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Block Copolymers by Transformation of "Living" Carbocationic into "Living" Radical Polymerization

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Controlled/"living" polymerization methods offer the best way to prepare well-defined polymers (controlled molecular weight, polydispersities, and terminal functionalities) in systems where the contribution of a side reaction is small.[1,2] The synthesis of block copolymers usually requires efficient controlled/"living" polymerization.[3]

During the past decade considerable advances have been made in "living" carbocationic polymerization processes for a variety of vinyl monomers,[2] including vinyl ethers,[4] isobutene,[5,6] styrene,[7−10] *p*-alkoxystyrene,[11] and *N*-vinylcarbazole.[12] For example, Sawamoto et al.[10] reported "living" cationic polymerization of styrene with an initiating system based on 1-phenylethyl chloride (1-PhEtCl) and tin tetrachloride ($SnCl_4$) in the presence of added tetra-*n*-butylammonium chloride (n-Bu_4NCl) using methylene chloride as solvent.

Extension of atom transfer radical addition (ATRA) to atom transfer radical polymerization (ATRP) provides a new and efficient way to conduct controlled/"living" radical polymerization.[13] With a variety of alkyl halides, R−X (X = Cl or Br), as the initiator and a transition metal species complexed by suitable ligand(s), CuX/2,2′-bipyridine, as the catalyst, ATRP of vinyl monomers such as styrene and (meth)acrylate proceeds in a "living" fashion.[14] The resulting polymers have a degree of polymerization predetermined by $\Delta[M]/[I]_o$ up to $M_n \approx 10^5$ and low polydispersity, $1.1 < M_w/M_n < 1.5$. For example, when an alkyl chloride, 1-PhEtCl, is used as initiator, and a CuCl/4,4′-diheptyl-2,2′-bipyridine or 4,4′-di-(5-nonyl)-2,2′-bipyridine complex is used as catalyst, styrene polymerized by repetitive atom transfer radical additions to yield a well-defined, high molecular weight polymer, with narrow molecular weight distribution ($M_w/M_n = 1.05$).[15]

Polymers with a variety of terminal functionalities can be obtained by "living" cationic polymerization, and some of the end functions may be useful for initiating another polymerization to give block copolymers. Several papers report well-defined block copolymers by the transformation of initiating sites from "living" cationic to anionic polymerization.[16−23] Another approach for block copolymers is the coupling reaction of two "living" homopolymers having antagonistic functions, such as carbocationic with group transfer,[24,25] or anionic polymerizations.[26] Commonly, these techniques include many steps and the number of monomers is limited to those which can be polymerized by cationic or anionic methods. There were attempts to combine "living" cationic polymerization with conventional radical polymerization. For example, methacrylonitrile[27] and benzyl methacrylate[28] were radically polymerized from well-defined poly(vinyl ethers) with terminal azo-initiating sites. Obviously, the second-stage free radical polymerization is not controlled in term of molecular weight and polydispersity, so that the product may be a mixture of desired block copolymers and the respective homopolymers.

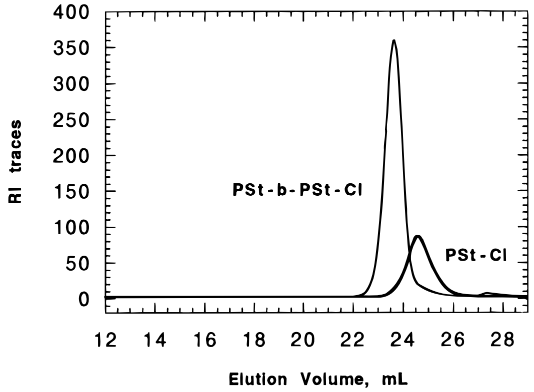


Figure 1. GPC chromatograms for PSt−Cl and PSt-*b*-PSt−Cl polymers shown in Table 1 (experiments 1 and 2).

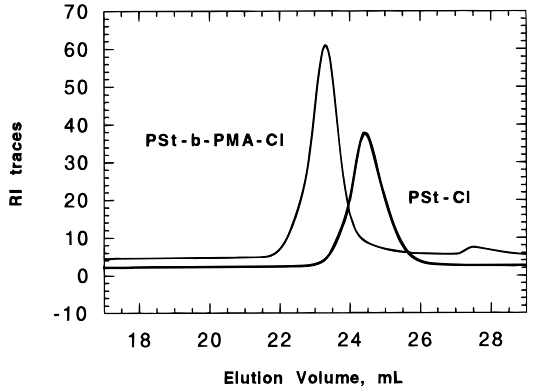
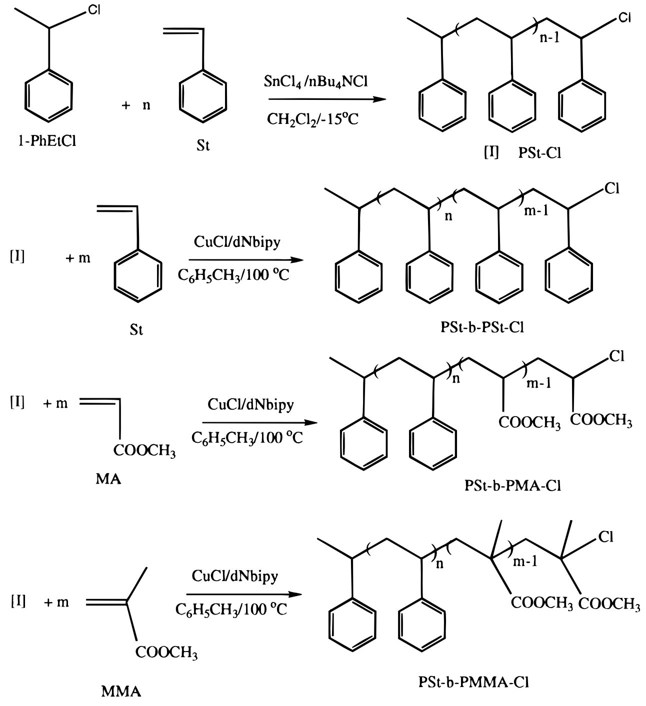


Figure 2. GPC chromatograms for PSt−Cl and PSt-*b*-PMA−Cl polymers shown in Table 1 (experiments 1 and 3).

Scheme 1



The preparation of block copolymers by the combination of "living" carbocationic with "living" radical polymerization has not yet been reported. This communication reports that polystyrene with chlorine termini, synthesized by "living" cationic polymerization, without any transformation, is an efficient macroinitiator for "living" ATRP of styrene and (meth)acrylates. Scheme

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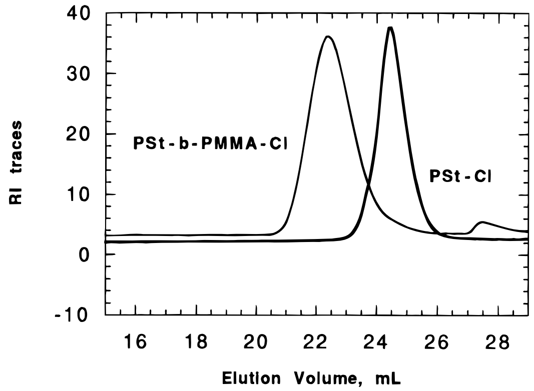

Figure 3. GPC chromatograms for PSt–Cl and PSt-*b*-PMMA–Cl polymers shown in Table 1 (experiments 1 and 4).

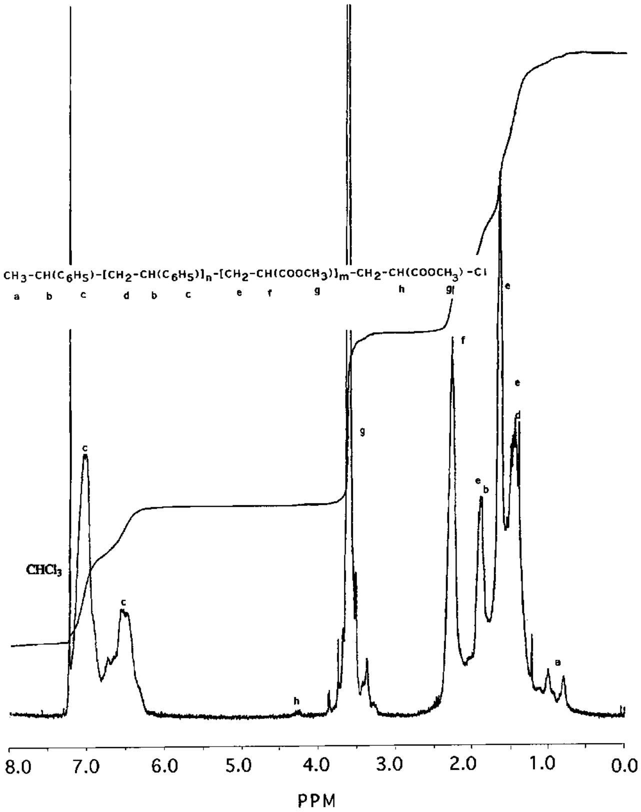

Figure 4. ^{1}H-NMR spectrum (CDCl$_3$) of PSt-*b*-PMA–Cl copolymers [M_n(GPC) = 6200, M_w/M_n = 1.20, M_n(NMR) = 6020].

1 describes the procedure for the synthesis of poly(styrene-*b*-styrene), poly(styrene-*b*-methyl acrylate), and poly(styrene-*b*-methyl methacrylate) copolymers.

Macroinitiators based on poly(styrene) with chlorine chain ends were obtained by "living" cationic polymerization of styrene with the 1-PhEtCl/SnCl$_4$ initiating system in the presence of *n*-Bu$_4$NCl at −15 °C in methylene chloride in a Schlenk flask under dry nitrogen (Table 1). After 30 min, polymerization was terminated by adding prechilled methanol. The polymers were purified by repeated dissolution-precipitation in dichloromethane/methanol, and dried under vacuum. The experimental number average molecular weight $M_{n,exp}$[29] was very close to the theoretical one, $M_{n,th}$ calculated by means of eq 1.[30] The molecular weight

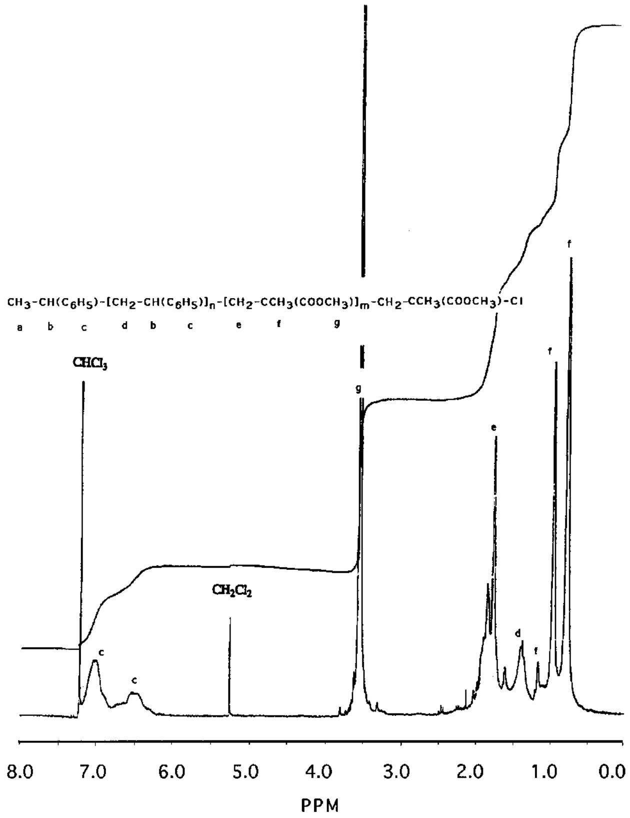

Figure 5. ^{1}H-NMR spectrum (CDCl$_3$) of PSt-*b*-PMMA–Cl copolymers [M_n(GPC) = 11 090, M_w/M_n = 1.57, M_n(NMR) = 10 300].

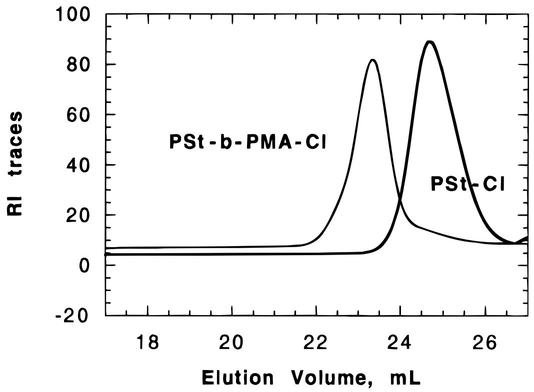

Figure 6. GPC chromatograms for PSt–Cl and PSt-*b*-PMA–Cl polymers obtained by one pot polymerization. Experimental conditions were identical to those in Table 1 (experiments 1 and 3).

Table 1. Results Obtained by Transformation of "Living" Cationic to "Living" Radical Polymerization[a]

expt	monomer	initiating system	temp, °C	M_{nth}	$M_{n,exp}$	M_w/M_n
1	$CH_2{=}CH(Ph)$	1-PhEtCl/SnCl$_4$/*n*-Bu$_4$NCl	-15	2080	2100	1.17
2	$CH_2{=}CH(Ph)$	PSt-Cl/CuCl/dNbipy	100	5100	5080	1.10
3	$CH_2{=}CH(COOMe)$	PSt-Cl/CuCl/dNbipy	100	6200	6330	1.20
4	$CH_2{=}CCH_3(COOMe)$	PSt-Cl/CuCl/dNbipy	100	10100	11090	1.57

[a] Conditions: experiment 1, $[St]_o = 1$ mol/L, $[1\text{-PhEtCl}]_o = 5 \times 10^{-2}$ mol/L, $[1PhEtCl]_o/[SnCl_4]_o/[nBu_4NCl]_o = 1/5/2$, CH_2Cl_2 solvent, conversion = 98%; experiment 2, $[St]_o = 3$ mol/L, $[PSt{-}Cl]_o = 0.1$ mol/L, $[PSt{-}Cl]_o/[CuCl]_o/[dNbipy]_o = 1/1/2$, $C_6H_5CH_3$ solvent, conversion = 98.5%; experiment 3, $[MA]_o = 4.76$ mol/L, $[PSt{-}Cl]_o = 0.1$ mol/L, $[PSt{-}Cl]_o/[CuCl]_o/[dNbipy]_o = 1/1/2$, $C_6H_5CH_3$ solvent, conversion = 99.5%; experiment 4 $[St]_o = 8$ mol/L, $[PSt{-}Cl]_o = 0.1$ mol/L, $[PSt{-}Cl]_o/[CuCl]_o/[dNbipy]_o = 1/1/2$, $C_6H_5CH_3$ solvent, conversion = 97.5%.

$$M_{n,th} = ([M]_o/[\text{initiator}]_o) \times (MW)_o \times \text{conversion} \quad (1)$$

distribution was narrow ($M_w/M_n = 1.17$), and end group analysis by ^{1}H-NMR showed that polystyrene contained the ...$-CH_2-CH(Ph)-Cl$ terminal group (broad signal of methine protons at $\approx$ 4.4 ppm). The polystyrene with terminal chlorine functionality was used as a macroinitiator in controlled/"living" radical polymerization. ATRP exhibits all of the experimental criteria of a "living" polymerization and is a general method for a large number of radically polymerizable monomers.

Thus polystyrene with chlorine chain end, poly(styrene)−Cl, was used to initiate homogeneous ATRP of styrene, methyl acrylate, and methyl methacrylate in the presence of catalyst based on CuCl and 4,4′-di-5-nonyl-2,2′-bipyridine (dNbipy).[31] Table 1 summarizes polymerization results in cationic polymerization of styrene (experimental 1), and homogeneous ATRP of styrene (St) (experimental 2), methyl acrylate (MA) (experimental 3) and methyl methacrylate (MMA) (experimental 4), initiated with poly(styrene)−Cl (PSt−Cl) and catalyzed by CuCl/dNbipy.

$M_{n,exp}$ values agree with $M_{n,th}$ which were calculated using eq 1 with the assumption that each polymer chain contains one terminal chlorine. The GPC chromatograms of starting PSt−Cl and PSt-*b*-PSt−Cl, PSt-*b*-PMA−Cl and PSt-*b*-PMMA−Cl copolymers are illustrated in Figure 1−3. The reaction mixtures from block copolymer synthesis were diluted with THF and injected directly into GPC in order to avoid any fractionation of the polymer sample during isolation. The GPC measurements showed that molecular weight distribution of block copolymers are unimodal and narrow. No signal attributed to starting macroinitiators is detected.

The structure of block copolymers was analyzed by ^{1}H NMR spectroscopy. Figures 4 and 5 illustrate 300 MHz ^{1}H NMR spectra of PSt-*b*-PMA−Cl and PSt-*b*-PMMA−Cl copolymers. The M_n determined from NMR spectra by integration of the aromatic protons of the macrointiator and the methoxy group from PMA and PMMA, agrees well with those determined by GPC. The tacticity of PMMA (based on CH_3 groups signals) was (rr) = 59%, (rm) = 32%, and (mm) = 9%.

The ability to apply the process to a one-pot transformation was demonstrated by the following experiment. In a Schlenk flask under nitrogen, the "living" PSt−Cl obtained by cationic polymerization was deactivated by adding methyl acrylate at −15 °C. After the temperature was raised, CH_2Cl_2, Lewis acid, and ester were removed under vacuum. A solution of CuCl/dNbipy in toluene was added to the PSt−Cl product, followed by the addition of required amount of methyl acrylate and the temperature was increased to 100 °C. Experimental conditions identical to those in Table 1 (experimental 3) were used. The GPC traces of macroinitiators and copolymer PSt-*b*-PMA−Cl confirm the successful one-pot transformation as shown in Figure 6, leading to a polymer with $M_n = 6300$ and $M_w/M_n = 1.21$.

In conclusion, we report a general method of transformation of "living" carbocationic into "living" radical polymerization, without any modification of initiating sites, and successful preparation of block copolymers. We have demonstrated that, a PSt−Cl prepared cationically can be used as an efficient macroinitiator for homogeneous "living" ATRP of styrene and (meth)acrylates. This procedure is now being tested for isobutene, which can be exclusively polymerized cationically and for the synthesis of the corresponding triblock copolymers.

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(29) $M_{n,exp}$ values were determined by size exclusion chromatography calibrated using polystyrene standards
(30) $[M]_o$ and $[\text{initiator}]_o$ represent the initial concentrations of monomer and initiator respectively and $(MW)_o$ is the molecular weight of monomer.
(31) General procedure for the homogeneous ATRP of styrene and (meth)acrylate: The following reagents were weighed in an appropriate amount into glass tube under ambient atmosphere: CuCl, dNbipy, monomer, and benzene, macroinitiator. Two "freeze−pump−thaw" cycles were performed on the content of each tube in order to insure that dioxygen 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 in order to quench the polymerization. Afterward, the individual tubes were broken and the contents were dissolved in 7 mL of THF. The percent conversion of each of the samples was measured using gas chromatography, and molecular weights and polydispersities were measured using size exclusion chromatography.

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