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Cationic Macromolecular Engineering Via Furan Derivatives

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SUMMARY: General methodologies for the synthesis of linear and star-block copolymers and functional polymers using furan derivatives are reviewed, based on a study of addition reactions of 2-substituted furans to living polyisobutylene (PIB^+). Rapid and quantitative mono-addition of 2-alkyl (and aryl)furans (2-R-Fu), a new class of non-(homo)polymerizable monomers, to PIB^+ has been observed in conjunction with $TiCl_4$ as Lewis acid in hexane/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. The resulting stable allylic cation ($PIB\text{-}Fu^+\text{-}R$) was found to be an efficient initiating species for the polymerization of methyl vinyl ether (MeVE). Using 2,5-*bis*[1-furanyl)-1-methylethyl]-furan, coupling of living PIB was found to be rapid and quantitative in hexanes(Hex)/CH_3Cl 60/40 or 40/60 (v/v) solvent mixtures at –80 °C in conjunction with $TiCl_4$, as well as in CH_3Cl at –40 °C with BCl_3 as Lewis acid. The kinetics of addition of 2-R-Fu to PIB^+ was investigated by UV-vis spectroscopy. Based on these results and those obtained with substituted 1,1-diarylethylenes earlier, the absolute rate constants of ionization (k_i), reversible termination (k_{-i}) and propagation (k_p) in the polymerization of IB have been determined. By a similar approach the corresponding rate constants have also been determined for the polymerization of styrene.

Introduction

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 mono-addition 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 has been shown to be well suited for quantitative end-functionalization with a variety of nucleophiles. The resulting diarylcarbenium ion was also found to be an efficient initiating species for the polymerization of reactive monomers. Recently, *bis*-DPE compounds have been successfully used as 'living' coupling agents for the synthesis of A_2B_2 star block copolymers. 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.$^{1)}$ A limitation of using

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diarylethylenes as capping agents is that quantitative capping can be obtained only under selected conditions. For instance, it is 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 discovered a new class of non-(homo)polymerizable monomers; 2-substituted furans as capping agents.

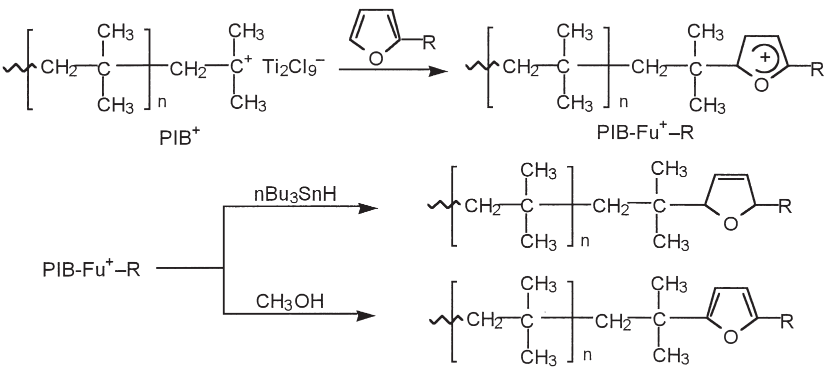
In this paper we report on new methodologies using furan derivatives as capping agents for the synthesis of functional polymers and block copolymers and on kinetic and mechanistic studies.

Results and Discussion

Capping with 2-alkylfurans. Although it has been known that 2-alkylfurans are highly reactive toward electrophilic attack at C–5 position, no attempt has been made on the synthetic utilization of 2-alkylfurans in the living cationic polymerization of vinyl monomers. Our mechanistic studies revealed that 2-alkylfurans, such as 2-methylfuran (2-MeFu), 2-*tert*-butylfuran (2-tBuFu), and 2-phenylfuran (2-PhFu), quantitatively add to living PIB, obtained in Hex/CH_2Cl_2 or CH_3Cl 60/40 (v/v) at -80 °C as shown in Scheme 1.2) Addition occurs exclusively at C–5 position and a stable tertiary allylic cation is generated at C–2 position which is further stabilized by the neighboring O-atom. The formation of the stable allylic cation (PIB-Fu^+-R) was further confirmed by trapping the resulting cation with tributyltin hydride (Bu_3SnH). Interestingly, quenching with methanol at –80 °C yielded 2-alkyl-5-PIB-furan, most probably due to the intermediate formation of an acetal, which eliminates methanol.

The stability of PIB-Fu^+-R with increasing temperature was studied in Hex/CH_2Cl_2 60/40 (v/v) by UV-vis spectroscopy (monitoring the maximum absorption at λ_{max} = 340 nm with R=Ph)3) or by trapping the remaining cations with Bu_3SnH (with R=tBu), followed by the analysis of the product by ^1H NMR spectroscopy.2) Both experiments verified that PIB-Fu^+-R is stable up to –40 °C, however it slowly eliminates H^+ at -20 °C. Importantly, decapping was not observed at any temperature, indicating that with 2-alkyl(or aryl)furans retro-addition (decapping) is absent or negligible.

Quantitative capping of living PIB with 2-R-Fu could also be achieved using the BCl_3/CH_3Cl/–40 °C system. Since the capping reaction of living PIB with DPE or DTE was found to be slow and incomplete under these conditions, it appears that 2-alkylfurans are



Scheme 1. Capping reaction of living PIB with 2-alkyl(or aryl)furans

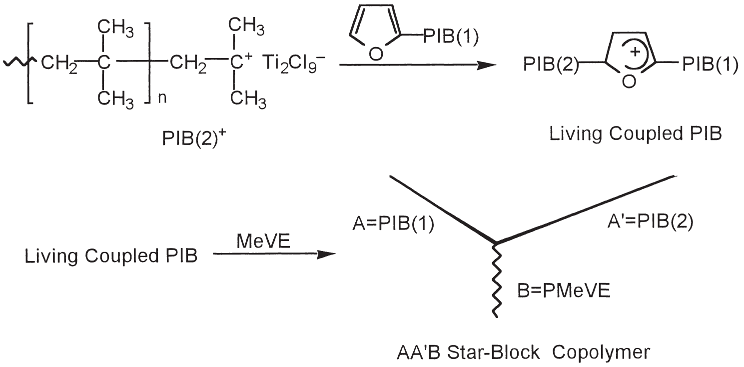
more suitable capping agents when the subsequent functionalization or block copolymerization should be carried out at elevated temperature.

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 using 2-tBuFu and 2-MeFu as capping agent for the synthesis of P(IB-b-MeVE) block copolymers by sequential monomer addition. 2) After capping at -80 °C, the Lewis acidity was moderated by the introduction of $Ti(OiPr)_4$ or $Ti(OEt)_4$ followed by the addition of MeVE. The temperature was then raised to 0 °C to polymerize MeVE. Characterization of the products by ^{1}H NMR spectroscopy and GPC indicated that the cross over was not quantitative. By column chromatography the cross over efficiency was determined to be 66% for 2-tBuFu and 75% for 2-MeFu. ^{13}C NMR and DEPT 135 spectra have shown that contrary to expectations, initiation is not from C-2 but from C-4 position. Therefore it appears that PIB-Fu$^+$-R is sterically hindered somewhat which adversely affects the efficiency of initiation of a second monomer.

The Synthesis of Furan Functional PIBs. Recently we reported4) the quantitative synthesis of furan functionalized PIBs by the reaction of polyisobutenyl diphenylcarbenium ion (PIB-DPE$^+$) with 2-Bu_3SnFu. Continuing our investigations we have found that the reaction between 2-Bu_3SnFu and living PIB$^+$ (i.e., without DPE capping) in Hex/CH_3Cl 60/40 (v/v) in the presence of $TiCl_4$ at -80 °C is also rapid and quantitative.2) In contrast the functionalization of living PIB with 2-Bu_3SnFu in the presence of BCl_3 in CH_3Cl at -40 °C failed as the PIBCl chain ends remained unreacted even after 15 hours. This may be attributed to transmetallation that gives rise to the formation of BCl_2Fu (and nBu_3SnCl) which is likely too weak to ionize PIBCl.

Reactions of Furan Functional PIBs. Since furan functional PIB (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.2) According to GPC and ^1H NMR spectroscopy, close to quantitative coupling of the two PIB chains was achieved in ~3h. The M_n of the product was almost equal to the sum of the M_ns of 2-PIB-Fu and living PIB, and the ^1H NMR spectrum of the coupled product exhibited a singlet at 5.8ppm since the 2 protons H^3 and H^4 on the ring are chemical shift equivalent.

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 may also be utilized to obtain *AB* type block copolymers. It is also apparent that ω-furan functionalized polymers may 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'* represents 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*). This scheme was experimentally verified by the synthesis and characterization of PIB-*s*-PIB'-*s*-PMeVE mixed



Scheme 2. Synthesis of AA'B tri-arm type star-block copolymers

tri-arm star block copolymer.[5)] Pure star-block copolymer was obtained upon purification of the crude product, contaminated by a small amount of homo-PIB (incomplete crossover) by column chromatography.

Coupling Reaction of Living Cationic Polymers. Since 2-alkylfurans add rapidly and quantitatively to living PIB to yield stable tertiary allylic cations, the living coupling reaction of living PIB was also studied using *bis*-furanyl compounds (Chart 1).[6)] Using *bis*-furanyl compounds with a methylene spacer group, such as DMF and FMF, as coupling agents, a higher degree of coupling was obtained with FMF (~85% by ^{1}H NMR) than with DMF (~35% by ^{1}H NMR). While the products obtained in the capping reaction of living PIB with 2-alkylfurans were colorless, the product obtained in the coupling reaction of living PIB by DMF or FMF exhibited a strong orange color. This observation indicates the presence of a well-known side reaction, i.e., hydride abstraction at α-position to the ring.

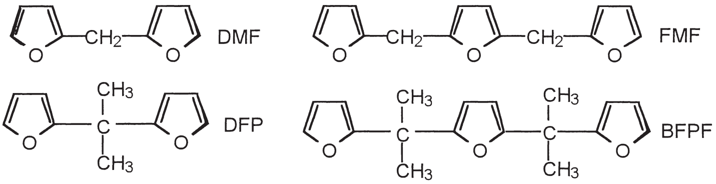
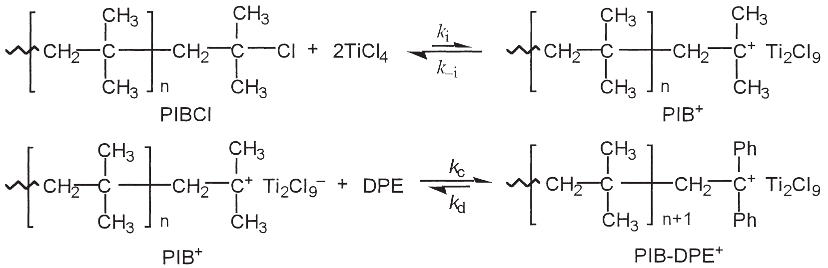


Chart 1. Structures of *bis*-furanyl compounds

This side reaction was circumvented using DFP or BFPF, which lacks hydrogen atoms at α-position to the ring, as a coupling agent. Using DFP as a coupling agent, however, the coupling reaction was less than quantitative (< 50%) indicating that the reactivity of the second furan ring decreases significantly upon monoaddition. When BFPF was used as a coupling agent, the coupling was complete within 30 min in Hex/CH_3Cl (60/40 or 40/60, v/v) solvent mixtures on the basis of spectroscopic as well as chromatographic analyses. The ^{1}H NMR spectrum of the final product lacked resonance signals for aromatic group as well as for PIB with a terminal-chloro group, indicating the absence of both monoadduct and unreacted PIB. Furthermore, the final product exhibited doubled M_n as well as lowered M_w/M_n confirming quantitative coupling of living PIB by BFPF. Efficient, albeit slow coupling was also achieved with bFPF in CH_3Cl at -40 °C in the presence of BCl_3. Unique applications of coupling living PIB with BFPF for the synthesis of hydroxyl, vinyl and dichlorosilyl telechelic PIB with controlled molecular weight have been described.[7)] The *bis*-dimethoxysilyl telechelic PIBs obtained upon quenching with methanol were quantitatively crosslinked by moisture at room temperature in the presence of catalytic amounts of tin(II) 2-ethyl-hexanoate.

Kinetic Aspects of the Capping Reactions. The capping reaction of living cationic polymers with non-(homo)polymerizable monomers comprises of two consecutive reactions as shown in Scheme 3 for PIB and DPE; (i) the ionization of dormant PIB (PIBCl) and (ii) the addition reaction of DPE to ionized PIB (PIB^+). Since capping gives rise to a stable and fully ionized cation with high molar absorption coefficient in the UV-vis region, the reaction rate can be conveniently measured by on-line UV-vis spectroscopy and related to the reactivity of the electrophile and π-nucleophile. We recently studied the addition of 1,1-diarylethylenes to hydrochlorinated IB *n*-mers, H-$[IB]_n$-Cl (*n* = 2, 3, 4, 36), in the presence of $TiCl_4$ in hexanes/CH_3Cl 60/40 (v/v) at −80 °C using on-line UV-visible spectroscopy.[8] Assuming steady state for $PIB^+\ Ti_2Cl_9^-$, i.e., $[PIB^+\ Ti_2Cl_9^-]$=const., the initial rate of capping for DPE is described by Equation 1.



Scheme 3. Ionization equilibrium of living PIB ($K_i = k_i/k_{-i}$) and capping/decapping equilibrium ($K_{cd} = k_c/k_d$)

$$\frac{d}{dt}[PIB - DPE^+ Ti_2Cl_9^-] = \frac{k_c k_i [PIBCl][TiCl_4]^2 [DPE]}{k_{-i} + k_c[DPE]} \qquad \text{Equation 1}$$

From the initial rate of formation of $PIB\text{-}DPE^+$ or $PIB\text{-}DTE^+$ the apparent rate constants of capping, k_cK_i could be calculated according to Eq. 1, when $k_{-i} >> k_c$[diarylethylene]. k_cK_i increased with increasing *n* for the capping with both DPE and DTE: For *n* = 3, 4, and 36, it was approximately three, four and five times higher, respectively, than for *n* = 2. Capping with DTE was approximately fifteen times faster than with DPE indicating a much higher reactivity of DTE. With increasing concentration of DTE, a change in the rate determining step from addition of the nucleophile to H-$[IB]_n^+$ ($k_{-i} >> k_c$[DTE]) to ionization of H-$[IB]_n$-Cl (k_{-i} <<

k_c[DTE]) was observed. The rate constant of ionization, k_i = 6 (n=2), 11 (n=3), and 15 (n=36) M^{-2} s^{-1} could then be calculated for the first time. Comparison of these k_i values with the corresponding k_cK_i values indicated that the observed increase of the apparent rate constant of capping with increasing chain length can be mainly ascribed to a similar increase in k_i and K_i, due to an increase of back-strain with increasing *n*.

Continuing our investigation on the addition reactions of non-(homo)polymerizable monomers to PIB^+ we employed 1,1-*bis*-(4-tert.-butylphenyl)ethylene, (DBE) and 2-PhFu, i.e., π-nucleophiles with increased nucleophilicity. As shown in Figure 1, virtually identical plots have been obtained with DTE, DBE and 2-PhFu, indicating diffusion limited addition with all three nucleophiles. While the nucleophilicity parameters (*N*) have not been determined for diarylethylenes, it has recently been determined for 2-PhFu (*N*=3.6),9) which in conjunction with the electrophilicity parameter of PIB^+ (*E*=7.5)10) also suggests diffusion controlled addition, according to the linear free energy relationship {k=s(N+E), s≅1}.10) Using the diffusion controlled second order rate constant of k_c~$3x10^9$ $M^{-1}s^{-1}$ K_i and k_{-i} could be calculated. On the basis of K_i and the apparent propagation rate constant of IB, obtained under identical conditions, the absolute propagation rate constant k_p (=$9x10^8$ $M^{-1}s^{-1}$) was determined. A similar approach was used to determine k_p (=$5x10^9$ $M^{-1}s^{-1}$) for styrene based on data in a recent report.11) These results are in good agreement with results of the diffusion clock method for IB (k_p=$6x10^8$ $M^{-1}s^{-1}$) reported earlier12) and with theoretical predictions based on the linear free energy relationship by Mayr.10) k_p for styrene however is ~10^6 times higher than that determined using the stopped-flow method.13) When the addition of the nucleophile to the polymer cation is diffusion limited, and the capped cationic ends do not initiate polymerization of the monomer, a simple competition experiment can also be used to determine k_p. Thus, the polymerization in the presence of capping agent (*C)* will stop short of completion when all chain ends are capped. From the limiting conversion or at low conversion more accurately from the limiting DP_n k_p can be calculated according to Equation 2.

$$DP_{n\mathrm{lim.}} = \frac{k_p[IB]_o}{k_c[PIBCl]} \ln \frac{[C]_o}{[C]_o - [PIBCl]} \qquad \text{Equation 2}$$

The polymerization of IB carried out in the presence of DTE or 2-MeFu (= $3x10^{-3}$ M= 1.5x [PIBCl]) indeed stopped at ~6% conversion. The ^{1}H NMR spectra of the products verified that all chain ends were capped. From DP_{nlim} k_p = 3 x 10^8 (for IB/2-MeFu), and 2 x 10^8 (for IB/DTE) M^{-1} s^{-1} was calculated.

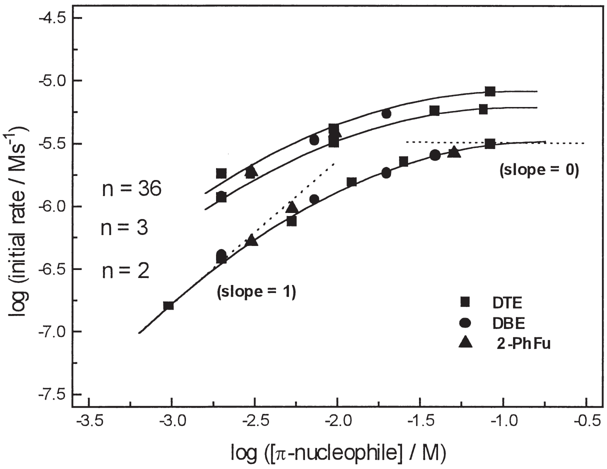


Figure 1. The log initial rate of capping versus log [π-nucleophile] for the capping reaction of hydrochlorinated IB *n*-mers in Hex/MeCl 60/40 (v/v) at –80 °C.

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