Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 1761–1770 **1761**
DOI: 10.1021/ma9025114

Introducing Polar Monomers into Polyisobutylene by Living Cationic Polymerization: Structural and Kinetic Effects

Katharina Hackethal, Diana Döhler, Susanne Tanner, and Wolfgang H. Binder*

Chair of Macromolecular Chemistry, Institute of Chemistry, Division of Technical and Macromolecular Chemistry, Faculty of Natural Sciences II (Chemistry and Physics), Martin-Luther Universität Halle-Wittenberg, Halle 06099, Germany

Received November 13, 2009; Revised Manuscript Received January 11, 2010

ABSTRACT: We report on the direct copolymerization of polar styrene monomers with isobutylene (IB) using living cationic polymerization with $TiCl_4$/TMPCl as initiators, for the first time opening the possibility to introduce polar moieties in a direct copolymerization approach into PIB polymers. The investigated polar styrene monomers contain pyridine (**1a**), collidine (**1b**, **1c**), thymine (**2c**), and/or triazole moieties (**2a**−**2c**). Copolymerization with styrene monomers **1a**, **1b**, and **2c** proceeded under incorporation of the comonomer into the PIB polymer (as proven by MALDI and NMR spectroscopy), whereas monomer **1c** was not incorporated and resulted in broad polydispersities of the resulting PIB polymers. Inline-IR kinetic measurements of the monomer consumption demonstrated strong effects of the monomer structure on the polymerization kinetics, with rates of polymerization (k_p) increasing up to a factor of 15. The addition of nonpolymerizable additives containing triazole moieties revealed a strong dependency on the attached residue R (R = hexyl (**3a**), phenyl (**3b**), *p*-methoxyphenyl (**3c**), *p*-methylphenyl (**3d**), *p*-chlorophenyl (**3e**)), with a decreasing rate of polymerization (k_p) in the order of **3e** > **3b** > **3c** > **3e** > **3a** = k_p(IB). Measurements of k_p/k_{-1} displayed significant changes with respect to homopolymerization of IB under the same conditions, proving that ion equilibria are disturbed by addition of the polar species during the IB polymerization.

Introduction

Polyisobutylene (PIB) can be prepared solely by free or living cationic polymerization of isobutene (IB), based on the well-known chemistry to reduce the concentration of the cationic intermediates by appropriate ion equilibria,[1,2] thus avoiding chain transfer reactions. As the monomer itself is limited in its structural variability, the quest for modification and property enhancement of PIB arises as an urgent need as PIB is used in many technical applications[3] as well as in special applications such as in medicine[4] and biology.[5] Solutions to increase the structural variability of PIB by introducing other monomer units can either be approached by copolymerization or via appropriate modifications at starting- or end-group moieties. Thus, the direct copolymerization of IB with monomers subjectable to cationic polymerization (such as styrene[6−13] vinyl ethers[5,14,15]) yields either statistical or block copolymers, thus expanding its structural and biological applications by the well-known modifications in thermal and chemical properties. Recently, a methylene-homologous polymer of PIB via a ROMP polymerization has been reported.[16] However, the direct introduction of highly polar monomers (i.e., those serving as hydrogen donor−acceptor structures[17]) into PIB via cationic polymerization has not been accomplished, as the complex equilibrium between "dormant = *tert*-chlorine-telechelic" and "active = cationic" species are often severely changed by the addition of even slightly polar additives, leading to either a quench of the living PIB cation or to the generation of *exo*-alkene end groups.[18] The use of specific polar additives to modify or improve control over the living cationic polymerization of IB is well-known and has been investigated extensively.[15] Thus, sterically hindered amines (i.e., pyridine, collidines, di-*tert*-pyridine), quaternary ammonium cations, DMSO, or esters can be used to effect improved control over molecular weight and polydispersity.[19] As recently pointed out by Storey et al.,[20] the use of such additives serves primarily to control the equilibrium between "dormant" and "active" species rather than to remove protic impurities or reduce the "cationicity" of the active (growing) species.

Another strategy to chemically modify PIB is directed toward the use of functional initiator[21,22] or quenching moieties.[18] Well-known examples include the use of nonpolymerizable quenchers with methanol (1,1-diphenylethylene/methanol),[23] furane,[24] 4-alkoxybenzene,[25] sulfonium,[26] and *N*-methylpyrrole moieties.[18] Other methods involve the "postmodification" of telechelic PIB's, introducing complex hydrogen bonds[27−30] or amines,[31] i.e., via azide/alkine "click" chemistry,[28,30,32−34] nucleophilic substitution reactions,[27,29,31] or activated chloromethyl ethers.[27] However, in these latter cases only the end group a PIB polymer can be modified, whereas a direct introduction of hydrogen bonding units by copolymerization has not been accomplished.

The present paper investigates the direct copolymerization of polar monomers (bearing hydrogen donor/acceptor moieties) with IB using the living cationic polymerization approach with $TiCl_4$/TMPCl as initiators. The polar moiety is introduced within a styrene moiety, as structural variations on the IB molecule are not possible due to the close proximity of the polar moiety to the growing cation, which would immediately destroy the livingness of the polymerization reaction (see Scheme 1). Polar moieties such as pyridine, collidine, and thymine units are investigated. As comparison, additional information on the copolymerization is obtained by inline-IR monitoring of the polymerization kinetics, comparing the polar monomers with the structurally related polar additives.

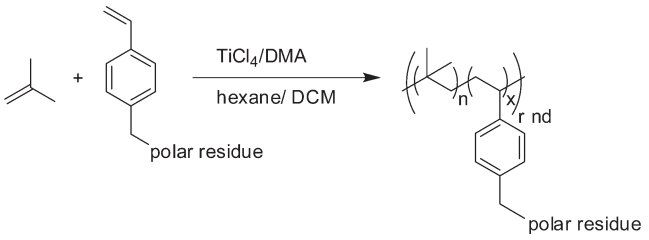
Experimental Part

Materials. Tetrahydrofuran (THF), toluene, and diethyl ether were dried over KOH and freshly distilled over Na and

*Corresponding author. E-mail: wolfgang.binder@chemie.uni-halle.de.

Published on Web 01/25/2010

Scheme 1



benzophenone. Hexane was distilled, heated under reflux with sulfuric acid, washed with water and NaOH-solution, dried over Na_2SO_4, and finally freshly distilled over CaH_2. Dichloromethane (DCM) was dried over KOH and freshly distilled over CaH_2. Styrene was destabilized by washing with NaOH solution and then with water and dried over Na_2SO_4 and freshly distilled over CaH_2. IB was piped through KOH for drying. 2-Chloro-2,4,4′-trimethylpentane (TMPCl) was synthesized as described in the literature,[35] and the pure product was stored in a freezer. All other reagents, in particular the alkynes **7a** (purity ≥95%), **7b** (purity ≥97%), **8c**, **8d** (purity 97%), and **8e** (purity 98%), were purchased from Sigma-Aldrich and used without further purification.

Instrumentation. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using $CDCl_3$ as solvent on a Varian Gemini 2000 FT-NMR spectrometer. For the interpretation of the spectra MestReC 4.7.0.0 was used. The chemical shifts were given in ppm, and the coupling constants were given in Hz.

Number-average molecular weights (M_n) and molecular weight distribution were determined using gel permeation chromatography (GPC) with THF as eluent in a flow rate of 1 mL/min on a Viscotek GPCmax VE 2001 using a refractive index detector (VE 3580 RI detector, Viscotek) and column set H_{HR} + GMH_{HR}-N (Viscotek, mixed bed). Calibration was made by polystyrene (1050−115 000 g/mol) and PIB standards (340−87 300 g/mol).

Inline monitoring of the IB polymerization was done with a Bruker Vertex 70 MIR spectrometer. The kinetic measurements were made with an attenuated total reflection (ATR) FT-IR fiber optics equipped with a diamante prism with a scan number of 20 scans per spectra in a resolution of 4 cm^{-1} so that one spectrum could be achieved within 9 s. Conventional IR measurements were carried out with an ATR-Golden Gate unit using a diamond crystal. The scan number was 32 scans per spectra with a resolution of 2 cm^{-1}.

Matrix-assisted laser desorption ionization (MALDI) time-of-flight (TOF) mass spectroscopy (MS) measurements were performed with a Bruker autoflex III smartbeam mass spectrometer equipped with a TOF analyzer and a nitrogen laser delivering 3 ns laser pulses at 337 nm. The positive ions were detected in the linear and reflectron mode. Polymer samples (2 mg/mL) in THF were prepared with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix (40 mg/mL in THF). To produce cations, silver trifluoroacetate (AgTFA) dissolved in THF at a concentration of 1 mg/mL was added to the matrix/analyte solution. The solutions were mixed in 10:5:1 volume ratio (matrix:analyte:salt). A volume of 0.5 μL of these solutions was deposited onto the target plate (stainless steel) and allowed to air-dry. MALDI-TOF-MS spectra were recorded with flexControl 3.0. Peaks were analyzed using flexAnalysis 3.0 software. For simulation DataAnalysis4.0 and IsotopePattern were used.

(*4-Pyridylethyl*)*-4-vinylbenzene* (***1a***). A solution of lithium diisopropylamine (LDA) (0.58 g, 5.37 mmol) in 5 mL of dry THF was added dropwise to a solution of picoline (0.50 g, 5.37 mmol) in 2 mL of dry THF at −80 °C under slow stirring. The reaction mixture was stirred for 1 h while slowly raising the temperature (after 1 h to −35 °C). Subsequently, a solution of **4** (10 mL reaction mixture of **4**; see Supporting Information) was added dropwisely under soft stirring, during which the solution was allowed to reach room temperature. After complete addition of **4** the mixture was heated to 40 °C and stirred for 3 days. For quenching the reaction 2 mL of methanol was added, and THF was removed under reduced pressure. The resulting oil was dissolved in dichloromethane and washed with deionized water and brine. The resulting solution was then dried over Na_2SO_4 and evaporated to dryness. The crude 1-(2-pyridylethyl)-4-vinylbenzene was purified by column chromatography (SiO_2, dichloromethane/methanol = 100/1; R_f = 0.36−0.14) to yield **1a**: 0.66 g (3.16 mmol, 63%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.46 (d, 2H, *J* = 6.03, Ar−H), 7.28 (d, 2H, *J* = 8.13, Ar−H), 7.08 (dd, 4H, *J* = 6.09, Ar−H), 6.68 (dd, 1H, *J* = 10.87, CH=C), 5.71 (d, 1H, *J* = 16.74, C=CH_2), 5.20 (d, 1H, *J* = 10.88, C=CH_2), 2,99 (s, 4H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.2 (C=N), 149.6 (*tert*C-hetero-Ar), 140.22 (*tertC*−CH_2), 136.42 (CH=), 135.6 (*tertC*−CH=CH_2), 128.5 (Ar), 126.2 (Ar), 123.8 (Ar), 113.2 (CH_2=), 36.87 (CH_2), 36.2 (CH_2).

(*4-(2,6-Dimethylpyridylethyl)-4-vinylbenzene* (***1b***) *and 1-(2-(4,6-Dimethylpyridylethyl)-4-vinylbenzene* (***1c***). The experimental procedure was adopted from ref 36. Butyllithium in hexane (2.5 M, 2 mL, 5 mmol) was dissolved in 1.2 mL of freshly distilled THF (solution A). Diisopropylamine (DIPA) (0.7 mL, 5 mmol) was dissolved in 15 mL of THF and added to solution A. After stirring for 15 min a solution of *sym*-collidine (0.67 mL, 5 mmol, dissolved in 2.5 mL of THF) was added dropwise to the reaction mixture. After complete addition the reaction mixture was cooled (to −50 °C) and stirred for 1 h at this temperature. Subsequently a solution of **4** (10 mL reaction mixture of **4**; see Supporting Information) in THF was added dropwise within 1 h while stirred at −50 °C. The reaction mixture was then allowed to reach room temperature and subsequently heated to 40 °C and stirred for 4 days, then cooled to 0 °C, and quenched by addition of 10 mL of cooled water. The organic phase was washed with 10% NaOH solution and the product was extracted with diethyl ether (3 × 30 mL) and dried over Na_2SO_4. After evaporation of the solvent the product was dissolved in hexane. Purification was carried out by column chromatography (SiO_2 (80 g), hexane:dichloromethane = 1:3); R_f = 0.4 (dichloromethane:hexane:methanol = 3:1:0.3). Because of still present impurities a second column chromatography was required. After drying the product excessively in high vacuum, the second purification with column chromatography (SiO_2 (160 g), hexane: ethyl acetate = 1:3) yielded two products. The main product was **1b**; the major second side product could be assigned to the regioisomer **1c** (R_f = 0.37). Yield: **1b** 230 mg (1 mmol, 20% o.th); **1c** 60 mg (0.25 mmol, 5% o.th).

(*4-(2,6-Dimethylpyridylethyl)-4-vinylbenzene* (***1b***). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.3 (d, 2H, *J* = 6.1, Ar−H), 7.11 (d, 2H, Ar−H), 6.76 (d, 2H, Ar−H), 6.68 (dd, 1H, *J* = 10.88, CH=C), 5.71 (d, 1H, *J* = 18.05, C=CH_2), 5.18 (d, 1H, *J* = 11.3, C=CH_2), 2.85 (m, 2H, CH_2), 2.81 (m, 2H, CH_2), 2.46 (s, 6H, Ar−CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.6 (*tert*C−N), 150.9 (*tertC*-hetero-Ar), 140.8 (*tertC*−CH_2), 136.6 (CH=), 135.6 (*tertC*−CH=CH_2), 128.6 (Ar), 126.2 (Ar), 120.4 (Ar), 113.2 (CH_2=), 36.9 (CH_2), 36.4 (CH_2), 24.4 (CH_3).

1-(2-(4,6-Dimethylpyridylethyl)-4-vinylbenzene (***1c***). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.3 (d, 2H, *J* = 6.1, Ar−H), 7.16 (d, 2H, Ar−H), 6.79 (d, 2H, Ar−H), 6.67 (dd, 1H, *J* = 10.88, CH=C), 5.7 (d, 1H, *J* = 18.05, C=CH_2), 5.18 (d, 1H, *J* = 11.3, C=CH_2), 2.99 (s, 4H, CH_2), 2.49 (s, 3H, Ar−CH_3), 2.23 (s, 3H, Ar−CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.3 (*tert*C=N), 157.6 (CH_3-*tertC*=N), 147.4 (CH_3-*tertC*-hetero-Ar), 141.6 (*tertC*−CH_2), 136.6 (CH=), 135.2 (*tertC*−CH=CH_2), 128.6 (Ar), 126.1 (Ar), 121.6 (Ar), 120.7 (Ar), 112.9 (CH_2=), 39.9 (CH_2), 35.9 (CH_2), 24.4 (CH_3−C=N), 20.9 (CH_3).

General Procedure for the Synthesis of the Triazoles 2a−2d and 3a−3e. The basic reaction conditions and reaction procedure were adopted from Yoo et al.[37] To a stirred mixture containing the acetylene (**7a**−**c**; **8a**−**e**; 0.5 mmol), the azide (**5**, **6**; 0.6 mmol)

and Cu(I)I (9.5 mg, 0.05 mmol) in THF (1.0 mL) and diisopropylamine (DIPA) (0.085 mL, 0.597 mmol) at 25 °C were added slowly. After the reaction mixture was stirred for 24 h at room temperature (RT), it was diluted with DCM (2 mL) and then quenched with saturated aqueous NH_4Cl solution (3 mL). The mixture was stirred for an additional 30 min at RT, and two layers were separated. The aqueous layer was extracted with DCM (3 × 5−10 mL), and the combined organic layers were washed additionally with saturated aqueous NH_4Cl solution until the aqueous layer stayed colorless. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude product was dissolved in DCM and purified by column chromatography (SiO_2, DCM or DCM/MeOH 100:1).

(*4-Butyl-1-(4-vinylbenzyl)-1H-1,2,3-triazole*) (**2a**). Yield: 128 mg (0.53 mmol, 94% o.th). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.4 (d, 2H, J = 8.2, Ar−H), 7.2 (m, 3H, Ar−H + triazole—H), 6.7 (dd, 1H, CH=C), 5.75 (d, 1H, J = 17.6, C=CH_2), 5.45 (s, 2H, Ar−CH_2), 5.28 (d, 1H, J = 10.8, C=CH_2), 2.67 (t, 2H, J = 7.7, alk—H), 1.6 (qi, 2H, J = 7.7, alk—H), 1.35 (qi, 2H, J = 7.5, alk—H), 0.89 (t, 3H, J = 7.4, alk—H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.8 (CH=), 138.0 (*tert*C−CH=CH_2), 135.9 (*tert*C−CH_2), 134.3 (*tert*C-triazole), 128.2 (Ar), 126.8 (Ar), 120.4 (CH-triazole), 114.8 (CH_2=), 53.8 (Ar−CH_2-triazole), 31.5 (CH_2), 25.4 (CH_2), 22.4 (CH_2), 13.8 (CH_3). IR (cm^{-1}): 3114.9, 3063.9, 2960.1, 2932.1, 2873.6, 2859.1, 1868.3, 1548.2, 1512.7, 1465.4, 1435.5, 1407.3, 1335.7, 1318.5, 1229.6, 1213.1, 1129.1, 1114.5, 1048.7, 994.1, 908.9, 859.2, 789.6, 762.1723.7, 702.6, 677.1.

(*4-Phenyl-1-(4-vinylbenzyl)-1H-1,2,3-triazole*) (**2b**). Yield: 141 mg (0.53 mmol, 96% o.th). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.8 (d, 2H, J = 7.1, Ar−H), 7.64 (s, 1H, triazole—H), 7.39-7.27 (m, 7H, Ar−H), 6.7 (dd, 1H, CH=C), 5.77 (d, 1H, J = 17.0, C=CH_2), 5.46 (s, 2H, Ar−CH_2), 5.28 (d, 1H, J = 11.6, C=CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.2 (CH=), 135.9 (*tert*C−CH_2), 133.9 (*tert*C−CH=CH_2), 130.8 (*tert*C-triazole), 128.8 (Ar), 128.3 (Ar), 128.1 (Ar), 126.9 (Ar), 125.7 (Ar), 119.3 (CH-triazole), 114.9 (CH_2=), 54.1 (Ar−CH_2-triazole). IR (cm^{-1}): 3088, 3044.9, 2959.6, 1725.9, 1512.7, 1482.5, 1462.9, 1442.4, 1428.3, 1408.2, 1345.2, 1286.9, 1223.2, 1208.7, 1189.3, 1134.1, 1076.2, 1049.5, 1018.6, 991.0, 974.7, 918.1, 857.4, 830.7, 779.4, 764.2, 738.2, 716.6, 692.1.

(*1-(1-(4-Vinylbenzyl)-1H-1,2,3-triazol-4-yl)-methylene-5-methyl-pyrimidine-2,4(1H,3H)-dione*) (**2c**). Acetonitrile was used as solvent instead of THF. Yield of **2c**: 0.661 mg (2.05 mmol, 89% (o.th.)). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16 (s, 1H, N−H), 7.56 (s, 1H, triazole−H), 7.39 (d, 2H, Ar−H), 7.31 (s, 1H, Thy−H), 7.23 (d, 2H, Ar−H), 6.7 (dd, 1H, CH=C), 5.77 (d, 1H, J = 17.0, C=CH_2), 5.46 (s, 2H, Ar−CH_2), 5.28 (d, 1H, J = 11.6, C=CH_2), 4.9 (s, 2H, Thy−CH_2), 1.88 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.7 (C=O), 153.5 (C=O), 140.1 (=*C*H−N), 136.2 (CH=), 135.8 (*tert*C−CH_2), 134.15 (*tert*C−C=), 133.3 (*tert*C-triazole), 128.5 (Ar), 126.9 (Ar), 120.0 (CH-triazole), 115.1 (CH_2=), 111.2 (*tert*C−CH_3), 56.0 (Ar−CH_2−triazole), 42.8 (triazole−CH_2−pyrimidine), 12.3 (CH_3). IR: 3131.2, 3033.2, 2832.9, 1682.5, 1647.0, 1513.5, 1464.8, 1380.2, 1351.1, 1338.3, 1308.9, 1342.8, 1215.4, 1133.8, 1063.7, 1029.1, 992.9, 903.5, 879.2, 781.3, 763.0, 721.3, 703.7, 559.9, 433.5, 473.8.

(*1-Benzyl-4-butyl-1H-1,2,3-triazole*) (**3a**). Yield: 100 mg (0.46 mmol, 83% o.th). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.4−7.17 (m, 5H, Ar−H + triazole−H), 5.47 (s, 2H, Ar−CH_2), 2.67 (t, 2H, J = 7.7, alk—H), 1.6 (qi, 2H, J = 7.7, alk−H), 1.35 (qi, 2H, J = 7.5, alk−H), 0.89 (t, 3H, J = 7.4, alk−H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 129.0 (Ar), 128.6 (*tert*C-triazole), 127.9 (Ar), 120.6 (CH-triazole), 54.3 (Ar−CH_2−triazole), 31.6 (CH_2), 25.4 (CH_2), 22.5 (CH_2), 13.9 (CH_2). IR: 3114.4, 3063.4, 2959.3, 2925.1, 2857.9, 1726.3, 1557.0, 1495.5, 1448.4, 1310.3, 1287.6, 1228.2, 1215.4, 1176.2, 1131.3, 1051.9, 1033.0, 856.8, 824.8, 747.8, 703.5, 673.3, 641.7.

(*1-Benzyl-4-phenyl-1H-1,2,3-triazole*) (**3b**). Yield: 115 mg (0.49 mmol, 88% o.th). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.8 (d, 2H, J = 7.1, Ar−H), 7.64 (s, 1H, triazole−H), 7.4−7.28 (m, 8H, Ar−H), 5.56 (s, 2H, Ar−CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.6 (*tert*C-triazole), 130.4 (*tert*C−CH_2), 129.1 (CH−triazole), 128.8 (Ar), 128.2 (Ar), 128.0 (Ar), 125.7 (Ar), 54.4 (Ar−CH_2−triazole). IR: 3121.7, 3096.0, 3064.6, 2972.5, 2936.6, 1607.6, 1496.9, 1483.4, 1466.7, 1455.4, 1441.9, 1426.8, 1356.8, 1320.2, 1224.6, 1205.8, 1155.6, 1074.9, 1049.2, 1028.5, 1003.2, 975.5, 913.3, 898.3, 827.3, 780.3, 765.0, 726.5, 708.0, 691.7.

(*1-Benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole*) (**3c**). Yield: 175 mg (0.45 mmol, 91% o.th). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.7 (d, 2H, J = 8.8, Ar−H), 7.55 (s, 1H, triazole−H), 7.4−7.28 (m, 5H, Ar−H), 6.91 (d, 2H, J = 8.8, Ar−H), 5.55 (s, 2H, CH_2), 3.8 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.6 (*tert*C−O), 148.0 (*tert*C-triazole), 134.7 (*tert*C−CH_2), 129.1 (CH−triazole), 128.7 (Ar), 128.0 (Ar), 126.9 (Ar), 123.2 (Ar), 118.7 (Ar-*tert*C-triazole), 114.2 (CH−O), 55.3 (CH_3−O), 54.3 (Ar−CH_2−triazole). IR: 3137.5, 3048.6, 2927.8, 2837.1, 2349.2, 2049.9, 1897.1, 1614.9, 1578.1, 1557.5, 1495.5, 1454.1, 1439.1, 1349.1, 1301.6, 1249.4, 1217.6, 1170.9, 1070.0, 1048.8, 1027.7, 972.8, 833.8, 794.8, 718.1, 658.2, 579.4, 532.4, 477.2.

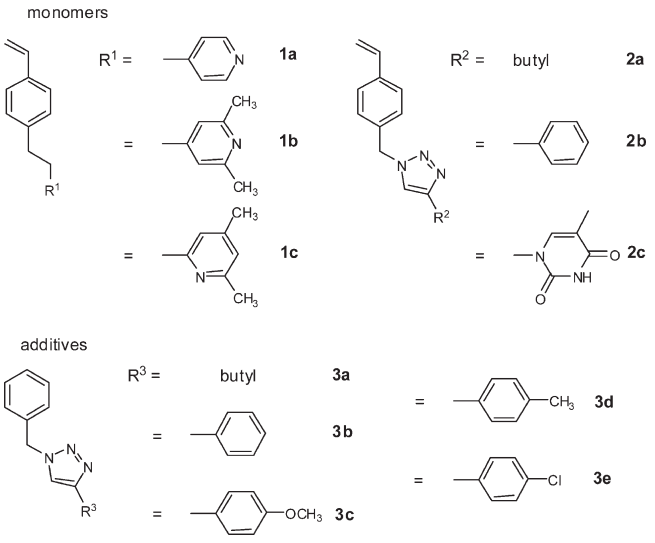
(*1-Benzyl-4-p-tolyl-1H-1,2,3-triazole*) (**3d**). Yield: 94 mg (0.38 mmol, 75% o.th). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.7 (d, 2H, J = 8.2, Ar−H), 7.6 (s, 1H, triazole-H), 7.4−7.25 (m, 5H, Ar−H), 7.18 (d, 2H, J = 7.8, Ar−H), 5.55 (s, 2H, CH_2), 2.3 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9 (*tert*C-triazole), 134.7 (*tert*C−CH_2), 129.4 (Ar), 129.1 (CH-triazole), 128.7 (*tert*C−CH_3), 128.0 (Ar), 127.8 (Ar), 125.6 (Ar), 54.4 (Ar−CH_2−triazole), 21.4 (CH_3). IR: 3145.3, 3019.0, 2955.7, 2916.4, 2858.3, 1683.2, 1602.9, 1586.1, 1495.6, 1452.9, 1348.7, 1222.9, 1182.4, 1136.8, 1067.3, 1047.4, 970.6, 827.1, 792.4, 718.5, 663.4, 604.9, 580.5, 512.7, 480.5.

(*1-Benzyl-4-(4-chlorophenyl)-1H-1,2,3-triazole*) (**3e**). Yield: 97 mg (0.43 mmol, 85% o.th). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.7 (d, 2H, J = 8.5, Ar−H), 7.62 (s, 1H, triazole-H), 7.4−7.34 (m, 5H, Ar−H), 7.3 (m, 2H, Ar−H), 5.56 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.14 (*tert*C-triazole), 134.49 (*tert*C−CH_2), 133.89 (*tert*C−Cl), 129.18 (Ar), 129.07 (Ar), 128.98 (Ar), 128.85 (Ar), 128.08 (Ar), 126.93 (Ar), 119.47 (Ar), 54.43 (Ar−CH_2−triazole). IR: 3117.4, 3069.2, 3040.8, 2950.3, 1682.9, 1606.3, 1551.2, 1478.3, 1452.2, 1432.7, 1403.3, 1344.8, 1225.8, 1207.9, 1186.4, 1136.1, 1090.8, 1068.7, 1051.9, 1012.9, 977.3, 809.9, 723.9, 707.4, 659.9, 583.6, 513.6, 474.9, 458.9.

General Procedure for PIB Polymerization. Polymerization and copolymerization were carried out in a two-necked Schlenk tube under an atmosphere of argon. A solution of hexane, DCM (60: 40, v:v) (20 mL) with *N,N*-dimethylacetamide (DMA) (c = 4.4×10^{-3} mol/L), and the Lewis base (2,6-di-*tert*-butylpyridine) (c = 2.5×10^{-3} mol/L) was cooled to −10 °C, and TMPCl was added. The comonomer (**1a**−**2c**) or the additives (**3a**−**3e**) or the amino bases in amounts of 1−7 mol % were added as solution in DCM to the reaction mixture. After initiator addition the polymerization mixture was cooled to final temperature of −80 °C, and IB (c = 1.2 mol/L) was added (prepared by condensation at −80) via a syringe. Finally, the co-initiator ($TiCl_4$ (final concentration the polymerization mixture is 0.124 mol/L)) was added to start the polymerization.[6] The overall volume of the polymerization was about 20 mL. The polymerization was conducted after complete conversion by kinetic measurements was determined and subsequently quenched with distilled MeOH (3 mL). The reaction mixture was then allowed to warm up to RT and precipitated in acetone (**2a**−**2c**) or acetone/methanol v:v 50:50 mixture (for **1a**−**1c**). The absence of residual monomer was checked by TLC (DCM/MeOH = 100/1). The precipitated polymer was dissolved in DCM, washed with $NaHCO_3$ solution and water, dried over Na_2SO_4, and filtered. The solvent was evaporated to dryness, and the resulting polymer was dried under high vacuum.[27]

Kinetic IR Monitoring. The progress of polymerization was monitored with attenuated total reflectance (ATR) probes. The probe was immersed in the polymerization medium and interfaced to a Bruker Vertex 70 FTIR unit by fiber-optic cables. A background spectrum (32 scans, resolution 4 cm^{-1}) was taken

Scheme 2



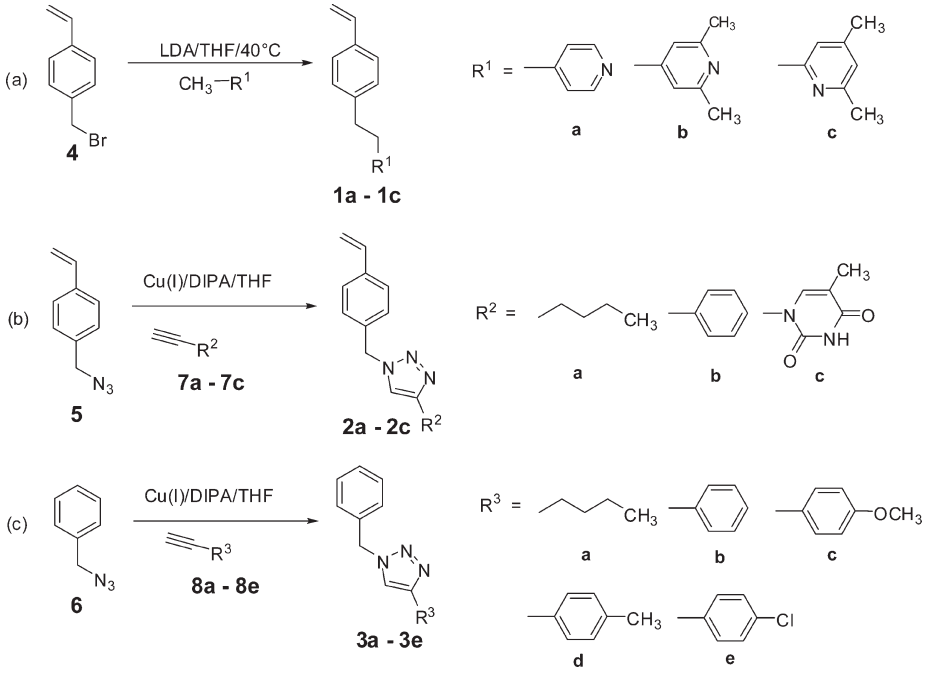
after the initiator, additives, and solvents were added. After initiation with $TiCl_4$, a spectrum (each spectrum consists of 20 scans and a resolution of 4 cm^{-1}) was collected every 9 s. Reaction conversion was determined by monitoring the $=CH_2$ wag at 887 cm^{-1} according to Storey et al.[38] (The overlap of the stretching vibration at 1655 cm^{-1} with a vibration of the active species at 1640 cm^{-1} (see Supporting Information Figure S 23) rendered the integration of the peak area impossible and was therefore not used.) Integration of the peak area leads to the values for the first-order kinetic plots. k_{app} values were determined from the ln-$[M_0]/[M_t]$ vs time (t) plots by selecting the linear range from $\ln[M_0]/[M_t] = 0$ to $\sim\ln[M_0]/[M_t] = 2.0$ (see eqs 1−3).

$$\ln [M]_0/[M]_t = k_{app}t \tag{1}$$

$$k_{app} = k_p K_{eq}[I]_0[LA]_0^2 \tag{2}$$

$$RN = (k_p[P_n^+Ti_2Cl_9^-][M])/(k_{-i}[P_n^+Ti_2Cl_9^-]) = k_p[M]/k_{-i} \tag{3}$$

Scheme 3. Synthesis of Monomers 1a−1c, 2a−2c and Additives 3a−3e[a]



[a] LDA = lithium diisopropylamine, DIPA = diisopropylamine, and THF = tetrahydrofuran.

Table 1. Copolymerization of IB with 1a in Comparison to Pure Picoline as Additive[a]

entry	monomer/additive	mol %	M_n[b] [g/mol]	M_w/M_n	incorp (%)[c]	conversion (%)[i]	k_{app} (10^{-3} s^{-1})	yield (%)	k_p[d] (10^8 s^{-1} M^{-1})	RN
1	−	0	2395[e]	1.1	−		20.1	90	1.54	2.47
2	**1a**	1	2800[e]	1.4	∼1	94	18.9	80	2.57	4.11
3		2	2800[e]	1.3	2.5	93	15.4	78	1.96	3.12
4		5	6300[f]	1.4	2.1	98	80.8	76	23.1	36.96
5		7	4000[f]	>2.3	0.75	83	6.9	70	−	−
6		1	9900[g]	1.3	0.3	96	17.1	82	7.69	12.29
7	picoline	1	4600[f]	1.2	−[h]	94	8.6	90	8.59	4.98
8		2	5600[e]	1.2	−[h]	97	19.3	85	4.9	7.84
9		5	4000[f]	1.1	−[h]	97	23.8	90	4.32	6.9

[a] [IB] = 1.2 M; [$TiCl_4$] = 0.128 M; [DtBP] = 2.2 mM; [DMA] = 5.4 mM; n-hexane-DCM v:v 60:40, −80 °C. [b] M_n determined by GPC measurement in THF as solvent, calibration with PIB standards (g/mol). [c] Determined by integration of 8.5−8.6 ppm (**1a**) vs 1.0−1.1 ppm (IB) ^{1}H NMR. [d] Determination by eq 3 (k_{-i} = 7.5 × 10^7 1/s, k_i = 15 1/(s M^2))[38] with k_p determined by combination of eqs 1 and 2 ($K_{eq} = k_i/k_{-i}$) with respect to the dimeric form of the LA ($[LA]_0^2$).[46] [e] Calcd M_n = 3000 g/mol; [IB] 1.2 M; [TMPCl] = 0.0224 M. [f] Calcd M_n = 6000 g/mol; [IB] 1.2 M; [TMPCl] = 0.0112 M. [g] Calcd M_n = 10 000 g/mol; [IB] 1.2 M; [TMPCl] = 0.0067 M. [h] Additive, no incorporation possible. [i] Determined by inline FTIR-spectroscopy $\ln[M]_0/[M]_t$ plot; limited by detection of concentrations below ∼0.07 mol/L (IB).

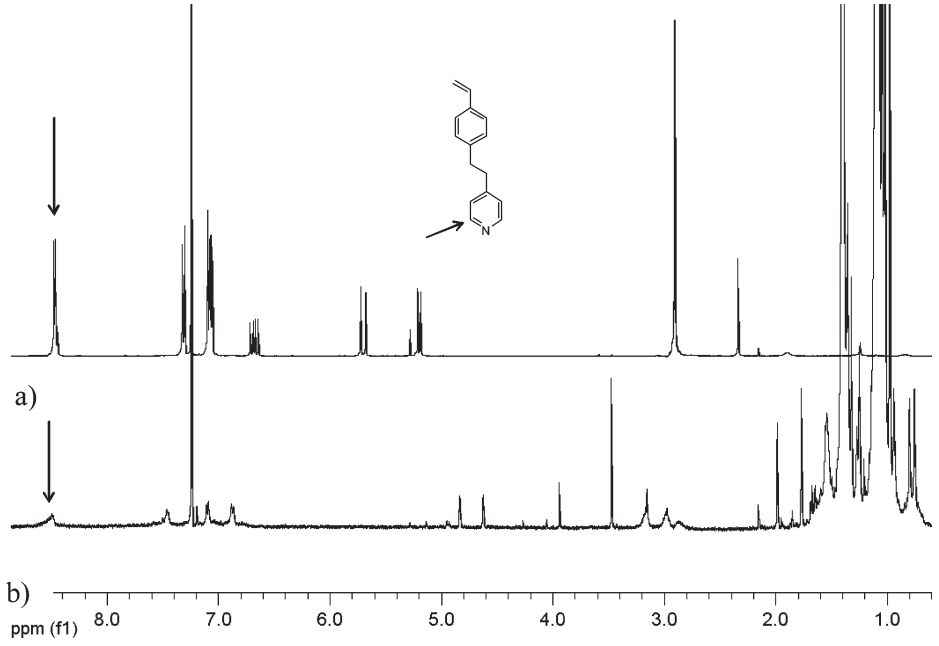


Figure 1. ^{1}H NMR of (a) pure comonomer **1a** and (b) PIB-**1a** copolymer with 1 mol % of **1a**, with respect to the integration of the pyridyl-C−H at 8.5 ppm **1a** vs the $-CH_2$ PIB at 1.4 ppm.

Calculation of k_p was then accomplished according to eq 2 using $k_{-i} = 7.5 \times 10^7$ 1/s and $k_i = 15$ 1/(s M^2) from Storey et al.[38]

Determination of k_p/k_{-i} According to Müller et al.[39] The rate constant of deactivation (k_{-i}) can be determined from the molecular weight distribution vs initiator concentration plot by linear curve fitting with a conversion of 100% according to eq 2 as derived by Müller et al.[39]

$$\mathrm{PDI} \approx 1 + 1/\beta(2/x - 1) \quad (4)$$

In this equation $\beta = k([\mathrm{I}]_0 k_p)^{1/2}$, where $[\mathrm{I}]_0$ is the initiator concentration, k_p the rate constant of propagation, and PDI the polydispersity index with PDI = M_w/M_n. Equation 1 is valid when the fraction of the chain end $[P^+LA_nCl^-]/[I]_0$ is $\leq 10^{-2}$ and $\beta \geq 10$. If exchange is not extremely slow, i.e., $\beta \gg \alpha$ (fraction of the active chains in equilibrium), this leads to an equation for $P_w \approx 1 + \gamma(1 + 1/\beta)$ (with $\gamma = \beta/\alpha$), and consequently, the polydispersity index (PDI) at $x = 1$ is

$$\mathrm{PDI} \approx 1 + 1/\beta = 1 + k_p/k_{-i}[\mathrm{I}]_0 \quad (5)$$

for $P_n \gg 1$. For determining k_p/k_{-i} different polymerizations with a variable initiator concentration ($[\mathrm{I}]_0 = 0.0026-0.022$ mol/L) were prepared, and the polydispersity index (PDI = 1.48−1.15) was determined by GPC-measurements (see Figure 7).

Results and Discussion

Concept. The structures of the used monomers investigated in the copolymerization reactions are given in Scheme 2. Thus, monomers **1a**−**1c** derived from styrene with attached pyridine and collidine moieties were investigated. An 1,2-ethylene chain was placed between the functional group and the styrene moiety in order to reduce eventual unfavorable electronic effects on the styrene moiety. In order to expand the structural variability, the triazole-containing monomers **2a**−**2c** were included, as their preparation can be easily accomplished by azide/alkine "click" reactions via *p*-azidomethylstyrene. In this case, the influence of the triazole moiety on the living cationic polymerization was studied as a concept for further modification of the PIB backbone. For comparison of all polar monomers the polymerization reactions with nonpolymerizable additives resembling the monomers **1a**−**1c** and **2a**−**2c** were studied with respect to their influence on the living cationic polymerization. Thus, pyridine, collidine, and picoline were used as polar additives resembling the chemical structures of monomers **1a**−**1c**; the additives **3a**−**3e** were used to study the influence of the triazole moiety and the attached alkyl/phenyl moieties on the polymerization process.

Monomer and Additive Synthesis. The synthesis of monomers **1a**−**1c** (see Scheme 3) was accomplished via a nucleophilic reaction between the lithiated collidines and 4-bromomethylstyrene (**4**) (see Supporting Information).[36,40,41] In-situ prepared 4-vinylbenzyl bromide (**4**) was directly used by coupling with picoline or *sym*-collidine deprotonated with a Li-organyl. The isomers **1a**−**1c** could be isolated up to 63% yield. Reaction of **4** with *sym*-collidine generated the isomeric products **1b** and **1c**, which could be separated by column chromatography and assigned unambiguously by 2D H−C long-range COSY-NMR analysis (see Supporting Information).

Monomers **2a**, **2b** and the additives **3a**−**3e** were prepared starting from 4-vinylbenzyl azide (**5**) and 4-azidomethylbenzene (**6**) synthesized according to the literature[42,43] via an azide/alkine "click" reaction[32,33] using THF as solvent, Cu(I)I, and diisopropylamine (DIPA) in the ratios of (0.08:1:1 = Cu(I):DIPA:azide) according to Yoo et al.[37] Monomer **2c** was prepared from 1-(prop-2-ynyl)-5-methylpyrimidine-2,4-(1*H*,3*H*)-dione (**7c**)[44] using reaction conditions from Tilliet et al.[45]

Copolymerization with Polar Monomers 1a−1c. As a first step, the copolymerization reactions of IB with monomer **1a** (containing a pyridyl unit attached to the styrene moiety) were investigated, adding 1−7 mol % of **1a** as comonomer directly to the polymerization mixture before starting the polymerization by addition of $TiCl_4$ as co-initiator at −80 °C (see Table 1). Solubility tests prior to the polymerization reaction ensured the solubility of the monomers in the final reaction mixture at −80 °C. The projected molecular weight was either 3000 or 6000 g mol^{-1}. Results of the polymerization reaction are shown in Table 1; incorporation of the comononer **1a** was determined by integration of the pyridyl

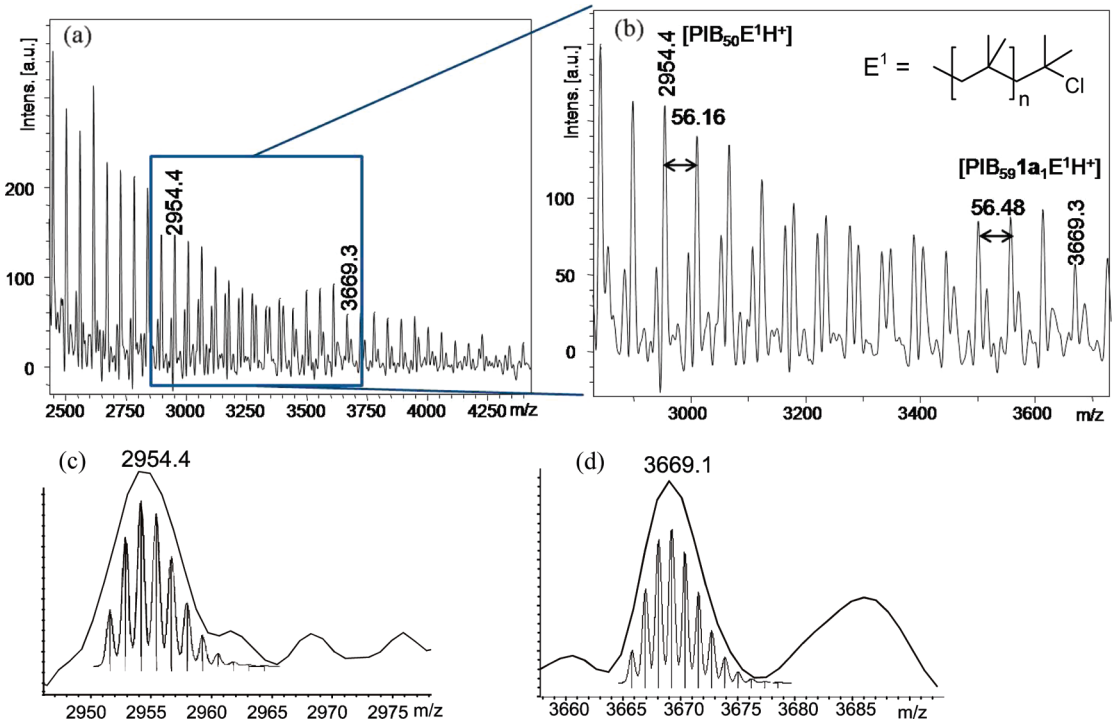


Figure 2. MALDI TOF MS of PIB-**1a** (as prepared from Table 1, entry 1) with one unit of incorporated **1a** in the second series (a, b). (c) Simulation for $[PIB_{50}E^1H^+]$ the first series. (d) Simulation for $[PIB_{59}\mathbf{1a}_1E^1H^+]$ as the second series (E^1 = *tert*-chloride).

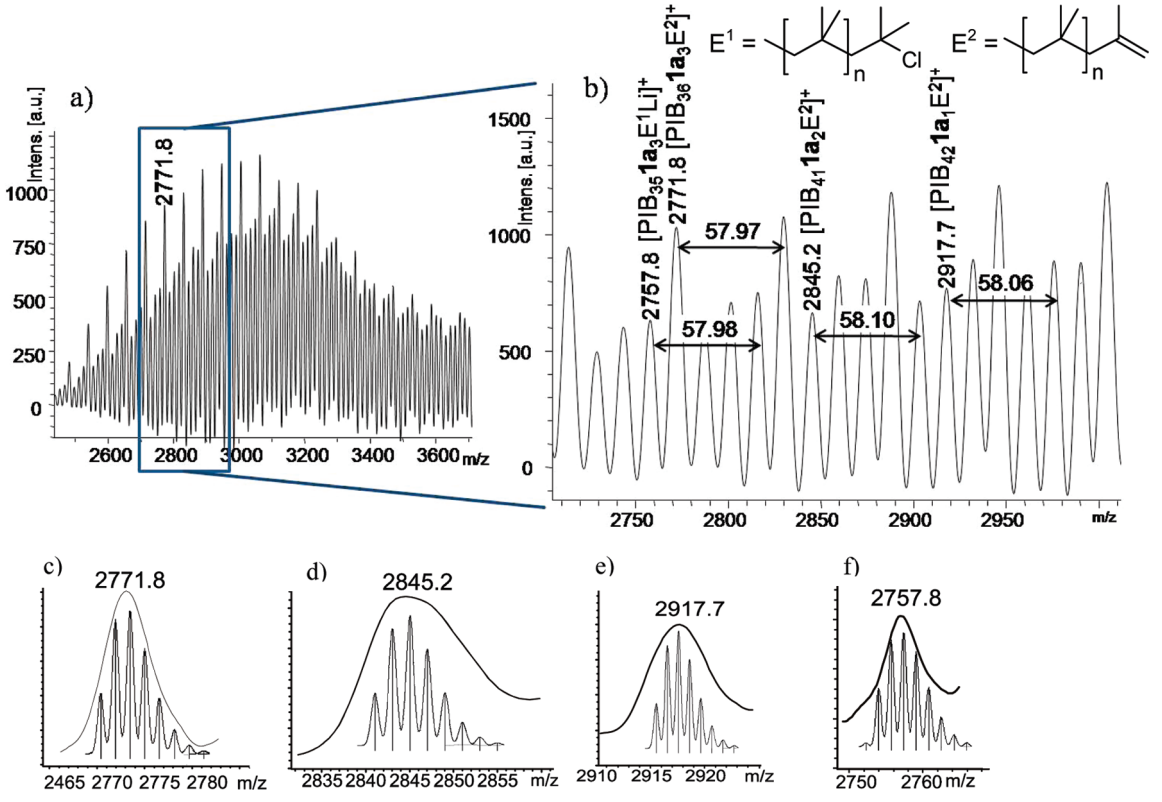


Figure 3. MALDI TOF MS PIB-**1a** (a) with expansion (b); (c–f) simulation of the isotopic pattern the four series (c) $[PIB_{35}\mathbf{1a}_3E^2]^+$, (d) $[PIB_{41}\mathbf{1a}_2E^2]^+$, (e) $[PIB_{42}\mathbf{1a}_1E^2]^+$, and (f) $[PIB_{35}\mathbf{1a}_3E^1Li]^+$ (E^1 = *tert*-chloride; E^2 = vinyl).

resonances at 8.46 ppm vs the main resonances of the PIB chain in the final polymer (precipitation of the polymer in acetone/methanol ensured the complete removal of eventually unreacted comonomer **1a** as judged by NMR spectroscopy and TLC).

Thus, the polymerization yields polymers with polydispersities below 1.4 upon addition of monomer **1a** up to 5 mol % (entries 2–4). At higher amounts (7 mol %, entry 5), the polymerization is no longer controlled, with polydispersities $M_w/M_n > 2.3$ and an expected molecular weight far below

the expectations. In a further series of experiments the addition of picoline as additive without the use of comonomer **1a** was probed in order to check for the influence of the pyridyl moiety on the polymerization (see entries 6−8), revealing low polydispersities but small to significant deviations from the expected molecular weights.

Incorporation of monomer **1a** was checked by ^{1}H NMR spectroscopy (see Table 1 and Figure 1) and MALDI-TOF methods (see Figures 2 and 3). As judged by NMR spectroscopy, the incorporation of monomer **1a** is possible up to ∼2.5 mol % (entries 2−5). However, at 7 mol % amount of comonomer **1a** less than 1 mol % is incorporated into the PIB polymer. Figure 2 shows the MALDI results of a polymer obtained in a copolymerization with 1 mol % of **1a** (see Table 1, entry 2) with a projected molecular weight M_n = 3000 g mol^{-1}. MALDI-mass spectrometry clearly shows two series of PIB polymer (all with the expected ∼56 g mol^{-1}): the first, low molecular weight series can be assigned to $PIB_nE^1H^+$ ions (n = 50) devoid of comonomer **1a**, where E^1 can be assigned as *tert*-chloride end group.

Simulation of the respective ions proves the assigments via excellent overlap of the simulated isotope pattern and the respective peak series (see Figure 2c,d). The higher molecular weight part clearly shows the expected incorporation of one unit of **1a**, visible as $[PIB_n\mathbf{1a}_1E^1H^+]$ ion (n = 59; E^1 = *tert*-chloride).

As the initially projected molecular weight of M_n = 3000 g mol^{-1} with 1 mol % **1a** as comonomer statistically only allows for the incorporation of ∼1 unit of **1a**, a higher molecular weight (M_n = 10 000 g mol^{-1}) under the same reaction conditions (1 mol % of **1a**, see Table 1, entry 6) was probed. MALDI results of this polymer are shown in Figure 3, clearly demonstrating the incorporation of one, two, and three monomeric units of **1a**, as visible in the four series via the respective ions (c) $[PIB_{35}\mathbf{1a}_3E^2]^+$, (d) $[PIB_{41}\mathbf{1a}_2E^2]^+$, (e) $[PIB_{42}\mathbf{1a}_1E^2]^+$, and (f) $[PIB_{35}\mathbf{1a}_3E^1Li]^+$ (with E^1 = *tert*-chloride; E^2 = vinyl).

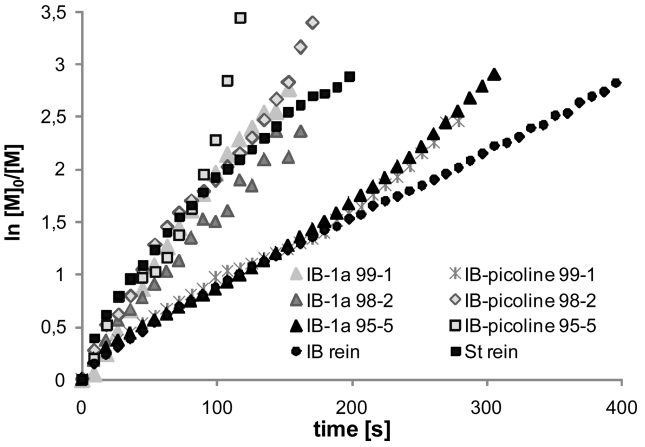


Figure 4. First-order plot of the copolymerization of IB with monomer **1a**. Conditions: *n*-hexane-DCM (v/v) 60:40; −80 °C; $[M]_0$ = 1.2 M, $[TMPCl]_0$ = 0.01 M; $[TiCl_4]$ = 0.128 M; [DtBP] = 2.2 mM; [DMA] = 5.4 mM.

This clearly demonstrates the successful incorporation of the polar comonomer **1a** into the growing PIB chains—a result unexpected with this level of (a) control over the polymerization reaction and (b) with respect to the amount of incorporated monomer. Therefore, a more detailed look on the reaction kinetics of the IB polymerization in the presence of either monomer **1a** or the analogous base picoline (structurally reminiscent of the picoline unit in **1a**) was conducted (see Figure 4). Basically, both types of polymerization reactions show linear $\ln[M_0]/[M]$ vs time (t) plots up to conversions of 92% or more, with an increase of the apparent rate of polymerization (k_p) by a factor of 2−4 (see also data for k_p and k_{app} in Table 1) as compared to the IB or styrene polymerization under exactly the same reaction conditions. Thus, the polymerization is enhanced by addition of up to 5 mol % of either monomer **1a** or pure picoline. As both—the comonomer **1a** and the pure additive picoline—yielded similar results, a purely stereoelectronic effect exerted from the closely present nitrogen in **1a** can be excluded, thus hinting toward a change in the equilibrium between the "dormant = *tert*-chlorine-telechelic" and the "active = cationic" species[20] rather than a removal of protic impurities or reduction in the "cationicity" of the actively (growing) species.

In order to check for the influence of small structural variations in monomer **1a**, the isomeric monomers **1b** and **1c** reminiscent of a collidine base were checked in a similar copolymerization. The data are shown in Table 2, and the respective kinetic investigations in are shown in Figure 5. Thus, already 1 mol % of **1b** leads to strongly increased polydispersities (M_w/M_n = 1.8) and a molecular weight above the expectations. Higher amounts of **1b** still lead to a definite loss of control over the polymerization reaction with mostly bimodal molecular weight distributions (see entries 1−3). Monomer **1c** behaves a little differently at 1 mol % but similarly at higher amounts (2 mol %). As comparison, *sym*-collidine as additive yielded comparably poor results, underlining the fact that these bases do not lead to controlled cationic homo- or copolymerization reactions. In both cases, however (see Figure 4), the kinetics show a linear monomer

Table 2. Copolymerization of IB with 1b and 1c in Comparison to *sec*-Collidine as Additive[a]

entry	monomer/additive	mol %	M_n[b] [g/mol]	M_w/M_n	incor (%)[c]	conversion (%)[g]	k_{app} (10^{-3} s^{-1})	yield (%) o.th	k_p[d] (10^8s^{-1} M^{-1})	RN
1	**1b**	1	9100	1.9	1	96	45.7	75	18.8	30.16
2		2	8700	1.8	0.4	98	61.8	80	24.4	38.99
3		5	6700	1.2	2	97	9.73	< 10	2.96	4.73
			255	1.8						
4	**1c**	1	4200	1.1	−[e]	92	19.1	75	3.64	5.82
5		2	800	1.1						
			2000	1.5	−[e]	–	–	–	–	–
6	*sym*-collidine	1	2800	1.2	−4[e]	95	62.9	89	4.84	7.74
7		2	6600	1.3	−[e]	97	23.5		7.07	11.24
8		5	–[f]	–[f]	–[f]	–[f]	–[f]	–[f]	–[f]	–[f]

[a] [IB] = 1.2 M, [TMPCl] = 0.01 M; $[TiCl_4]$ = 0.128 M; [DtBP] = 2.2 mM; [DMA] = 5.4 mM; *n*-hexane−DCM v:v 60:40, −80 °C; calcd M_n = 6700 g/mol. [b] M_n determined by GPC measurement in THF as solvent, calibration with PIB standards (g/mol). [c] Determined by integration of 6.8−7.1 ppm **1b**, **1c** vs 1.0−1.1 ppm (IB) ^{1}H NMR. [d] Determination by eq 3 (k_{-i} = 7.5 × 10^7 1/s, k_i = 15 1/(s M^2))[38] with k_p determined by combination of eqs 1 and 2 (K_{eq} = k_i/k_{-i}) with respect to the dimeric form of the LA ($[LA]_0^2$).[46] [e] No incorporation detected. [f] No polymerization observed. [g] Determined by inline FTIR spectroscopy $\ln[M]_0/[M]_t$ plot; limited by detection of concentrations below ∼0.07 mol/L (IB).

consumption and a significant acceleration of the polymerization in comparison to picoline as additive or monomer **1a**. Incorporation of monomer **1b** in amounts up to ~2 mol % were detected by ^{1}H NMR spectroscopy and MALDI (see Supporting Information for detailed spectra).

Copolymerization with Triazole-Containing Monomers 2a−2c. As the structural variability and also synthetic accessability of the monomers **1a−1c** were quite limited, a simpler structural approach to styrene-type monomers was investigated. Coming up with the azide/alkine "click" reaction,[32,33,47−49] the monomers **2a−2c** with a 4-(methylene-triazole) moiety were prepared and investigated toward their influence and incorporation during a living cationic polymerization of IB. All monomers **2a−2c** (see Table 3) did not show a living copolymerization of IB, as clearly visible by high polydispersities and strong deviations from the expected molecular weights.

However, despite the fact that the incorporation could not be detected with ^{1}H NMR spectroscopy (sensitivity limit ~1%), it was possible to detect the species with one incorporated monomer unit **2c** within the MALDI spectrum (see Figure 6). As the absolute amount of incorporation must be low, a preferential desorption of the strongly ionic species $[PIB\mathbf{2c}_1Li]^+$, $[PIB\mathbf{2c}_2]^+$, and $[PIB\mathbf{2c}_2Ag]^+$ with respect to the pure $[PIBLi]^+$ can be assumed and also expected. Thus, the obviously extremely low incorporation of **2c** is visible quite strongly in the respective MALDI spectra.

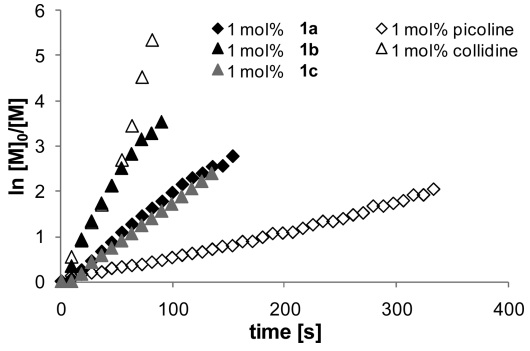


Figure 5. First-order plot of the copolymerization of IB with monomers **1a**, **1b**, and **1c**. Conditions: *n*-hexane−DCM (v/v) 60:40; −80 °C; $[M]_0$ = 1.2 M, $[TMPCl]_0$ = 0.01 M; $[TiCl_4]$ = 0.128 M; [DtBP] = 2.2 mM; [DMA] = 5.4 mM.

Copolymerization with Triazole-Containing Additives 3a−3d. In order to check for the influence of the triazole moiety on the IB polymerization, the use of the triazole-containing additives **3a−3d** was probed, as shown in Table 3 (entries 6−12) and Figure 7. Thus, the kinetics upon addition of 1 mol % **3a−3d** as additives were followed by inline monitoring of the IB polymerization. Except for additives **3a** and **3d** (containing a butyl moiety and a 4-methylphenyl moiety, respectively, at the triazole moiety), the polymerization reaction displayed low polydispersities of the obtained polyisobutylenes. A slight electronic influence of the substituent of the triazole moiety is seen, with electron-donating moieties (such as PhMe (**3d**), Ph−OCH_3 (**3c**), and butyl (**3a**) leading to strongly enhanced rates of polymerization, whereas Ph−Cl (**3e**) and Ph (**3b**) display significantly reduced polymerization rates. As these substances do not act as comonomers but just as additives during the polymerization, this kinetic effect can only be explained by changes of the equilibrium between active/dormant species during the living cationic polymerization. A comparison of comonomer **2b** and the additive **3b** at higher amounts of 1, 2, and 7 mol % (for data see Supporting Information Figure S 24) leads to a still living polymerization with a reduction of the rate constants by a factor of ~10 (7 mol % of **2b**) and ~3 (7 mol % of **3b**) with increasing amount of **2b** or **3b**, respectively.

From these data, it seemed conclusive that the triazoles, whether or not as additive of comonomer, lead to a change in the equilibrium between the active/dormant species during the IB polymerization. Measurements of the equilibrium constant K of this ion equilibrium can be achieved either by inline UV spectroscopy or via indirect methods, such as determination of M_w/M_n at low conversions as used by Storey et al.[20] As low-temperature UV spectroscopy or probe sampling at (−80 °C) could not be achieved, the indirect method as discussed by Müller et al.[39] was used, relying on measurements of M_w/M_n at 100% conversion by variations of the initiator concentration $[I_0]$ (see Experimental Part) and determining k_p/k_{-i} by plotting M_w/M_n vs $[I_0]$ (see Experimental Part, eqs 4 and 5). Thus (see Figure 8), a value for $k_p/k_{-i} = 15.52$ can be determined for 1 and 2 mol % of additive **3b**. Using the so-determined k_p/k_{-i} value, the rate constant of initiation (k_i) can be calculated via eq 6, with k_i the rate constant of initiation, k_{-i} the rate constant of deactivation, k_p the rate constant of propagation, the apparent rate constant (k_{app}), $[I]_0$ as the starting concentration of

Table 3. Kinetic Values of the Copolymerization of IB with 1 mol % of the Polar Monomers 2a−2c in Comparison to the Polymerization of IB in the Presence of the Polar Additives 3a−3d[a]

entry	monomer/ additive	mol % corr to IB	M_n[b] [g/mol]	M_w/M_n	conversion (%)[g]	incor (%)[c]	k_{app} (10^{-2} s^{-1})	yield (%)	k_p[d] (10^8 s^{-1} M^{-1})	RN
1	**2a**	1	12000	5.9		−[e]	n.d.	< 5	–	–
2	**2b**	1	3600	1.6	97	< 1	8.72	86	14.2	22.8
3	**2b**	2	3100	1.5	97	< 1	3.94	85	5.5	8.58
4	**2b**	7	5400	1.3	90	< 1	0.63	85	1.5	2.46
5	**2c**	1	3100	1.5	97	< 1	2.98	85	4.19	6.7
6	**3a**	1	5800	2.3	95	–[f]	0.57	80	1.5	2.4
7	**3b**	1	2000	1.3	94	–[f]	8.16	90	7.4	11.84
8	**3b**	2	5200	1.3	91	–[f]	1.60	85	3.8	6.06
9	**3b**	7	2000	1.3	97	–[f]	3.00	80	2.7	4.35
10	**3c**	1	7500	1.2	97	–[f]	3.58	87	12.2	19.45
11	**3d**	1	7300	1.8	99	–[f]	19.20	90	63.5	101.6
12	**3e**	1	5200	1.2	98	–[f]	1.65	85	3.8	6.03

[a] [IB] = 1.2 M; [TMPCl] = 0.01 M; [DtBP] = 2.5×10^{-3} mol/L, $[TiCl_4]$ = 0.124 mol/L, [DMA] = 4.41×10^{-3} mol/L, *n*-hexane−DCM (v/v) 60:40; −80 °C; calcd M_n = 6000 g/mol. [b] M_n determined by GPC measurement in THF as solvent, calibration with PIB standards (g/mol). [c] Determined by integration of 5.4−5.5 pmm (**2a−2c**) vs 1.0−1.1 ppm (IB) ^{1}H NMR spectroscopy. [d] Determination by eq 3 ($k_{-i} = 7.5 \times 10^7$ 1/s, $k_i = 15$ 1/(s M^2))[38] with k_p determined by combination of eqs 1 and 2 ($K_{eq} = k_i/k_{-i}$) with respect to the dimeric form of the LA ($[LA]_0^2$).[46] [e] No signals from the comonomer visible in ^{1}H NMR. [f] Additive, no incorporation possible. [g] Determined by inline FTIR spectroscopy $\ln[M]_0/[M]_t$ plot; limited by detection of concentrations below ~0.07 mol/L (IB).

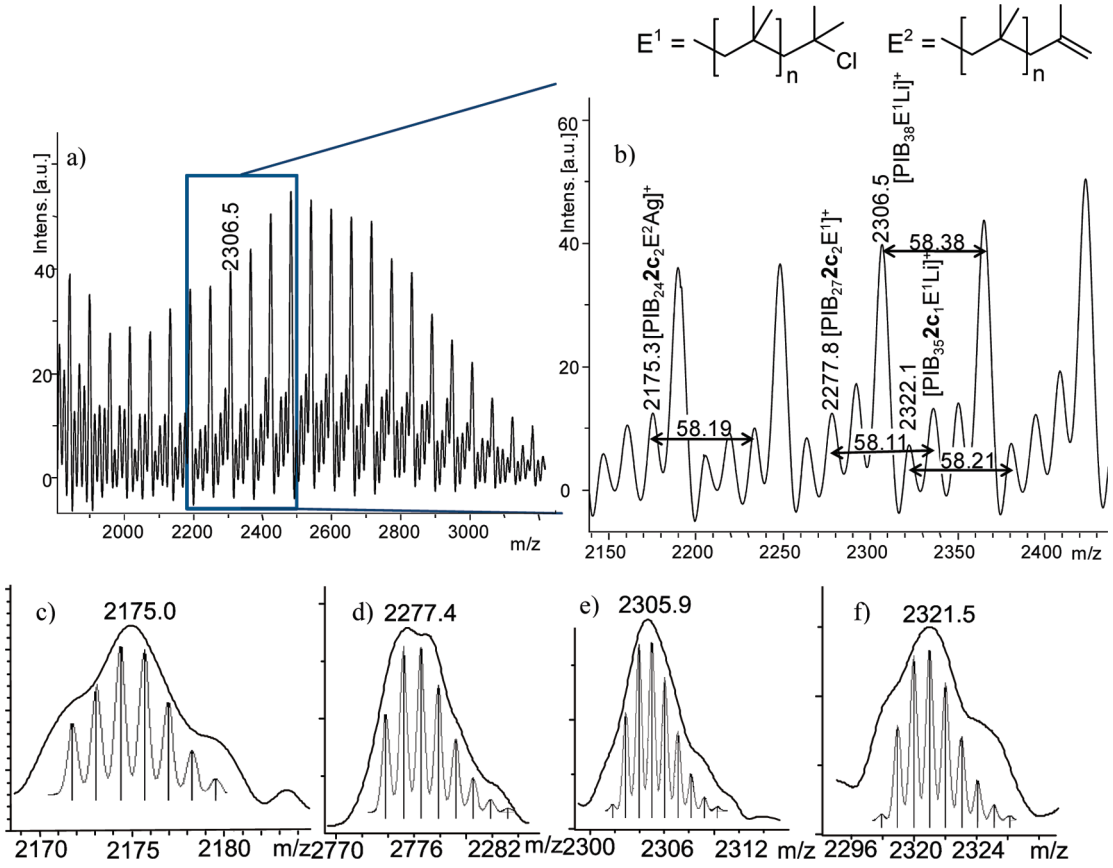


Figure 6. (a, b) MALDI-TOF MS of PIB-**2c** with (c–f) simulation of the isotopic pattern four series: (c) $[PIB_{24}\mathbf{2c}_2E^2Ag]^+$, (d) $[PIB_{27}\mathbf{2c}_2E^1]^+$, (e) $[PIB_{38}E^1Li]^+$, and (f) $[PIB_{35}\mathbf{2c}_1E^1Li]^+$ (E^1 = *tert*-chloride; E^2 = vinyl).

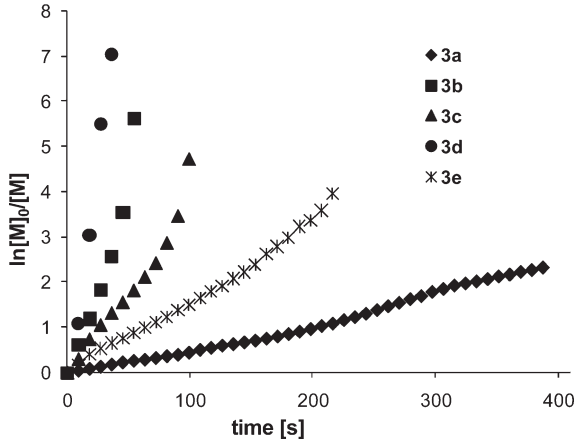


Figure 7. First-order kinetic plots of IB polymerization in presence of 1 mol % additive **3a** to **3e**. *n*-Hexane–DCM (v/v) 60:40; −80 °C; $[M]_0$ = 1.2 M, $[TMPCl]_0$ = 0.01 M; $[TiCl_4]$ = 0.128 M; [DtBP] = 2.2 mM; [DMA] = 5.4 mM.

the initiator, and $[TiCl_4]$ the starting concentration of the Lewis base.

$$k_i = k_{app}/([I]_0[TiCl_4]^2(k_{-i}/k_p) \quad (6)$$

Using this equation with the determined value (Table 3, entry 7) k_i = 34.19 1/(s M^2) can be calculated. This value is about double of the value reported in literature by Storey et al.[38] (k_i = 15.5 1/(s M^2)). We thus conclude that the ion equilibrium of this polymerization is disturbed by addition of the triazole-containing additive **3b**.

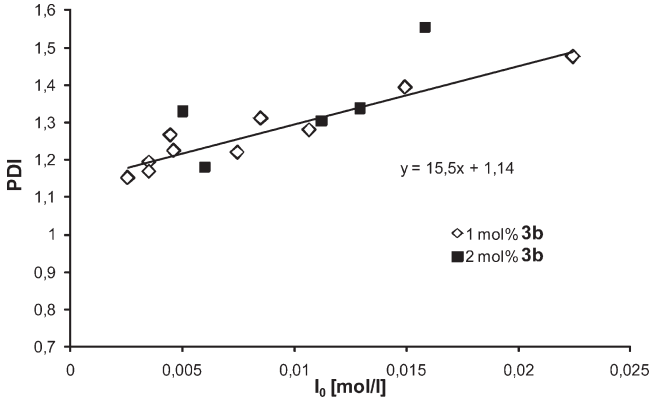


Figure 8. Determination of k_p/k_{-i} by Müller with 100% conversion → k_p/k_{-i} = 15.52.

Conclusion

We have studied the direct copolymerization of polar styrene monomers containing pyridine (**1a**), collidine (**1b**, **1c**), thymine (**2c**), and/or triazole moieties (**2a**–**2c**) with IB using living cationic polymerization. Whereas the copolymerization with the styrene monomers **1a**, **1b**, and **2c** proceeded under incorporation of up to 2 mol % of the comonomer into the PIB polymer as proven by MALDI methods and NMR spectroscopy, the comonomer **1c** was not incorporated and resulted in broad polydispersities of the resulting PIB polymers. For structural comparison, the triazole-containing additives **3a**–**3d** (1 mol %) were probed in the IB polymerization under the same conditions, revealing a strong structural effect, especially for the additives **3a** and **3d** (containing a butyl moiety and a 4-methylphenyl moiety,

respectively, bound to the triazole moiety), which lead to high polydispersities and an uncontrolled polymerization reaction. Inline IR kinetic measurements of the monomer consumption demonstrated strong effects of the comonomer structure **1a**−**1d** on the polymerization kinetics, with rates of polymerization (k_p) increasing up to a factor of 15 with respect to the native (living) IB polymerization. Moreover, the addition of nonpolymerizable additives containing triazole moieties revealed a strong dependency on the attached residue R (R = hexyl (**3a**), phenyl (**3b**), *p*-methoxyphenyl (**3c**), *p*-methylphenyl (**3d**), *p*-chlorophenyl (**3e**)), with a decreasing k_p in the order of **3e** > **3b** > **3c** > **3e** > **3a** = k_p/k_{-1}. Measurements of k_p/k_{-1} of the triazole-containing additive **3b** demonstrated a change by a factor of ∼4.5 to the homopolymerization of IB under the same conditions, proving that ion equilibria are disturbed by addition of polar species during the IB polymerization. The presented method for the first time opens the possibility to introduce polar moieties in a direct copolymerization approach into PIB polymers via living cationic polymerization. Investigations of the copolymerization with other polar comonomers are in progress in our laboratories.

Acknowledgment. Grants from the DFG INST 271/249-1, INST 271/247-1, and INST 271/248-1 are gratefully acknowledged.

Supporting Information Available: $^1H/^{13}C$ NMR spectra for monomers **1a**−**2c** and additives **3a**−**3e**, C−H long-range COSY NMR spectra of **1b** and **1c**; preparative procedures for **4**, **5**, **6**, and **7c**; MALDI TOF MS spectra for poly(IB-*rnd*-**2c**) polymer; IR online measurement spectra showing the overlapping IB stretching band and an active species; conversion vs time plots obtained from inline IR for poly(IB-*rnd*-**2b**) in comparison to PIB in the presence of additive **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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