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Living Coupling Reaction in Living Cationic Polymerization. 3. Coupling Reaction of Living Polyisobutylene Using Bis(furanyl) Derivatives

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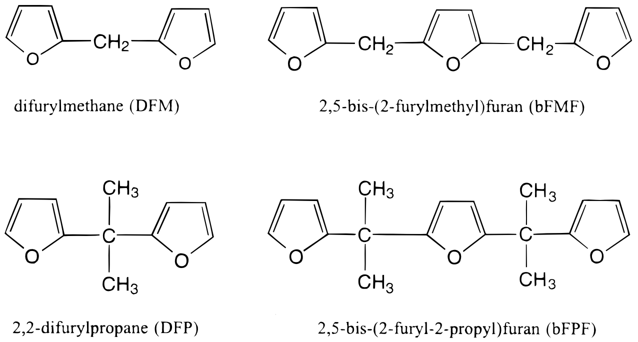
ABSTRACT: Living coupling reactions of living polyisobutylene (PIB) with bis(furanyl) compounds, 2,2-difurylmethane (DFM), 2,5-bis(2-furylmethyl)furan (bFMF), 2,2-difurylpropane (DFP), and 2,5-bis(2-furyl-2-propyl)furan (bFPF) were investigated in the presence of $TiCl_4$ as Lewis acid in hexanes/CH_3Cl 60/40 and 40/60 (v/v) at −80 °C and with bFPF in conjunction with BCl_3 in CH_3Cl at −40 °C. The products obtained with DFM and bFMF were slightly colored most probably due to α-hydride abstraction and the development of conjugated structures. DFP and bFPF, lacking α-hydrogens, yielded colorless products. In hexanes/CH_3Cl 60/40 (v/v), coupling was very slow and incomplete after 2 h with DFM and DFP, which was ascribed to deactivation of the second furanyl ring after monoaddition. Coupling was faster with bFMF; however, the coupling efficiency was only 85% after 2 h due to some side reactions that consumed bFMF. Coupling was rapid and quantitative with bFPF in the presence of $TiCl_4$ in hexanes/CH_3Cl 60/40 (v/v) at −80 °C. Increasing the solvent polarity to hexanes/CH_3Cl 40/60 (v/v) further increased the rate by 2-fold. Efficient, albeit slow, coupling was also achieved with bFPF in CH_3Cl at −40 °C in the presence of BCl_3. The mechanism of the coupling reaction was investigated in the presence of $TiCl_4$ in hexanes/CH_3Cl 60/40 (v/v) at −80 °C by quenching the reaction mixture with tributyltin hydride after complete coupling had been achieved. Identification of the product structure by ^1H NMR spectroscopy verified the formation of stable dications upon coupling and confirmed that this reaction is a living coupling reaction.

Introduction

Coupling reactions of living cationic polymers are important in the preparation of telechelic polymers when initiators containing unreactive (or protected) functional groups are utilized. Coupling is also valuable in the preparation of ABA type triblock copolymers by coupling living AB diblock copolymers, especially when crossover from monomer B to monomer A is inefficient. Several coupling agents for living poly(vinyl ethers) and poly(α-methylstyrene) have been reported in cationic polymerization,[1] but quantitative coupling was limited to living oligomers. We have reported on a facile and quantitative coupling of ω-isopropenyl functional PIB with catalytic amounts of triflic acid in hexanes (Hex) at −80 °C.[2] Rapid and quantitative coupling of living PIB, obtained in Hex/methyl chloride (CH_3Cl) 60/40 (v/v) at −80 °C in conjunction with $TiCl_4$, has also been reported recently with 1,3-bis[2-(3-trimethylsilyl)propenyl]benzene as coupling agent.[3]

We have also disclosed a more general approach based on methodologies of using non(homo)polymerizable monomers in living cationic polymerization, the living coupling reaction of living cationic polymers. We have achieved rapid and quantitative coupling of living PIB using bis(diphenylethylene) (bis-DPE) compounds such as 2,2-bis[4-(1-phenylethenyl)phenyl]propane (BDPEP), where two DPE moieties are separated by a spacer group.[4,5] Very recently, we extended the concept of using non(homo)polymerizable monomers in carbocationic macromolecular design and synthesis to 2-alkylfurans. Rapid and quantitative monoaddition of 2-methyl-, 2-*tert*-butyl-, and 2-phenylfuran to living PIB has been observed in conjunction with $TiCl_4$ as Lewis acid in Hex/CH_2Cl_2 (or CH_3Cl) 60/40 (v/v) at −80 °C and with BCl_3 in CH_3Cl even at −40 °C.[6,7] In contrast to DPE and derivatives, retroaddition (decapping) was not observed even at 0 °C. In conjunction with $TiCl_4$, however, a slow decomposition of the furanyl carbocation by proton elimination took place at −20 °C. Upon capping the living PIB chain ends with 2-alkylfurans, a stable carbocation is generated which was shown to initiate the polymerization of methyl vinyl ether (MeVE), to yield poly(IB-*b*-MeVE) block copolymers.[8]

Chart 1



The aforementioned advantages of 2-alkylfurans over DPE and derivatives incited us to investigate various difuranyl compounds as coupling agents. Difuranyl compounds shown in Chart 1 have been disclosed by Gandini and Salon in US 5,260378. According to the invention, these compounds can be used to prepare cationic diblock copolymers such as poly{IB-*b*-styrene(St)}. First, IB is polymerized in the presence of furan derivative in conjunction with $EtAlCl_2$ in CH_2Cl_2 at −20 °C. After 30 min, unreacted IB is removed and St is added. The polymerization reportedly yields low molecular weight block copolymers; however, the blocking efficiency was not reported. Since the polymerizations of IB or St are not living under these conditions,

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homoPIB and homoPSt almost certainly contaminate the diblock copolymer. Considering that the cation formed upon addition of PIB^+ (or PSt^+) to the bis(furanyl) compound is unstable at −20 °C, it most likely rapidly eliminates H^+.

In the present publication we report on the applications of difuranyl derivatives as living coupling agents, in the living cationic polymerization of IB.

Experimental Part

Materials. 2,6-Di-*tert*-butylpyridine (DTBP) (Maybridge Chemical Co., MCC) was purified by vacuum distillation from CaH_2. CH_3Cl was passed through in-line gas purifier columns, (1.0 ft long) 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 under N_2, from CaH_2, just before use. Hexanes (Hex) were rendered olefin-free by refluxing it over concentrated sulfuric acid for 48 h. They were 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 under N_2.

2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared by passing dry HCl through a 30% solution of 2,4,4-trimethyl-1-pentene in dried and distilled CH_2Cl_2 at 0 °C for 3 h. The solvent and excess HCl were removed on the rotavap, and the crude product was purified by distillation from CaH_2.

Titanium(IV) chloride ($TiCl_4$, 99.9%, Aldrich) and boron trichloride (BCl_3, 99.9%, Aldrich) were used as received. Difurylmethane (DFM), 2,5-bis(2-furylmethyl)furan (bFMF), 2,2-difurylpropane (DFP), and 2,5-bis(2-furyl-2-propyl)furan (bFPF) were synthesized according to the literature.[9]

Procedures. A representative process for IB polymerization and coupling is described below. The concentrations given reflect the concentrations in the polymerization solution. $TiCl_4$ (2×10^{-2} M) was mixed with 2,6-di-*tert*-butylpyridine (DTBP) (3×10^{-3} M) in a mixture of Hex/CH_3Cl 60/40 (v/v) at −80 °C for 5 min. TMPCl (2×10^{-2} M) was introduced next, followed by the immediate addition of IB (1 M), and allowed to polymerize. The total polymerization volume was 400 mL.

After the conversion of IB was close to 100% (90 min), the coupling agent 2,5-bis(2-furyl-2-propyl)furan (bFPF) or 2,2-difurylpropane (DFP) (1.1×10^{-2} M) was introduced as a solution in Hex/CH_3Cl 60/40 (v/v). The coupling reaction was allowed to proceed for 3 h and then was quenched with excess prechilled methanol. The polymer was recovered and purified three times by reprecipitation from Hex/methanol. It was dried overnight under vacuum and characterized by gel permeation chromatography (GPC) and ^1H NMR spectroscopy.

Characterization. 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. THF was used as eluent at a flow rate of 1.0 mL/min, and PSt standards were used to construct the universal calibration curve. The detector signals (RI, UV, and differential viscosity) were recorded on a PC computer for molecular weight and molecular weight distribution determination using the Viscotek TriSEC GPC-viscometry software. ^1H NMR spectroscopy was carried out on a Bruker 250 MHz instrument. Spectral peak assignments were carried out by the use of ACD/HNMR 1.0 computer software from Advanced Chemistry Development Inc.

Results and Discussion

Table 1. Coupling of Living PIB in the Presence of $TiCl_4$ in Hex/CH_3Cl 60/40 (v/v) at −80 °C[a]

	[bis(furan)]/[TMPCl]	[$TiCl_4$]/[TMPCl]	PIBCl, %	monoadded, %	coupled, %
DFP	0.55	1.0	51	32	17
	0.55	2.2	27	48	25
	0.51	8.0	14	39	47
bFPF	0.55	1.0	60	18	22
	0.55	2.2	0	28	72
	1.0	2.2	0	62	38
	0.51	2.2	0	16	84
	0.51	4.0	0	10	90
	0.51	8.0	0	10	90

[a] Reaction conditions: for IB polymerization, [TMPCl] = 2×10^{-2} M, [DTBP] = 3×10^{-3} M, [IB] = 1 M. Polymerization time 90 min. Coupling reaction time 180 min. Coupling reaction volume 20 mL.

We started our investigations by employing difurylmethane (DFM) (Chart 1), at a close to stoichiometric ratio ([DFM]/[TMPCl] = 0.52) in hexanes/CH_3Cl 60/40 (v/v) in the presence of $TiCl_4$ at −80 °C. At [$TiCl_4$] = 4.4×10^{-2} M after 2 h, the M_n of the product increased only by 21% ($M_{\mathrm{ncontrol}} = 2400$, $M_{\mathrm{ncoupled}} = 2900$). The product composition was determined by ^1H NMR spectroscopy by comparing the two protons on the coupling agent (positions C4 and C4′) of the coupled chains, at 5.85 ppm to the two protons of the unreacted $\sim CH_2{-}C(CH_3)_2{-}Cl$ ends at 1.95 ppm, and the single proton at the C5 position of the unreacted external furanyl ring at 7.3 ppm for the monoadded product. It was determined that 35% of the living PIB chains coupled, 30% remained unreacted, and 35% monoadded product was also present. The low coupling efficiency (defined as the percent of PIB chains that coupled) was attributed to deactivation of the second ring upon monoaddition of living PIB. A similar rationalization has already been used to explain the finding that 1,3-bis(1-phenylethenyl)benzene (MDDPE) is an inefficient living coupling agent for living PIB.[4] Rapid and quantitative coupling, however, has been accomplished with bis-DPE compounds such as BDPEP, where the two DPE moieties are separated by a spacer group. Following the same strategy, to increase the separation between the two furan rings, bFMF (Chart 1) was synthesized and employed in coupling reactions under conditions identical to that used for DFM. Coupling was much faster with bFMF compared to DFM, as indicated by the increase of the molecular weight from 2400 to 4000 in 7 min and to 4700 within 60 min. According to ^1H NMR spectroscopic analysis of the product, 85% coupling efficiency was achieved after 60 min. Interestingly, the peaks at 7.3 ppm, which would indicate the presence of unreacted coupling agent and/or monoadded product, were absent. The GPC chromatogram of the product displayed a small peak at higher molecular weights, indicating a possible side reaction consuming the coupling agent.

A general observation with both coupling agents was that the products exhibited a slight yellow to brown color. It is well documented that hydride abstraction at the α-position to the rings may cause the formation of conjugated structures and the development of color.[10] The lower than 100% coupling efficiency and the formation of colored products in coupling reactions with DFM and bFMF prompted us to investigate other bis(furanyl) derivatives. To eliminate the formation of colored products during coupling, DFP and bFPF (Chart 1), which do not contain α-hydrogen to the rings, were synthesized and employed as coupling agents.

The results of coupling experiments carried out with DFP and bFPF are summarized in Table 1.

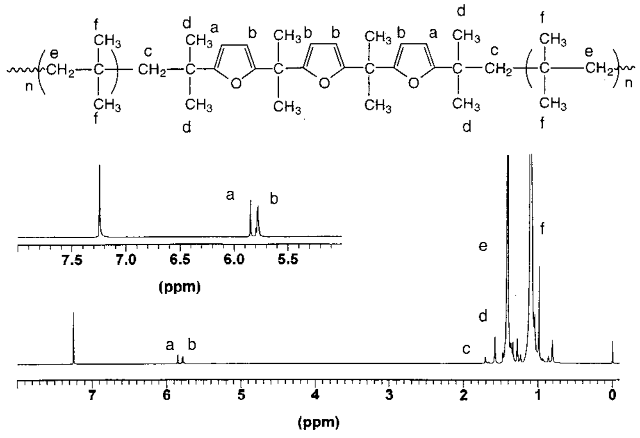


Figure 1. ^{1}H NMR spectrum of bFPF coupled PIB. Reaction conditions: [TMPCl] = 2×10^{-2} M, [DTBP] = 3×10^{-3} M, $[TiCl_4]_{pol} = 2 \times 10^{-2}$ M, [IB] = 1 M, solvent Hex/CH_3Cl 60/40 (v/v), $[TiCl_4]_{coupl} = 8 \times 10^{-2}$ M, [bFPF] = 7.65×10^{-3} M, $M_{ncontrol} = 3300$, $M_{ncoupled} = 6000$.

Similarly to DFM, DFP was found to be ineffective as a coupling agent most probably due to same reason, i.e., deactivation of the second ring upon monoaddition. Although the rate of coupling increased with increasing $[TiCl_4]$, even at a $[TiCl_4]$/[TMPCl] ratio of 8, 14% of the PIB ends remained unreacted after 3 h. Therefore, further experimentation with DFP was discontinued, and we continued our investigation with bFPF only.

With bFPF, coupling was relatively slow at $[TiCl_4]$/[TMPCl] = 1 as 60% of PIB ends remained unreacted in 3 h. The rate increased with increasing $TiCl_4$ concentration, and PIBCl completely disappeared in 3 h at $[TiCl_4]$/[TMPCl] = 2.2. However, the coupling efficiency was only 72% and 38% at [bFPF]/[TMPCl] = 0.55 and 1, respectively. The product distribution at [bFPF]/[TMPCl] = 1 (62% monoadded and 38% coupled) is somewhat different from the expected statistical distribution (50% monoadded and 50% coupled), assuming that the two furanyl rings react independently. This may indicate that the second addition is somewhat slower than the first one. Thus, using a stoichiometric amount of coupling agent is very important. This is an important difference in comparison with bis-DPE compounds, where the second addition was found to be much faster than the first one, and therefore, quantitative coupling was also obtained in the presence of excess bis-DPE. When the [bFPF]/[TMPCl] ratio was decreased to 0.51, at $[TiCl_4]$/[TMPCl] $\geq$ 2.2 close to quantitative coupling was observed in 3 h.

In Figure 1 the ^{1}H NMR spectrum of a representative sample of coupled PIB is shown along with the assignments.

Essentially quantitative coupling is indicated by the disappearance of the methylene and methyl signals at 1.69 and 1.95 ppm due to $-CH_2C(CH_3)_2Cl$ chain ends as well as the absence of signals at 7.3 ppm that correspond to monoadded product. The re-formation of the furan rings to which the two PIB chain are attached is attributed to quenching with methanol, resulting in the intermediate formation of an acetal, which eliminates methanol (see Scheme 1). A similar observation has already been reported when the product of capping living PIB with 2-alkylfurans was quenched with methanol.[6] In Figure 2, the GPC RI traces of the starting and the coupled PIB are overlaid for comparison.

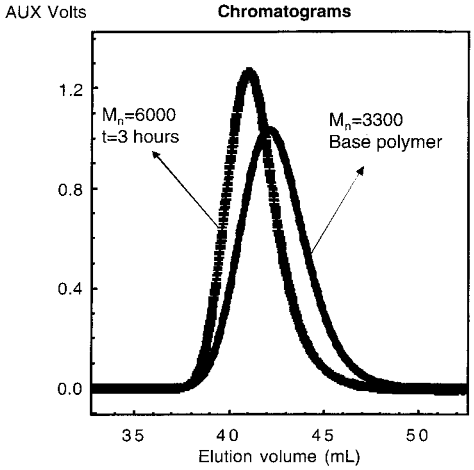
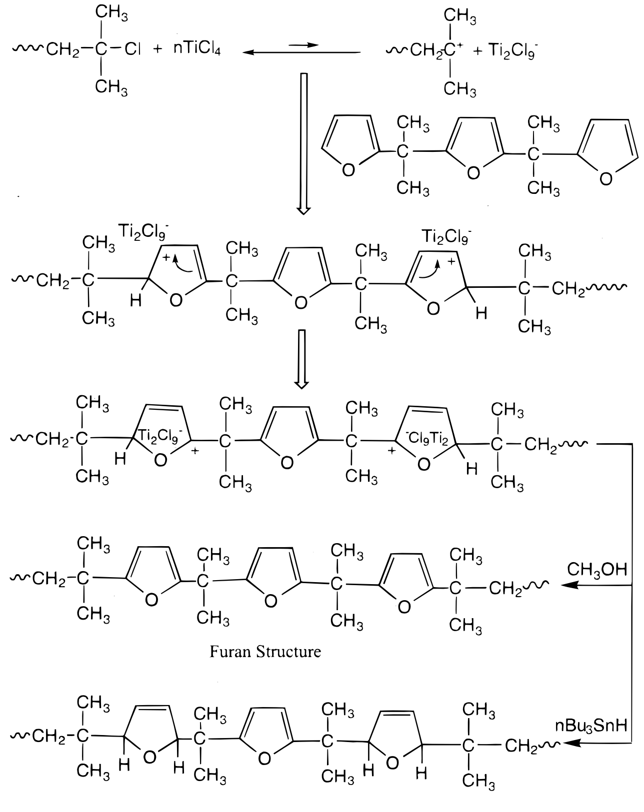


Figure 2. Overlaid GPC RI traces of the starting and coupled PIBs.

Scheme 1. Coupling Reaction with BFPF



Furan Structure

2,5-Dihydrofuran Structure

The mechanism of the coupling reaction was investigated by quenching the coupling reaction with tributyltin hydride (nBu_3SnH) to trap the intermediate carbocations. Since quenching with nBu_3SnH results in the formation of 2,5-dihydrofuran rings[6] that are different from furan rings, the mechanism can be probed by ^{1}H NMR spectroscopy (Figure 3).

In agreement with previous results, it was determined that the addition of living PIB takes place at position 5 on the furan rings. The resulting 2,5-dihydrofuran structure shown in Scheme 1 perfectly agrees with the ^{1}H NMR spectrum in Figure 3.

The effect of the solvent polarity on the rate of coupling was also studied. In Figure 4 the coupling efficiency obtained in Hex/CH_3Cl 60/40 and 40/60 (v/v) is plotted against the reaction time.

According to the results, coupling in Hex/CH_3Cl 40/60 (v/v) is approximately 2 times faster than in Hex/

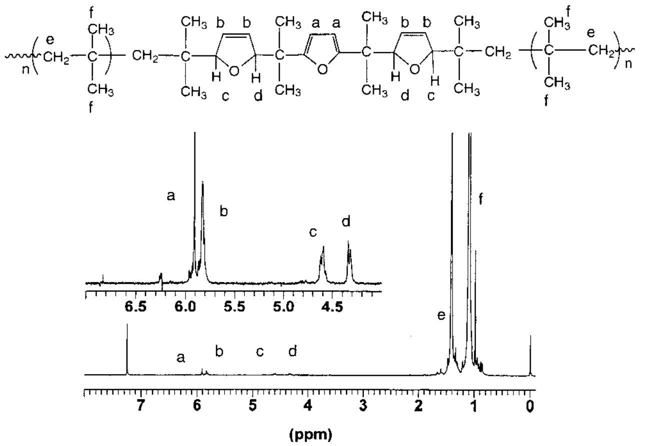


Figure 3. ^{1}H NMR spectrum of the coupled product after quenching the coupling reaction with nBu_3SnH.

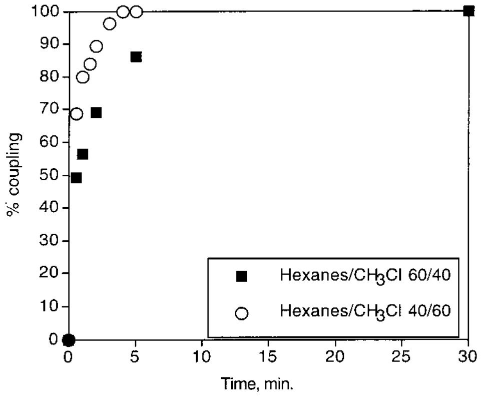


Figure 4. Effect of solvent polarity on the rate of coupling in conjunction with $TiCl_4$ at −80 °C. Reaction conditions: 1. Hex/CH_3Cl 60/40 (v/v): [TMPCl] = 2.03×10^{-2} M, [DTBP] = 3×10^{-3} M, $[TiCl_4]_{pol} = 2 \times 10^{-2}$ M, [IB] = 1 M, $[TiCl_4]_{coupl} = 8 \times 10^{-2}$ M, [bFPF] = 9.17×10^{-3} M; 2. Hex/CH_3Cl 40/60 (v/v): [TMPCl] = 2.0×10^{-2} M, [DTBP] = 3×10^{-3} M, $[TiCl_4]_{pol} = 2 \times 10^{-2}$ M, [IB] = 1 M, $[TiCl_4]_{coupl} = 8 \times 10^{-2}$ M, [bFPF] = 7.9×10^{-3} M.

CH_3Cl 60/40 (v/v). This can be attributed to the larger extent of ionization in the more polar medium.

Coupling of living PIB was also studied in conjunction with BCl_3 in CH_3Cl at −40 °C. Coupling was very slow, as close to complete coupling was achieved only after 14 h. The low rate of coupling is attributed to the extremely low concentration of active PIB^+ ends, which also necessitated using a very long polymerization time (6 h) to reach complete IB conversion. The plot of M_n vs coupling reaction time is shown in Figure 5.

It should be pointed out that living coupling of living PIB has not yet been accomplished and may be unattainable with bis-DPE compounds in conjunction with BCl_3 due to retroaddition at this temperature, and therefore, this is the first example of successful living coupling of living PIB using BCl_3.

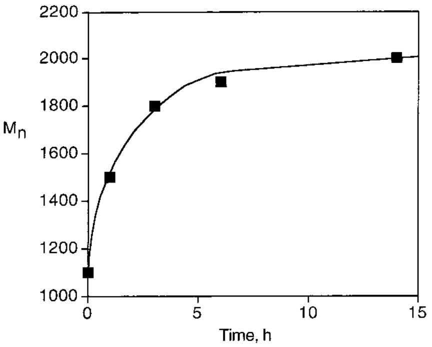


Figure 5. M_n versus time plot for the coupling reaction of living PIB in conjunction with BCl_3 in CH_3Cl at −40 °C. Reaction conditions: for IB polymerization, [TMPCl] = 2.4×10^{-2} M, [DTBP] = 4×10^{-3} M, $[BCl_3] = 2.5 \times 10^{-1}$ M, [IB] = 0.478; for coupling reaction, $[BCl_3] = 5 \times 10^{-1}$ M, [bFPF] = 1.1×10^{-2} M.

Conclusion

2,5-Bis(2-furyl-2-propyl)furan (bFPF), an inexpensive and readily obtainable bis(furanyl) compound, is an efficient coupling agent for living PIB in the presence of $TiCl_4$ as Lewis acid in Hex/CH_3Cl 60/40 and 40/60 (v/v) at −80 °C and in conjunction with BCl_3 in CH_3Cl at −40 °C. Monoaddition somewhat decreases the reactivity of the second furanyl active site in bFPF, and precise stoichiometry is therefore necessary to achieve complete coupling. Coupling results in the formation of stable dications; i.e., this reaction is a living coupling reaction which therefore could potentially be utilized for the synthesis of other macromolecular architectures such as A_2B_2 heteroarm star-block copolymers, center functionalized polymers, etc.

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