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Cationic Macromolecular Design and Synthesis Using Furan Derivatives

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ABSTRACT: General methodologies for the synthesis of block copolymers and functional polymers using furan derivatives are reported on the basis of a study of addition reactions of 2-substituted furans to living polyisobutylene (PIB^+). Rapid and quantitative monoaddition of 2-methylfuran (2-MeFu) and 2-*tert*-butylfuran (2-tBuFu) to PIB^+ has been observed in conjunction with $TiCl_4$ as Lewis acid in hexanes (Hex)/CH_2Cl_2 or CH_3Cl 60/40 v/v at −80 °C and with BCl_3 in CH_3Cl at −40 °C, in the presence of proton trap. Upon monoaddition, the formation of the stable allylic cation was confirmed by trapping the resulting cation with tributyltin hydride, which yielded PIB with dihydrofuran functionality. Quenching with methanol resulted in the quantitative formation of 2-alkyl-5-PIB-furan. The stable allylic cation was found to be an efficient initiating species for the polymerization of methyl vinyl ether (MeVE), yielding P(IB-*b*-MeVE) block copolymers by sequential monomer addition with up to 75% crossover efficiency. 2-PIB-Fu, a polymeric capping agent, was obtained in quantitative yields in a reaction of PIB^+ with 2-Bu_3SnFu in Hex/CH_3Cl 60/40 v/v in the presence of $TiCl_4$ at −80 °C. In a subsequent reaction of 2-PIB-Fu with living PIB^+, under conditions similar to capping PIB^+ with 2-tBuFu, close to quantitative coupling of the two PIB chains was achieved. The concept of coupling a living cationic polymer with an ω-furan functional polymer to obtain AB-type linear block copolymers and for the synthesis of ABC- and AA′B-type three-arm star-block copolymers is presented.

Introduction

Since the introduction of the foundation and methodology of using non(homo)polymerizable monomers in cationic macromolecular engineering 5 years ago, we have gained significant insight in the scope and limitations of this technique. The importance of non(homo)-polymerizable monomers, such as 1,1-diphenylethylene (DPE) or 1,1-ditolylethylene DTE, in cationic macromolecular design and synthesis, arises from their application in the capping reaction of living cationic polymers. A quantitative monoaddition of DPE or DTE, to a living chain end, i.e., a capping reaction, results in a stable and completely ionized cationic living chain end, which was shown to be well suited for quantitative end functionalization with a variety of nucleophiles.[1,2] The resulting diphenylcarbenium ion was also found to be an efficient initiating species for the polymerization of reactive monomers.[3−10] Mechanistic and kinetic aspects of the capping reactions as well as applications for the synthesis of novel chain-end functionalized polymers and block copolymers have been reviewed recently.[11−14]

A limitation of using DPE or substituted DPEs as capping agents is that quantitative capping can be obtained only under selected conditions. For instance, it is exceedingly difficult to achieve complete capping of PIB^+ with DPE at −40 °C with $TiCl_4$, or even at −80 °C with BCl_3, due to the low equilibrium constants of capping/decapping under these conditions. Recently, we have started experimentations with furan derivatives as capping agents. Although it has been known that 2-alkylfurans are highly reactive toward electrophilic attack at the C-5 position,[15] no attempt has been made in the synthetic utilization of 2-alkylfurans in the living cationic polymerization of vinyl monomers. Razzouk et al.[16] reported that 2-methylfuran is an excellent chain transfer agent in the polymerization of IB in conjunction with $EtAlCl_2$ in CH_2Cl_2 in the temperature range of −23 to 0 °C. We have recently reported quantitative monoaddition of 2-*tert*-butylfuran to polyisobutenyl diphenylcarbenium ($PIB\text{-}DPE^+$) ions.[2] Diaddition was not observed, apparently due to steric hindrance brought about by the 2-*tert*-butyl substituent. It occurred to us that 2-*tert*-butylfuran and perhaps other 2-alkylfurans

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could also add to living PIB^+ (and to other living cationic polymers) quantitatively without homopolymerization. It was anticipated that, upon addition exclusively at the C-5 position, a stable tertiary allylic cation, stabilized by the vicinal O atom, would be generated at the C-2 position. The resulting cation may be used to initiate monomers possessing high reactivity. Likewise, the capped polymer cation may be quenched with a nucleophile to introduce a particular functional group. This invention thus provides a new method of capping living cationic polymer chain ends and makes possible the synthesis of novel functionalized polymers and block copolymers.

In this paper we report on new methodologies using furan derivatives as capping agents for the synthesis of functional polymers and block copolymers.

Experimental Section

Materials. 2,6-Di-*tert*-butylpyridine (DTBP) (Maybridge Chemical Co., MCC) was purified by distillation from CaH_2. Methyl vinyl ether (MeVE) (98+%, Aldrich) was purified by passing the gaseous monomer through a column of CaH_2 before condensing it at −80 °C. CH_3Cl was passed through in-line gas purifier columns packed with BaO/Drierite and condensed at −80 °C prior to polymerization. CH_2Cl_2 was purified by washing it with 10% aqueous NaOH and then with distilled water until neutral and dried over anhydrous $MgSO_4$ overnight. It was refluxed for 24 h and distilled from CaH_2, just before use. Hexane (Hex) was rendered olefin free by refluxing it over concentrated sulfuric acid for 48 h. It was washed with 10% NaOH aqueous solution and then with deionized water until neutral and stored over $MgSO_4$ for 24 h. It was refluxed over CaH_2 overnight and distilled.

Titanium(IV) chloride ($TiCl_4$, 99.9%, Aldrich) and boron trichloride (BCl_3, 99.9%, Aldrich) were used as received. Titanium(IV) ethoxide ($Ti(OEt)_4$, tech., Aldrich) was rendered free from excess ethanol by leaving it under vacuum while stirring overnight. It was stored under N_2 at −20 °C and evacuated again at least for an hour just before use. $Ti(OiPr)_4$ (99.999%) and 2-(tributylstannyl)furan (2-Bu_3SnFu) (97%, Aldrich) were used as received. 2-Methylfuran (2-MeFu 99%, Aldrich) was distilled from CaH_2 the day before use and stored at −20 °C. 2-*tert*-Butylfuran (2-tBuFu) was synthesized according to the literature.[17]

2-(Tributylstannyl)-5-methylfuran was synthesized as follows: 10.8 mL (0.12 mol) of 2-methylfuran was added dropwise to a mixture of 40 mL of 2.5 M solution of BuLi in Hex (0.10 mol) and 50 mL of anhydrous ether while the temperature was kept at 10 °C. After the addition, the mixture was kept at room temperature for 40 min and then was cooled to 0 °C. 22.0 mL (0.09 mol) tributylstannyl chloride was added dropwise, and the mixture was stirred for an additional 30 min at room temperature. It was poured into 200 mL of distilled water, the organic phase was separated, and the aqueous phase was extracted with 2 × 100 mL of ether. The organic layers were combined and dried overnight over anhydrous $MgSO_4$. The solvents were removed on the rotavap, and the crude product was purified by vacuum distillation, yielding 17.73 g of 2-(tributylstannyl)-5-methylfuran (40% yield). The ^1H NMR spectrum and assignments are available in the Supporting Information.

2,5-Bis(tributylstannyl)furan was synthesized according to the following procedure: To a 100 mL three-neck reaction flask equipped with a magnetic stirrer, a condenser, and a dropping funnel were placed 50 mL of dried and distilled Hex, 15 mL of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), and 3 mL (41.2 mmol) of furan. Under stirring, 42 mL of BuLi (105 mmol, 2.5 M in Hex) was added dropwise. The reaction mixture was refluxed for 90 min, and under reflux 30 mL of nBu_3SnCl (110 mmol) was added dropwise. Refluxing continued for an additional 2 h, and the reaction was quenched with 100 mL of distilled water. The organic phase was separated, and the aqueous phase was washed with 2 × 50 mL of Hex. The organic phases were combined and washed with distilled water and dried over anhydrous Na_2SO_4 overnight. The solvent was evaporated on the rotavap, leaving behind a brown liquid, from which 2,5-bis(tributylstannyl)furan (10.6 g, yield = 40%) was recovered by fractional distillation using a vigreux column. The structure of the product was verified by ^1H NMR spectroscopy. The ^1H NMR spectrum and assignments are available in the Supporting Information.

2-*tert*-Butyl-5-(2,4,4-trimethyl-2-pentyl)furan was synthesized according to the following procedure (all solutions were prepared at room temperature and cooled to −80 °C before mixing): 0.06 mL of DTBP dissolved in 10 mL of Hex was placed to a 250 mL round-bottom reaction flask equipped with an overhead stirrer and cooled to −80 °C. Under stirring a solution of 0.5 mL of $TiCl_4$ in 10 mL of Hex and 16.7 mL of CH_2Cl_2 was added and mixed for 5 min. The solution of 0.4455 g of 2-chloro-2,4,4-trimethylpentane (TMPCl) in 15 mL of Hex was added next, followed by the immediate addition of a solution of 0.3906 g of 2-*tert*-butylfuran dissolved in 5.5 mL of Hex and 10.1 mL of CH_2Cl_2. The concentrations of the reactants at −80 °C were $[TMPCl] = 5 \times 10^{-2}$ M, $[DTBP] = 6 \times 10^{-3}$ M, $[TiCl_4] = 7.6 \times 10^{-2}$ M, and $[2\text{-tBuFu}] = 5.25 \times 10^{-2}$ M. After 60 min the reaction mixture was quenched with prechilled methanol. It was washed three times with distilled water, and the organic phase was dried overnight over anhydrous Na_2SO_4. The solvents were evaporated on the rotavap to give 0.5540 g (78% yield) of product, the structure of which was verified by ^1H NMR spectroscopy. ^1H NMR spectrum: 5.8 ppm (2H, s), 1.62 ppm (2H, s), 1.31 ppm (6H, s), 1.25 ppm (9H, s), 0.75 ppm (9H, s).

The synthesis and purification of all other materials have been described.[7,8]

Procedures. All polymerizations were carried out in a stainless steel glovebox.[8] With BCl_3 as Lewis acid, the polymerization of IB and capping of the living PIB with 2-tBuFu were carried out according to the following representative procedure. Into a 500 mL reaction flask equipped with an overhead stirrer was placed 264 mL of CH_3Cl. Under stirring, the solutions of DTBP and BCl_3 in CH_3Cl were added. After 5 min mixing, TMPCl in CH_3Cl was introduced followed by the immediate addition of IB. The polymerization was allowed to proceed for 7 h, and then equal volumes of the solution were delivered into 20 mL/culture tubes at −40 °C. A solution of 2-tBuFu in CH_3Cl was added next, and the reaction mixtures were quenched at different times to determine the extent of capping. The concentrations of the reactants at −40 °C were as follows: $[DTBP] = 4 \times 10^{-3}$ M, $[BCl_3] = 0.5$ M, $[TMPCl] = 2.4 \times 10^{-2}$ M, $[IB] = 0.6$ M, and $[2\text{-tBuFu}] = 4.8 \times 10^{-2}$ M.

The polymerization of IB and capping reactions with 2-tBuFu or 2-MeFu in the presence of $TiCl_4$ were carried out in a Hex/CH_2Cl_2 or CH_3Cl 60/40 v/v solvent mixture at −80 °C. A representative procedure for the sequential block copolymerization of IB and MeVE is as follows (all solutions were prepared at room temperature and cooled to −80 °C before mixing): into a 250 mL round-bottom reaction flask equipped with overhead stirrer was placed 19.5 mL of Hex which was cooled to −80 °C. 30 mL CH_2Cl_2 was added next. After the temperature was equilibrated at −80 °C, a solution of 0.07 mL of DTBP in 10 mL of Hex was added followed by the addition of 0.66 mL of $TiCl_4$ dissolved in 10 mL of Hex and 10 mL of CH_2Cl_2 and allowed to mix for 5 min. 0.1485 g TMPCl dissolved in 20 mL of Hex was added next followed by the immediate addition of 2.8 mL of IB at −80 °C. After 30 min polymerization (complete conversion), 0.1302 g of 2-tBuFu dissolved in 6 mL of Hex and 4 mL of CH_2Cl_2 was added. About 15 min later a solution of 1.25 mL of $Ti(OiPr)_4$ in 5 mL of Hex and 5 mL of CH_2Cl_2 was added and reacted for 5 min. 2.7 mL MeVE was added last at −80 °C. After 3 h at −80 °C the temperature was raised to 0 °C. The final concentrations of the reactants at −80 °C were as follows: $[TMPCl] = 1 \times 10^{-2}$ M, $[DTBP] = 3 \times 10^{-3}$ M, $[TiCl_4] = 6 \times 10^{-2}$ M, $[IB] = 0.36$ M, $[2\text{-tBuFu}] = 1.05 \times 10^{-2}$ M, $[Ti(OiPr)_4] = 4.2 \times 10^{-2}$ M, and $[MeVE] = 0.68$ M. At 0 °C the polymerization was allowed to proceed for 75 min and then was quenched with prechilled methanol. The mixture was poured into 10% ammoniacal methanol. The product was dissolved in CH_2Cl_2, and insolubles were filtered. The solvent was evaporated, the polymer was redissolved in tetrahydrofuran (THF), and a few drops of 10% ammoniacal methanol were added to precipitate dissolved titanium compounds which were not removed by filtration. The solution was dried overnight over anhydrous Na_2SO_4, and the solvent was removed. Control samples quenched with methanol after capping, purified, and analyzed by ^1H NMR spectroscopy indicated that capping was $\sim$100% after 15 min reaction time (disappearance of the peaks at $\sim$1.69 ppm $\{PIB-CH_2-C(C\boldsymbol{H}_3)_2Cl\}$ and $\sim$2.0 ppm $\{PIB-C\boldsymbol{H}_2-C(CH_3)_2Cl\}$ and appearance of new peaks at $\sim$5.8 ppm $\{PIB-CH_2-C(CH_3)_2-\boldsymbol{Fu}-C(CH_3)_3\}$ and $\sim$1.72 ppm $\{PIB-C\boldsymbol{H}_2-C(CH_3)_2-Fu-C(CH_3)_3\}$). The capping procedure with 2-MeFu was the same as with 2-tBuFu. In addition to the peaks at $\sim$5.8 and $\sim$1.72 ppm, the ^1H NMR spectrum of the products exhibited a peak at 2.25 ppm due to the $-CH_3$ group at position 2 on the furan ring.

Molecular weights were measured using a Waters HPLC system equipped with a Waters model 510 HPLC pump, a Waters model 486 tunable absorbance (UV/vis) detector, an on-line refractometer/viscometer dual detector (model 250) equipped with Data Manager DM 400 (Viscotek Inc.), a Waters model 712 WISP sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. The THF was used as eluent at a flow rate of l.0 mL/min. The detector signals (RI, UV, and DP) were recorded on a PC for molecular weight and molecular weight distribution determination using the Viscotek TriSEC GPC−viscometry software. Refractive index increments (dn/dc) of 0.063 mL/g[18] for PMeVE in THF were used. The dn/dc for the diblock was calculated using dn/dc values for PIB and PMeVE and the composition of diblock copolymer. The crossover efficiency was determined by column chromatography on silica gel.[19] ^1H and ^{13}C NMR spectroscopy were carried out on a Bruker 250 MHz instrument. ^1H NMR and ^{13}C NMR spectral peak assignments were carried out by the synthesis of model compounds and the use of ACD/HNMR 1.0 and ACD/CNMR 1.1 computer software from Advanced Chemistry Development Inc.

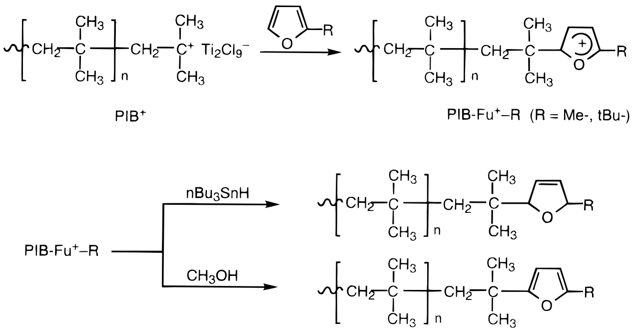
Results and Discussion

Capping with 2-Alkylfurans. Furan displays a variety of structural features that results in its unique chemical behavior. It is a bifunctional molecule and its primary mode of reaction is electrophilic substitution. It has higher reactivity than benzene, and the presence of oxygen induces orientation of the attacking electrophile at C-2 and C-5 positions which are of equal reactivity. As a result of two highly reactive positions in furan, a dark-colored, hexanes-insoluble material was obtained when living PIB^+ was reacted with furan in the presence of $TiCl_4$ at −80 °C, most likely due to oligomerization of furan.

Controlled monoaddition to electrophiles may be achieved by blocking one of the two positions by placing a substituent. In contrast to furan itself, we found that living PIB^+ chain ends can be capped by 2-alkylfurans. Homopolymerization and other side reactions were found to be absent under selected conditions. Thus, living PIB, obtained by the TMPCl/$TiCl_4$ initiating system in Hex/CH_2Cl_2 or CH_3Cl 60/40 v/v in the presence of DTBP at −80 °C, was reacted with 2-MeFu and 2-tBuFu in slight stoichiometric excess according to Scheme 1.

The formation of the stable allylic cation ($PIB-Fu^+-R$) was confirmed by trapping the resulting cation with tributyltin hydride, which according to the ^1H NMR spectrum of the product (Figure 1) yielded PIB with 2,5-dihydrofuran functionality in quantitative yield. Characteristic resonance signals of the chloro-terminated PIB ($\sim CH_2C(CH_3)_2C\boldsymbol{H}_2C(C\boldsymbol{H}_3)_2Cl$), i.e., the methylene and methyl protons next to the chloro group at 1.96 and 1.67 ppm, were absent.

Scheme 1. Capping Living PIB with 2-Alkylfurans



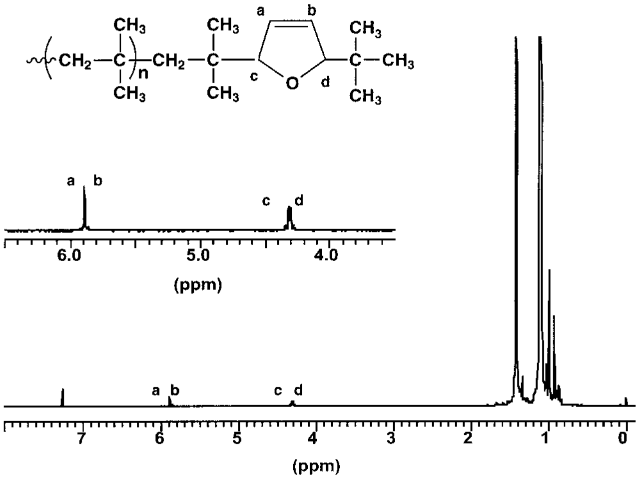


Figure 1. ^1H NMR spectrum of 2-*tert*-butyl-5-PIB-2,5-dihydrofuran.

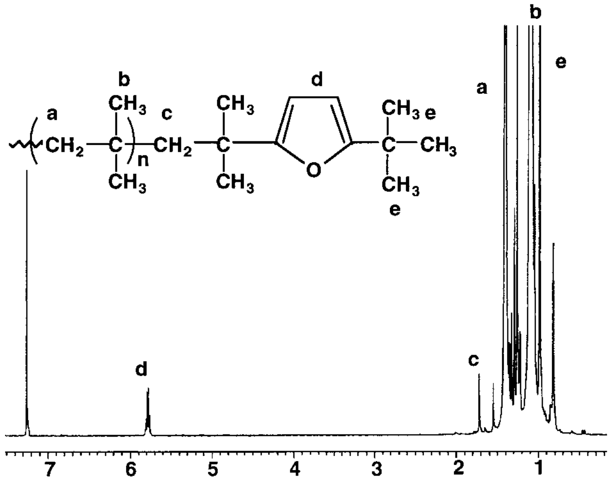


Figure 2. ^1H NMR spectrum of 2-*tert*-butyl-5-PIB-furan.

Interestingly, quenching $PIB-Fu^+-R$ with methanol at −80 °C resulted in the quantitative formation of 2-(methyl- or *tert*-butyl)-5-PIB-furan, most probably due to the intermediate formation of an acetal group which eliminates methanol. The ^1H NMR spectrum of 2-*tert*-butyl-5-PIB-furan is shown along with the assignments in Figure 2.

The spectrum is similar to that of 2-*tert*-butyl-5-(2,4,4-trimethyl-2-pentyl)furan (see Experimental Section) which was used as a model compound to confirm the assignments. Peak intensities at 5.8 ppm (2*H* on C3 and C4, in Fu ring) and 1.4 ppm ($-C\boldsymbol{H}_2(CH_3)_2-$Fu) confirmed one 2-alkylfuran ring per chain end. Identical results were obtained when 2-MeFu was employed as a capping agent. The ^{1}H NMR spectral assignments are as follows. **(**a**)** 2-Me-5-PIB-Fu: 5.80 ppm (m, 2H), $PIBCH_2C(CH_3)_2\boldsymbol{Fu}CH_3$, 2.25 ppm (s, 3H), $PIBCH_2C(CH_3)_2FuC\boldsymbol{H}_3$, 1.75 (s, 2H), $PIBC\boldsymbol{H}_2C(CH_3)_2FuCH_3$. (b**)** 2-Me-5-PIB-2,5H-Fu: 5.80 ppm (m, 2H), PIB-2,5H-***Fu***-CH_3, 4.90 ppm (m,1H) PIB-2,5***H***-Fu-CH_3, 4.45 ppm (d, 1H), PIB-2,***5H***-Fu-CH_3.

To determine the stability of the PIB-Fu$^+$-R cation, after complete capping of living PIB was achieved with 2-tBuFu in Hex/CH_2Cl_2 60/40 (v/v) at −80 °C, the reaction mixture was allowed to warm to −40, −20, and 0 °C, and at these temperatures Bu_3SnH was added to trap the remaining cations.[20] The products were then isolated and characterized by ^{1}H NMR spectroscopy. Importantly, decapping was not observed at any temperature, which indicates that with 2-alkylfurans retroaddition is absent or negligible; i.e., capping is irreversible, or the apparent equilibrium constant of capping/decapping is very high. However, two different end groups, dihydrofuran and furan functionalities, were observed in the ratio of 9/1, 5/5, and 0.1/9.9 at −40, −20, and 0 °C, respectively. We hypothesized that the furan functionality is due to proton elimination, and these ratios reflect the decreasing stability of the chain ends since the extent of proton elimination (that results in furan functionalities) increases with increasing temperature. Subsequent capping experiments with 2-phenyl-Fu (2-PhFu) using *on-line* UV−vis spectroscopy reported elsewhere[21] confirmed our hypothesis; the resulting allylic cation, PIB-Fu$^+$-Ph, was found to be stable up to −40 °C and slowly eliminated H^+ at −20 °C.

BCl_3 was also found to be an efficient Lewis acid in the capping reaction of living PIBCl with 2-tBuFu. Quantitative capping of living PIB (M_n = 1500), prepared using the TMPCl/BCl_3/IB/CH_3Cl/−40 °C system, was obtained within 60 min reaction time.

Block Copolymerization via Capping with 2-Alkylfurans Upon capping the living PIB chain ends with 2-alkylfurans, a stable carbocation is generated which may be used to initiate the polymerization of highly reactive monomers such as vinyl ethers. This concept was tested first using 2-tBuFu as capping agent for the synthesis of P(IB-*b*-MeVE) block copolymers by sequential monomer addition. After capping at −80 °C, the Lewis acidity was moderated by the introduction of $Ti(OiPr)_4$ followed by the addition of MeVE. The temperature was then raised to 0 °C to polymerize MeVE.[8] The product was characterized by ^{1}H NMR spectroscopy and GPC, which indicated the presence of 2-tBu-5-PIB-Fu, i.e., that the crossover was not quantitative. By column chromatography the crossover efficiency was determined to be 66%. Modifying the reaction conditions, such as increasing the reaction time at −80 °C (before raising the temperature to 0 °C), or increasing the solvent polarity from Hex/CH_2Cl_2 60/40 to 40/60 v/v, or replacing $Ti(OiPr)_4$ with $Ti(OEt)_4$, did not increase the crossover efficiency. However, higher MeVE polymerization rates were found when $Ti(OiPr)_4$ was used to tune the Lewis acidity (~100% conversion in 75 min) compared to that with $Ti(OEt)_4$ (67% conversion in 120 min), at $[Ti(OR)_4]/[TiCl_4] = 0.6$. In Figure 3 the overlaid GPC RI traces of the starting PIB and the block copolymer before and after separation from homo-PIB are shown.

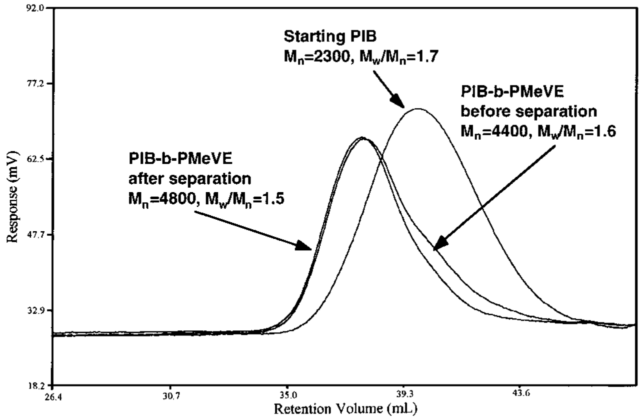


Figure 3. Block copolymerization of IB with MeVE. Reaction conditions: [TMPCl] = 1×10^{-2} M, [DTBP] = 3×10^{-3} M, [$TiCl_4$] = 6×10^{-2} M, [IB] = 3.6×10^{-1} M, [$Ti(OiPr)_4$] = 4.2×10^{-2} M, [tBuFu] = 1.05×10^{-2} M, [MeVE] = 6.8×10^{-1} M, Hex/CH_2Cl_2 60/40 v/v. Polymerization time: IB, 30 min at −80 °C; MeVE, 110 min at 0 °C.

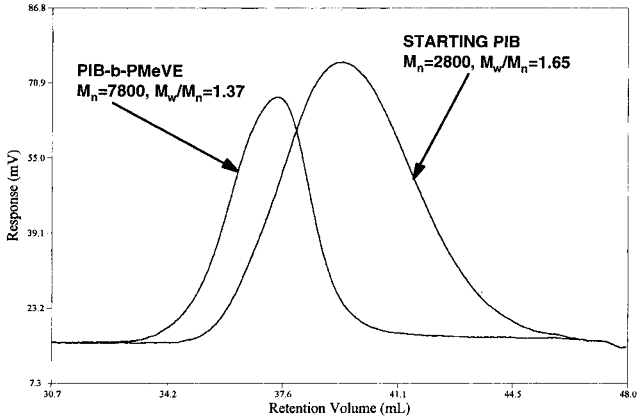


Figure 4. GPC RI traces of the starting PIB and the purified diblock. [$Ti(OiPr)_4$] = 4.2×10^{-2} M, [MeVE] = 0.68 M, 60 min at −80 °C and 80 min at 0 °C, 75% crossover efficiency. Other reaction conditions provided in Figure 3 and Table 1.

Table 1. Column Chromatography on Silica Gel of the PIB-*b*-PMeVE Diblock[a]

no.	eluant	vol (mL)	Wpi (g)	ΣWpi (g)	% Wpi	Σwpi (%)
1	Hex	20	0.0755	0.0755	8.31	8.31
2	Hex	40	0.0112	0.0867	1.23	9.55
3	Hex	60	0.0000	0.0867	0.00	9.55
4	Hex	80	0.0000	0.0867	0.00	9.55
5	Hex	100	0.0000	0.0867	0.00	9.55
6	THF	120	0.0000	0.0867	0.00	9.55
7	THF	140	0.5750	0.6617	63.32	72.87
8	THF	160	0.1949	0.8566	21.46	94.33
9	THF	180	0.0053	0.8619	0.58	94.91
10	THF	200	0.0081	0.8700	0.89	96.12

[a] Total amount of polymer loaded in the column, 0.9081 g. Wpi: the weight of polymer in sample *i* obtained from the column. [2-MeFu] = 1.1×10^{-2} M. Other reaction conditions provided in Figure 3.

Capping of living PIB with 2-MeFu was also used in the synthesis of P(IB-*b*-MeVE) block copolymers by sequential monomer addition. The GPC RI traces of the starting PIB and that of the purified diblock are overlaid in Figure 4. The crossover efficiency using 2-MeFu was found to be 75%, determined by column chromatography (Table 1), i.e., somewhat higher than that obtained using 2-tBuFu under identical conditions.

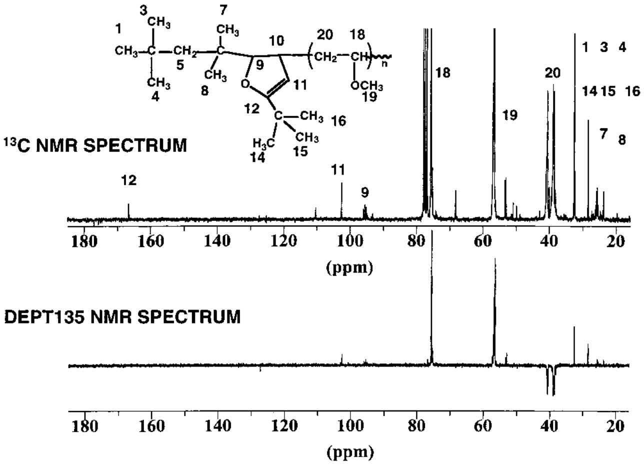


Figure 5. Overlaid ^{13}C NMR and DEPT 135 spectra of a PIB-*b*-PMeVE copolymer.

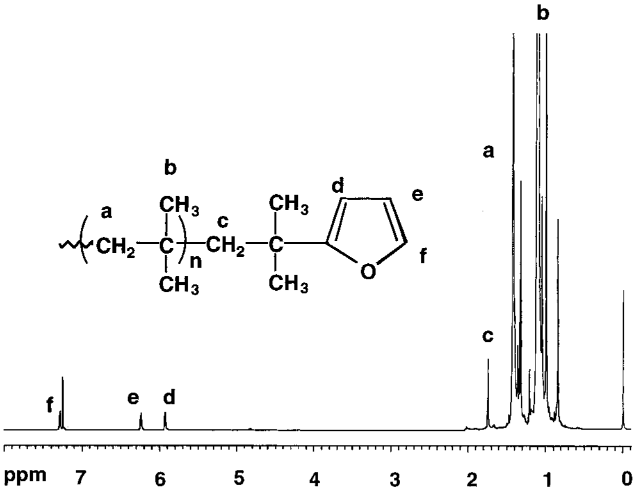


Figure 6. ^{1}H NMR spectrum of furan functionalized PIB.

The relatively low crossover efficiency prompted us to investigate the crossover mechanism. In Scheme 1, the cation at position 2 is a stable tertiary allylic cation next to an oxygen atom. The *tert*-butyl group, which prevents diaddition of 2-tBuFu, however, also imposes significant steric hindrance on the approach of MeVE, and therefore initiation is more likely from C-4, which is less sterically hindered. This was verified by the careful study of the overlaid ^{13}C NMR and DEPT 135 spectra shown in Figure 5. The positions of carbons 11 and 12 for the furan ring in the ^{13}C NMR spectrum are very characteristic and can be assigned unambiguously. It can be clearly seen that the peak due to C-12, which is olefinic and is not connected to any protons, disappears in the DEPT 135 experiment while C-11 gives a positive methine peak (=CH−).

It is likely that initiation of MeVE is also from the C-4 position using MeFu as capping agent.

The Synthesis of Furan Functional PIBs. Recently, we reported[2] the quantitative synthesis of furan functionalized PIBs by the reaction of polyisobutenyl diphenylcarbenium ion (PIB-DPE$^+$) with 2-Bu$_3$SnFu. Continuing our investigations, we have found that the reaction between 2-Bu$_3$SnFu and living PIB$^+$ (i.e., without DPE capping) in Hex/CH$_3$Cl 60/40 v/v in the presence of TiCl$_4$ at −80 °C is also rapid, yielding 2-PIB-Fu in 7 min. The ^{1}H NMR spectrum of the product 2-PIB-Fu is shown in Figure 6.

Quantitative addition was indicated by the disappearance of the peaks at 1.9 ppm (PIB−C$\boldsymbol{H}_2$−C(CH$_3$)$_2$−Cl) and 1.69 ppm (PIB−CH$_2$−C(C$\boldsymbol{H}_3$)$_2$−Cl). A new set of peaks at 1.8, 5.9, 6.23, and 7.3 ppm appeared due to the presence of the furan ring at the chain end. The chemical shifts of the carbon atoms of the furan ring are very characteristic in the ^{13}C NMR spectrum and are as follows: C^2, 163 ppm; C^3, 104 ppm; C^4,110 ppm; and C^5, 140 ppm.

In contrast to the quantitative capping of living PIB with with 2-tBuFu, the functionalization of living PIB (M_n = 1500) with 2-Bu$_3$SnFu in the presence of BCl$_3$ in CH$_3$Cl at −40 °C failed as the PIBCl chain ends remained unreacted even after 15 h reaction time. Since BCl$_3$ (0.5 M) was present in large excess over 2-Bu$_3$SnFu (4.8 × 10^{-2} M), transmetalation that gives rise to the formation of BCl$_2$Fu (and nBu$_3$SnCl), which is likely too weak to ionize PIBCl, may explain the results. This raises an important question about the mechanism of the reaction between PIBCl, TiCl$_4$, and 2-Bu$_3$SnFu. Is the transfer of furan group the result of direct interaction of the PIB$^+$ living ends with 2-Bu$_3$SnFu, or does it take place via rapid transmetalation between 2-Bu$_3$SnFu and TiCl$_4$ which gives rise to TiCl$_3$Fu in the first step, followed by ionization of PIBCl and furan group transfer by TiCl$_3$Fu? Although a detailed investigation of mechanism was not the main goal of this study, knowledge of the mechanism would have significant synthetic consequences, as this will become clear later.

Transmetalation reactions and particularly the reaction of titanium halides with organoaluminum, -zinc, -magnesium, etc., compounds are well documented in the literature. The products of transmetalation reactions have also been exploited in preparative organic chemistry. The mechanisms of reactions in the presence of the two metal compounds such as the Lewis acid promoted addition of allylstannanes to aldehydes, ketones, acetals, and other functions however have been debated. Boaretto et al.[22] proposed that the actual species that react with aldehydes are the allylmetal compounds which arise upon fast transmetalation between allyltributylstannanes and Bu$_2$SnCl$_2$, BF$_3$, or TiCl$_4$. A similar observation was reported by Denmark and co-workers,[23] who found that metathesis of allyltrimethylstannane with SnCl$_4$ is instantaneous and quantitative at −80 °C and concluded that allyltrimethylstannane is not involved in the reaction with the aldehyde when free SnCl$_4$ is present. Metathesis was also found to be faster than addition with fully complexed SnCl$_4$, i.e., in the absence of free SnCl$_4$. In contrast, Keck at al.[24] reported that transmetalation is only important under conditions where free uncomplexed SnCl$_4$ is present.

On the basis of the above references, it was not surprising that, upon mixing TiCl$_4$ with 2-Bu$_3$SnFu in Hex/CH$_3$Cl 60/40 v/v at −80 °C, Bu$_3$SnCl was obtained in quantitative yield as determined by the ^{1}H NMR spectrum of the isolated product. Organotitanium compounds could not be isolated most likely due to decomposition when the temperature was allowed to rise to room temperature since most alkyltitanium compounds are not stable above −40 °C. In the functionalization reaction of PIB$^+$ with 2-Bu$_3$SnFu, TiCl$_4$ is always used in excess over the PIB chain ends; therefore, transmetalation may be a competitive reaction. To determine whether TiCl$_3$Fu, the product of transmetalation, maybe the true reactant, preformed PIBCl was reacted with premixed TiCl$_4$ and 2-Bu$_3$SnFu in Hex/CH$_3$Cl 60/40 v/v

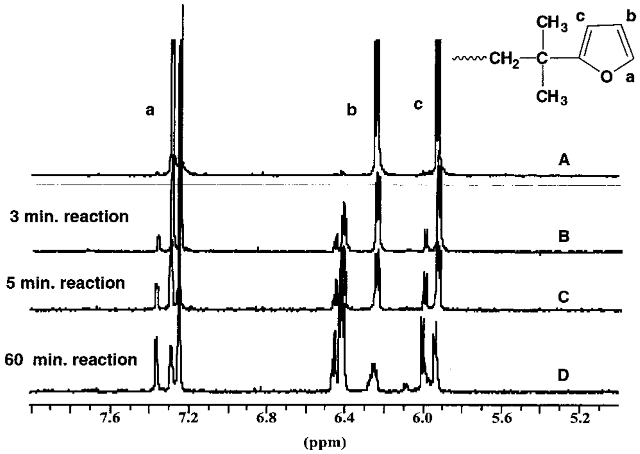


Figure 7. Overlaid ^{1}H NMR spectra of furan functionalized PIBs obtained under various conditions.

solution at −80 °C. The reaction was carried out using different premixing times between $TiCl_4$ and 2-Bu_3SnFu and varying reaction times with PIBCl. The premixing time however did not affect the results. In Figure 7 the ^{1}H NMR spectra of the products in the region between 5 and 8.0 ppm are shown for 3 and 60 min reaction time.

For comparison, the spectrum of PIB-Fu (spectrum A) is also shown. With 3 min reaction time the product composition was 75% PIB-Fu, 13% unreacted PIBCl, and 12% unidentified side products (Figure 7, spectrum B). Identical results were obtained when PIBCl was substituted with 2-chloro-2,4,4-trimethylpentane (TMPCl) as a model compound. Surprisingly, when the reaction time was increased to 60 min, only ∼25% functionalization was observed along with unidentified side products as indicated in Figure 7 (spectrum D). This finding is not in accord with the results of the in situ functionalization, and therefore the two reaction mechanisms may be different.

Regardless of the reaction mechanism, i.e., direct substitution at C-2 of 2-Bu_3SnFu by PIB^+ or rapid transmetalation followed by ionization and Fu group transfer by $TiCl_3Fu$, 2,5-bis(tributylstannyl)furan could be considered as a coupling agent. However, when a stoichiometric amount of 2,5-bis(tributylstannyl)furan was reacted for up to 1 h with living PIB, coupling was absent; i.e., the increase of the M_n was not observed. Similarly, both reaction mechanisms should yield 2-PIB-5-methylfuran using 2-tributylstannyl-5-methylfuran. ^{1}H NMR spectroscopic analysis of the isolated product obtained after 30 min reaction in Hex/CH_3Cl 60/40 v/v at −80 °C however indicated that although the PIBCl chain ends completely disappeared, 2-PIB-5-methylfuran was obtained in very low yield (10%). These results suggest that the mechanism may be different from the two discussed above and may involve addition to the 5-position of the furan ring in 2-Bu_3SnFu followed by proton transfer from C-5 to C-2, i.e., substitution of the Bu_3Sn− group.

Reactions of Furan Functional PIBs. We have shown that rapid and quantitative monoaddition of t-BuFu to living PIB^+ can be achieved. Since furan functional polyisobutylene (2-PIB-Fu) can be considered as a polymeric capping agent, 2-PIB-Fu was expected to react with living cationic polymers in coupling reactions. The proof of this concept was obtained in a reaction of 2-PIB-Fu with living PIB^+ under conditions similar to capping PIB^+ with 2-tBuFu. The M_n and M_w/M_n of the products obtained after different reaction times are shown in Figure 8. According to GPC (Figure 9) and ^{1}H NMR spectroscopy, close to quantitative coupling of the two PIB chains was achieved in ∼3 h. The M_n of the product was almost equal to the sum of the M_n's of 2-PIB-Fu and living PIB, and the ^{1}H NMR spectrum of the product, similar to that shown in Figure 2, exhibited a singlet at 5.8 ppm since the two protons H^3 and H^4 on the ring are chemical shift equivalent.

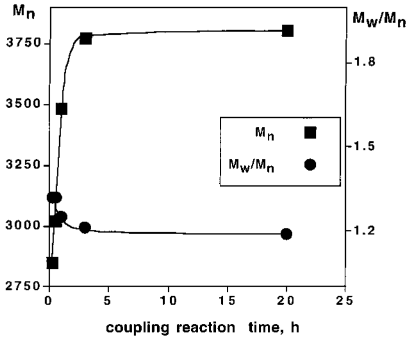


Figure 8. M_n and M_w/M_n versus reaction time in the reaction of living PIB (M_n = 3000) with PIB-Fu (M_n = 1200). Polymerization conditions for living PIB: [TMPCl] = 2 × 10^{-3} M, [$TiCl_4$] = 3.6 × 10^{-2} M, [IB] = 0.1 M, Hex/CH_3Cl 60/40 (v/v) −80 °C, IB polymerization 60 min.

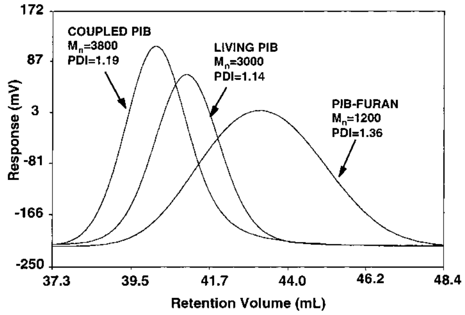


Figure 9. Overlaid GPC RI traces of the living PIB^+, PIB′-Fu, and the coupled PIB−Fu-PIB′ product. Reaction conditions provided in Figure 8.

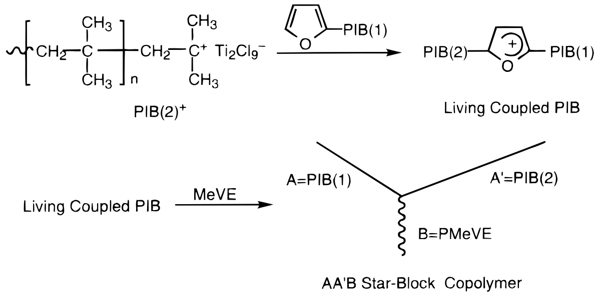
While the concept of coupling a living cationic polymer with an ω-furan functional polymer has been demonstrated above using living PIB^+ and 2-PIB-Fu, more importantly, coupling can also be utilized to obtain AB-type block copolymers. It is also apparent that ω-furan functionalized polymers can be used as precursor polymers for the synthesis of ABC and AA′B-type three-arm star-block copolymers, where for instance A and A′ represent PIB segments with different molecular weights and B and C represent chemically different block segments, such as PMeVE or polystyrene. To illustrate this concept, the strategy for the synthesis of AA′B-type star-block copolymers, where A = PIB(1), A′ = PIB(2), and B = PMeVE, is shown in Scheme 2. It involves the coupling reaction of PIB(1) with ω-furan functionality (A) with living PIB(2) of a different molecular weight (A′), followed by the chain-ramification polymerization of MeVE to yield the PMeVE block segment (B). A preliminary report on the synthesis of PIB-*s*-PIB′-*s*-PMVE according to Scheme 2 is published elsewhere.[25]

Research is in progress in our laboratory in all of the above areas.

Conclusion

We have shown that quantitative monoaddition of 2-alkylfurans to living polyisobutylene takes place in

Scheme 2. Synthesis of AA′B Triarm Type Star-Block Copolymers



the temperature range of −80 to −40 °C, in conjunction with TiCl$_4$ or BCl$_3$ as Lewis acid, resulting in the formation of a stable allylic cation. It appears therefore that general methodologies developed by us earlier using non(homo)polymerizable monomers in cationic macromolecular design and synthesis of block copolymers and functional polymers apply to 2-alkylfurans. A major advantage of using furan derivatives over DPE derivatives is that since retroaddition does not take place, quantitative capping can be achieved under much less restricted experimental conditions. The allylic cation generated also appears to be more stable and somewhat sterically hindered which appears to adversely affect the efficiency of initiation of a second monomer. It is also noteworthy that polymeric capping agents can be readily prepared by a simple reaction between living PIB and 2-Bu$_3$SnFu. The 2-PIB-Fu obtained in this reaction quantitatively adds to living PIB, which opens up new avenues to prepare AB-type linear block copolymers, as well as ABC- and AA′B-type three-arm star-block copolymers.

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Supporting Information Available: The ^{1}H NMR spectra of 2-(tributylstannyl)-5-methylfuran and 2,5-bis(tributylstannyl)furan. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hadjikyriacou, S.; Fodor, Zs.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32* (6), 1137.
(2) Hadjikyriacou, S.; Faust, R. *Polym. Mater. Sci. Eng.* **1997**, *76*, 300.
(3) Fodor, Zs.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31* (12), 1983.
(4) Fodor, Zs.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32* (3), 575.
(5) Li, D.; Faust, R. *Macromolecules* **1995**, *28*, 1383.
(6) Li, D.; Faust, R. *Macromolecules* **1995**, *28*, 4893.
(7) Hadjikyriacou, S.; Faust, R. *Macromolecules* **1995**, *28*, 7893.
(8) Hadjikyriacou, S.; Faust, R. *Macromolecules* **1996**, *29*, 5261.
(9) Li, D.; Hadjikyriacou, S.; Faust, R. *Macromolecules* **1996**, *29*, 6061.
(10) Mayr, H.; Roth, M.; Faust, R. *Macromolecules* **1996**, *29*, 19.
(11) Bae, Y. C.; Fodor, Zs.; Faust, R. *Polym. Prepr.* **1996**, *37* (1), 801.
(12) Charleux, B.; Moreau, M.; Vairon, J. P.; Hadjikyriacou, S.; Faust, R. *Macromol. Symp.* **1998**, *132*, 25.
(13) Schlaad, H.; Erentova, K.; Faust, R.; Charleux, B.; Moreau, M.; Vairon, J. P.; Mayr, H. *Macromolecules* **1998**, *31*, 8058.
(14) Cationic Macromolecular Design Using Non(homo)polymerizable Monomers. In *Cationic Polymerization and Related Processes;* Puskas, J. E., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1999.
(15) Gotta, F. M.; Mayr, H. *J. Org. Chem.* **1998**, *63*, 9769.
(16) Razzouk, H.; Bouridah, A.; Gandini, A.; Cheradame, H. In *Cationic Polymerization and Related Processes;* Goethals, E. J., Ed.; Academic Press: New York, 1984; p 355.
(17) Fitzpatrick, J. E.; Milner, D. J.; White, P. *Synth. Commun.* **1982**, *12* (6), 489.
(18) Cotts, B. D. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1381.
(19) Pernecker, T.; Kennedy, J. P. *Polym. Bull.* **1992**, *29*, 27.
(20) Basso, N.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1046.
(21) Kwon, Y.; Hadjikyriacou, S.; Faust, R.; Cabrit, P.; Moreau, M.; Charleux, B.; Vairon, J.-P. *Polym. Prepr.* **1999**, *40* (2), 681.
(22) Boaretto, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1987**, *321*, 199.
(23) Denmark, E. S.; Wilson, T.; Willso, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 984.
(24) Keck, E. G.; Andrus, M. B.; Castellino, S. *J. Am. Chem. Soc.* **1989**, *111*, 8136.
(25) Yun, J.; Hadjikyriacou, S.; Faust, R. *Polym. Prepr.* **1999**, *40* (2), 1041.

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