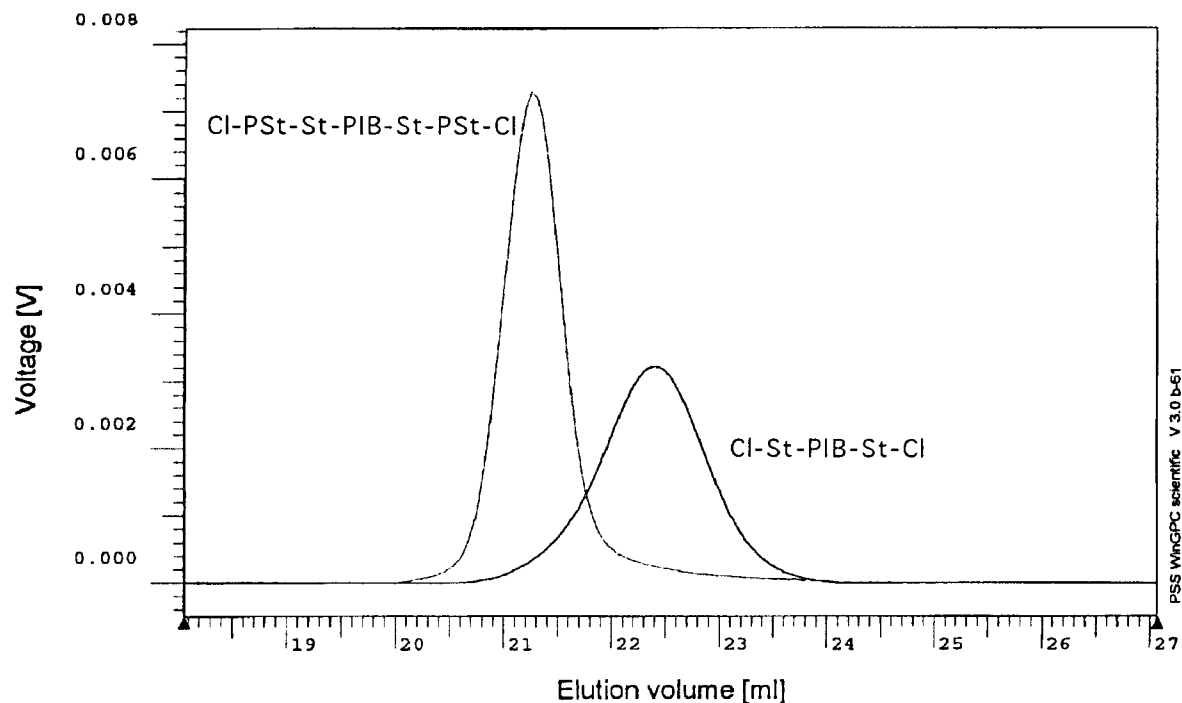
Table I. Results Obtained by Transformation of "Living" Cationic to "Living" Radical Polymerization

Exp	Monomer	Initiating System	Temp °C	M_{th}	$M_{n,exp}$	M_w/M_n
1	IB/St	dCuOMe/TiCl ₄ /DTBP	-80	7500	7800	1.31
2	St	dPIB-St-Cl/CuCl/dNbipy	100	13370	13350	1.18
3	MA	dPIB-St-Cl/CuCl/dNbipy	100	11800	12200	1.41
4	MMA	dPIB-St-Cl/CuCl/dNbipy	100	23100	22500	1.45
5	IBA	dPIB-St-Cl/CuCl/dNbipy	100	17270	18850	1.44
6	IB/St	dCuOMe/TiCl ₄ /DTBP	-80	30000	28800	1.31
7	St	dPIB-St-Cl/CuCl/dNbipy	100	48000	48820	1.14
8	MA	dPIB-St-Cl/CuCl/dNbipy	100	32000	31810	1.42
9	MMA	dPIB-St-Cl/CuCl/dNbipy	100	33000	33500	1.47
10	IBA	dPIB-St-Cl/CuCl/dNbipy	100	48000	49500	1.21

dCuOMe = *p*-dicumyl methyl ether; dPIB-St-Cl = Cl-St-PIB-St-Cl; Conditions: Exp. 1 [IB]₀ = 1 mol/L, [St]₀ = 4.5×10^{-2} mol/L, [dCuOMe]₀ = 7.5×10^{-3} mol/L, [dCuOMe]₀/[TiCl₄]₀/[DTBP]₀ = 1/25/0.5, CH₂Cl₂/Hexane = 4/6 v solvent, conversion = 99.8%; Exp. 2 [St]₀ = 2.67 mol/L, [dPIB-St-Cl]₀ = 0.025 mol/L, [dPIB-St-Cl]₀/[CuCl]₀/[dNbipy]₀ = 1/1/2, C₆H₅CH₃ solvent, conversion = 98.9%; Exp. 3 [MA]₀ = 2.32 mol/L, [dPIB-St-Cl]₀ = 0.025 mol/L, [dPIB-St-Cl]₀/[CuCl]₀/[dNbipy]₀ = 1/1/2, C₆H₅CH₃ solvent, conversion = 99.2%; Exp. 4 [MMA]₀ = 7.65 mol/L, [dPIB-St-Cl]₀ = 0.025 mol/L, [dPIB-St-Cl]₀/[CuCl]₀/[dNbipy]₀ = 1/1/2, C₆H₅CH₃ solvent, conversion = 97.1%; Exp. 5 [IBA]₀ = 2.64 mol/L, [dPIB-St-Cl]₀ = 0.025 mol/L, [dPIB-St-Cl]₀/[CuCl]₀/[dNbipy]₀ = 1/1/2, C₆H₅CH₃ solvent, conversion = 97.19%; Exp. 6 [IB]₀ = 1 mol/L, [St]₀ = 4.5×10^{-2} mol/L, [DiCuOMe]₀ = 2×10^{-3} mol/L, [dCuOMe]₀/[TiCl₄]₀/[DTBP]₀ = 1/25/0.5, CH₂Cl₂/Hexane = 4/6 v solvent, conversion = 99.8%; Exp. 7 [St]₀ = 8.7 mol/L, [dPIB-St-Cl]₀ = 0.025 mol/L, [dPIB-St-Cl]₀/[CuCl]₀/[dNbipy]₀ = 1/1/2, conversion = 98.0%; Exp. 8 [MA]₀ = 1.28 mol/L, [dPIB-St-Cl]₀ = 0.025 mol/L, [dPIB-St-Cl]₀/[CuCl]₀/[dNbipy]₀ = 1/1/2, C₆H₅CH₃ solvent, conversion = 99.1%; Exp. 9 [MMA]₀ = 1.60 mol/L, [dPIB-St-Cl]₀ = 0.025 mol/L, [dPIB-St-Cl]₀/[CuCl]₀/[dNbipy]₀ = 1/1/2, C₆H₅CH₃ solvent, conversion = 98.1%; Exp. 10 [IBA]₀ = 4.74 mol/L, [dPIB-St-Cl]₀ = 0.025 mol/L, [dPIB-St-Cl]₀/[CuCl]₀/[dNbipy]₀ = 1/1/2, conversion = 97.3%.

tional silylketene acetal macroinitiator. The subsequent GTP of MMA by PIB macroinitiator resulted in PMMA-*b*-PIB-*b*-PMMA triblock copolymer for-

mation with the blocking efficiency about 55%. A common feature of these techniques is that they include many steps and the number of monomers

**Figure 1.** GPC chromatograms for Cl-St-PIB-St-Cl and Cl-PSt-*b*-St-PIB-St-*b*-PSt-Cl polymers shown in Table I (Experiments 6 and 7).

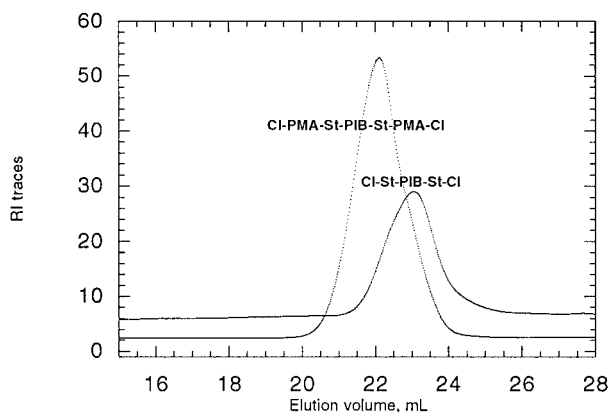


Figure 2. GPC chromatograms for Cl-St-PIB-St-Cl and Cl-PMA-*b*-PIB-St-*b*-PMA-Cl polymers shown in Table I (Experiments 1 and 3).

is limited to those that can be polymerized by cationic or anionic methods.

Atom Transfer Radical Polymerization (ATRP) was recently reported as a new and powerful route to the synthesis of well-defined (co)polymers of such monomers as styrene, acrylates, methyl methacrylate,^{14–19} acrylonitrile,²⁰ and isobutene.²¹ The resulting polymers have a degree of polymerization predetermined by $\Delta[M]/[I]_0$ up to $M_n \approx 10^5$ and low polydispersity, $1.1 < M_w/M_n < 1.5$. ATRP is a versatile tool for preparation of random, block,^{18,19} alternating,²¹ and gradient²² copolymers with controlled molecular weight, narrow polydispersities, and desired architecture.

Recently, we reported a general method of transformation of “living” carbocationic into “living” radical polymerization, and successful preparation of block copolymers, without any modifica-

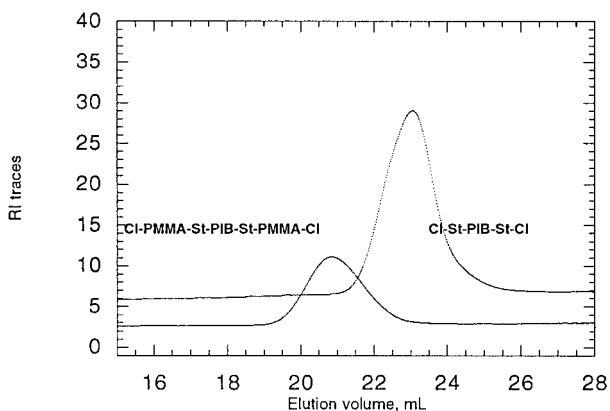


Figure 3. GPC chromatograms for Cl-St-PIB-St-Cl and Cl-PMMA-*b*-PIB-St-*b*-PMMA-Cl polymers shown in Table I (Experiments 1 and 4).

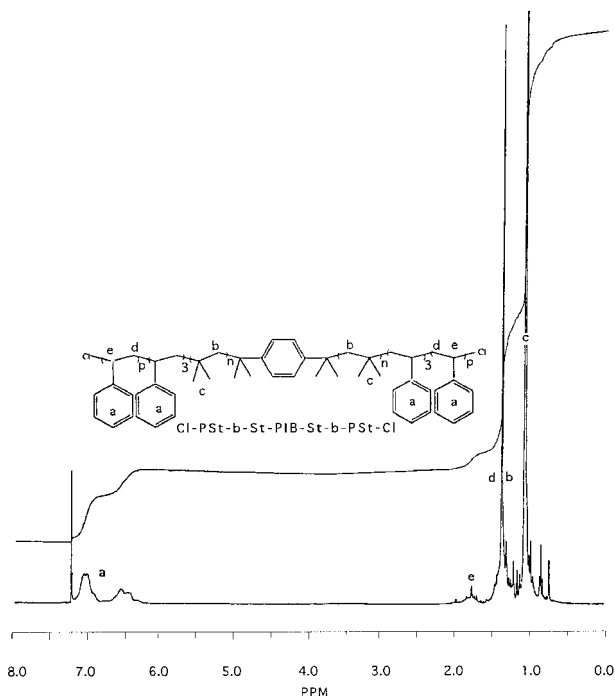


Figure 4. ^1H -NMR spectrum (CDCl_3) of Cl-PSt-*b*-PIB-St-*b*-PSt-Cl triblock copolymers [M_n (GPC) = 13,350, M_w/M_n = 1.18, M_n (NMR) = 13,200].

tion of chain ends.²³ For example, polystyrene with chlorine chain ends, synthesized by “living” cationic polymerization was used as an efficient macroinitiator for homogeneous “living” ATRP of styrene and (meth)acrylates. This communication reports synthesis of ABA-type block copolymers produced by the same procedure, using a PIB midblock obtained cationically and flanked by styrene or meth(acrylate) outer block prepared by ATRP. Thus, α,ω -difunctional PIB, Cl-PIB-Cl capped with several units of styrene, Cl-St-PIB-St-Cl, synthesized by “living” carbocationic polymerization, without any modification of chain ends, is an efficient difunctional initiator in “living” ATRP of styrene (St), methyl acrylate (MA), isobornyl acrylate (IBA) and methyl methacrylate (MMA) leading to Cl-PSt-*b*-St-PIB-St-*b*-PSt-Cl, Cl-PMA-*b*-St-PIB-St-*b*-PMA-Cl, Cl-PIBA-*b*-St-PIB-St-*b*-PIBA-Cl, and Cl-PMMA-*b*-St-PIB-St-*b*-PMMA-Cl triblock copolymers, as shown in Scheme 1.

The difunctional macroinitiators Cl-St-PIB-St-Cl with chlorine chain ends were obtained by “living” cationic polymerization of isobutene with *p*-dicumyl methyl ether/ TiCl_4 initiating system in the presence of 2,6-di-*tert*-butylpyridine (DTBP) at -80°C in methylene chloride/hexane as a solvent in a Schlenk flask under dry-box nitrogen

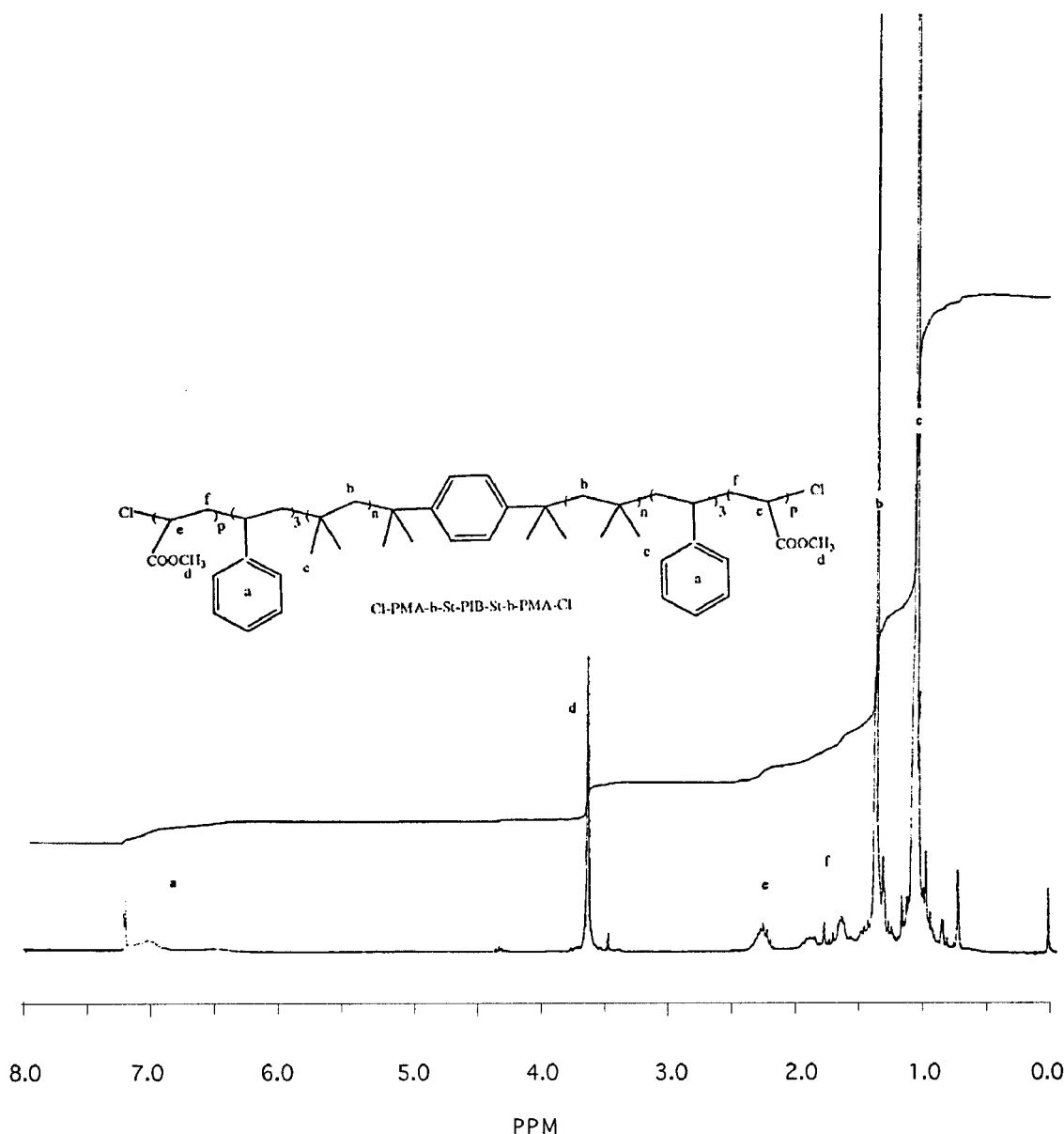


Figure 5. ^1H -NMR spectrum (CDCl_3) of Cl-PMA-*b*-PIB-St-*b*-PMA-Cl triblock copolymers [$M_n(\text{GPC}) = 12,200$, $M_w/M_n = 1.41$, $M_n(\text{NMR}) = 12,500$].

atmosphere (Table I). After 60 min of reaction the "living" PIB was capped with an average three to four units of styrene and polymerization was quenched with prechilled methanol. The polymers were purified by repeated dissolution-precipitation in dichloromethane/methanol, and dried under vacuum. The experimental number average molecular weight $M_{n,\text{exp}}$ ²⁴ was very close to the theoretical one, M_{th} calculated by means of eq. (1)²⁵

$$M_{\text{th}} = ([M]_0/[\text{Initiator}]_0$$

$$\times (\text{MW})_0 \times \text{conversion}. \quad (1)$$

The molecular weight distribution was narrow ($M_w/M_n = 1.31$) and the structure of α,ω -difunctional macroinitiator was confirmed by ^1H -NMR spectroscopy. This symmetric telechelic PIB flanked with a few units of styrene, which in turn, was capped with terminal chlorine functionalities, and was used as a macroinitiator in controlled/"living" radical polymerization. ATRP exhibits all of the experimental criteria of a "living"

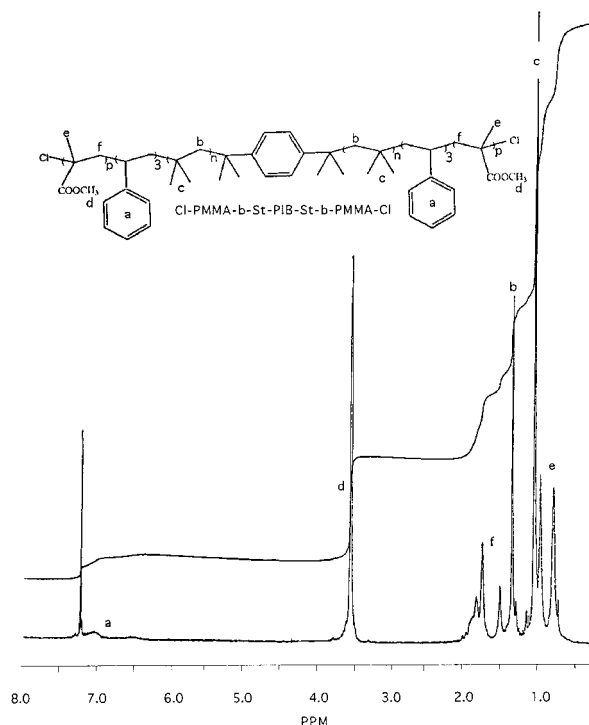


Figure 6. ^1H -NMR spectrum (CDCl_3) of Cl-PMMA-*b*-PIB-St-*b*-PMMA-Cl triblock copolymers [$M_n(\text{GPC}) = 23,100$, $M_w/M_n = 1.45$, $M_n(\text{NMR}) = 22,800$].

polymerization and is a general method for the polymerization of a large number of radically polymerizable monomers.

Thus, Cl-St-PIB-St-Cl, was used to initiate homogeneous ATRP of styrene, methyl acrylate, and methyl methacrylate in the presence of catalyst based on copper chloride (CuCl) and 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbipy). Table I summarizes representative polymerization results in cationic polymerization of isobutene and styrene (Experiments 1 and 6), and homogeneous ATRP of styrene (St) (Experiments 2 and 7), methyl acrylate (MA) (Experiments 3 and 8), isobornyl acrylate (IBA) (Experiments 5 and 10) and methyl methacrylate (MMA) (Experiments 4 and 9), initiated with Cl-St-*b*-PIB-St-Cl and catalyzed by $\text{CuCl}/\text{dNbipy}$.²⁶

$M_{n,\text{exp}}$ values agree with M_{th} , which were calculated using eq. (1) and assuming that each polymer chain contains two chlorine chain ends. The GPC chromatograms of starting Cl-St-PIB-St-Cl and Cl-PSt-*b*-St-PIB-St-*b*-PSt-Cl, Cl-PMA-*b*-St-PIB-St-*b*-PMA-Cl, and Cl-PMMA-*b*-St-PIB-St-*b*-PMMA-Cl triblock copolymers are illustrated in Figures 1–3. The reaction mixture from triblock copolymers synthesis was diluted with THF and injected di-

rectly into GPC to avoid any fractionation of the polymer sample during isolation. The GPC measurements showed that molecular weight distributions of triblock copolymers were unimodal and narrow. No signal attributed to starting macroinitiators was detected. Higher polydispersities observed for (meth)acrylate copolymers probably originate in slower crosspropagation step.

The structure of block copolymers was analyzed by ^1H -NMR spectroscopy. Figures 4–6 illustrate 300 MHz ^1H -NMR spectra of Cl-PSt-*b*-St-PIB-St-*b*-PSt-Cl, Cl-PMA-*b*-St-PIB-St-*b*-PMA-Cl, and Cl-PMMA-*b*-St-PIB-St-*b*-PMMA-Cl triblock copolymers. The M_n was determined from NMR spectra by integration of $-\text{CH}_2-$ protons of the PIB initiator, aromatic protons from PSt and of the methoxy group from the PMA and PMMA segments. All are close to values determined by GPC. The tacticity of PMMA (based on α $-\text{CH}_3$ group signals) was (rr) = 59%, (rm) = 32%, (mm) = 9%.

The phase separation in thermoplastic elastomers based on polyisobutene is illustrated by DSC measurements, showing two distinct glass transitions for the PIB block at -71°C and PSt block at 91°C (Table I, Experiment 7). Similar results were obtained for triblock copolymers with PMMA ($T_g = 94^\circ\text{C}$) and PIBA ($T_g = 93^\circ\text{C}$) (Table I, Experiments 9–10).

In conclusion, we have reported on a general method for the transformation of “living” carbocationic into “living” radical polymerization, without any modification of chain ends, which is now available for the preparation of ABA block copolymers. For example, a Cl-St-PIB-St-Cl prepared cationically was used as an efficient difunctional macroinitiator for homogeneous “living” ATRP of styrene and (meth)acrylates. This procedure is now being tested for other monomers (e.g., vinyl ethers) polymerizable only by cationic mechanism.

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24. $M_{n,exp}$ values were determined by size exclusion chromatography calibrated using linear polystyrene standards.
25. $[M]_0$ and $[Initiator]_0$ represent the initial concentrations of monomer and initiator, respectively, and $(MW)_0$ is the molecular weight of monomer.
26. General procedure for the homogeneous ATRP of styrene, (meth)acrylate: the following reagents were weighed in an appropriate amount into a glass tube under an ambient atmosphere: CuCl, dNbipy, monomer, toluene, macroinitiator. Two "freeze-pump-thaw" cycles were performed to ensure that oxygen was removed from the polymerization solution. Each tube was sealed under vacuum. The tubes were placed in an oil bath thermostated at 100°C. After 12 h the tubes were removed from the oil bath and cooled at 0°C to quench the polymerization. Afterwards, the individual tubes were broken and the contents were dissolved in 7 mL of THF. Percent conversion of each samples was measured using gas chromatography, molecular weights and polydispersities were measured using size exclusion chromatography.