Synthesis and Analysis of Telechelic Polyisobutylenes for Hydrogen-Bonded Supramolecular Pseudo-Block Copolymers

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Received July 2, 2003; Revised Manuscript Received December 18, 2003

ABSTRACT: New telechelic polyisobutylenes (PIB) with hydrogen-bonding motifs were prepared. Nucleobases such as thymine, uracil, and cytosine as well as chelate-type hydrogen-bonding donor−acceptors were affixed onto the end groups of the PIB. Starting with PIB of defined molecular weight, prepared by living cationic polymerization, hydroxyterminated PIB was generated, which subsequently was transformed into the corresponding chloromethyl ether. Reaction with silylated nucleobases furnished the final nucleobase-telechelic PIB in high yields. The chelate-type PIB was prepared by a sequence of nucleophilic/addition reaction steps adapted to the low solubility of PIB polymers in polar solvents. The structure of the PIB polymers was proven by ^{1}H NMR, ^{13}C NMR, and MALDI−TOF MS analysis proving the complete conversion between the reaction steps in quantitative yields. The pure PIB polymers with specific hydrogen bonding patterns will allow the investigation of supramolecular pseudo-block copolymers.

Introduction

The use of intermolecular interactions to organize the threedimensional structure of polymers has attracted increased attention during the past few years.[1] Directed hydrogen bonds[2] have shown equally effective in comparison to "conventional" intermolecular bonds such as metal complexes,[3] $\pi-\pi$ stacking,[4] and ionic forces,[5] since they allow the tuning of binding constants between several 1 M^{-1} up to 10^6 M^{-1} by use of a specific hydrogen-bond matching pair.[6] Additionally the ability to select specific intermolecular bonding combinations within several possibilites[7] (i.e.: favoring A−B contact over A−A or B−B binding) is unique to hydrogen bonds, thus offering new types of supramolecular arrangements. When affixed properly to small molecules[8] or polymers,[9] hydrogen bonds can induce new types of ordering and organization within materials, leading to supramolecular polymers.[10] The positioning of hydrogen bonds at specific positions within polymer chains can generate tunable materials with new properties such as thermoplastic behavior[11] and controlled rheological properties[12] as well as controlled molecular architectures.[13]

A necessary requirement for the investigation of this type of materials is the controlled synthesis of telechelic polymers with appropriately positioned hydrogen donor/acceptor moieties. Several direct methods such as ROMP,[14] Ziegler−Natta,[15] ATRP,[16] anionic,[17] and free radical polymerizations[18] as well as efficient postmodification methods[19] can be combined to generate telechelics with hydrogen bonding substituents, defined chain lengths and low polydispersities. The synthesis of telechelic polymers with hydrogen-bonding motifs derived from nucleobase structures has been described by a variety of authors.[17,19,20] Usually, conventional nucleophilic substitution methods derived from the well-known chemistry of nucleosides are adapted to this purpose. Critical for the attachment of nucleobases (such as thymine, uracil, cytosine, or adenine) is the site specific and regiospecific substitution due to the presence of more than one nucleophilic site at the respective nucleobase appropriate for substitution.

The present publication reports on the synthesis and analysis of telechelic poly(isobutylenes) "PIB" with defined hydrogen-bonding motifs at their chain ends (Scheme 1). The combination between the living polymerization of polyisobutylene with hydrogen bonding motifs is attractive due to two reasons: On one hand, the quasi-living polymerization of PIB[21] allows the exact tailoring of telechelics with defined chain lengths, low polydispersity, and defined functionalization[21d] due to the absence of chain transfer- and termination reactions. On the other hand, PIB polymers are extremely flexible, low-T_g polymers, allowing the study of the influence of hydrogen-bonding structures in mixtures with complementing stiff-rod systems (such as the poly(ether ketones) recently described in our group[22]). Thus, phase separation effects in dependence of hydrogen-bonding strength yielding pseudo-block copolymers can be studied impressively.[22c] Therefore, two types of PIB polymers were prepared: telechelic PIB with a thymine (**1a**), uracil (**1b**), or cytosine (**1c**) residue reminiscent of bonding patterns in DNA, as well as chelate-type bonding structures with multiple hydrogen bonding arrays **1d** derived from Lehn et al.[23] There is a stability difference of more than 10^3 between the triple hydrogen bonds in **1a**−**1c** (K_{assn} is approximately 1000 M^{-1}) compared to the multiple hydrogen bonds in **1d** (K_{assn} $>10^6$ M^{-1}).

The quasi-living cationic polymerization of polyisobutylene (PIB) is not compatible with the polar nature of hydrogen bonds. Additionally, there is a limited solubility of PIB in a variety of solvents normally appropriate for the nucleophilic displacement chemistry useful for the introduction of nucleobases. Thus, two main points

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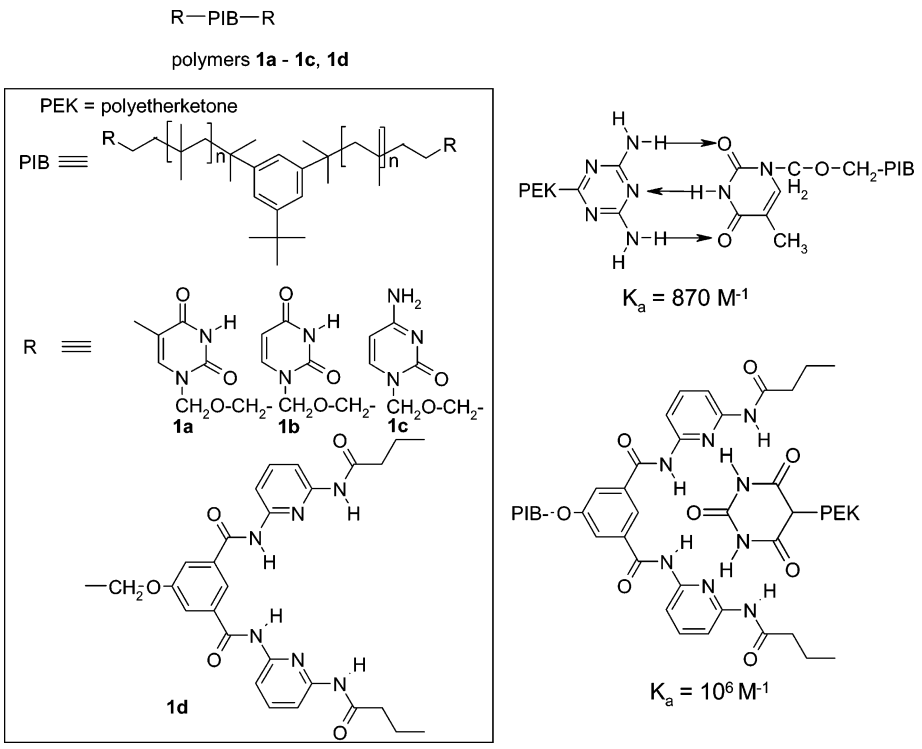
10.1021/ma034924t CCC: $27.50
Published on Web 02/10/2004

Scheme 1



have been investigated within this publication: the development of a protocol for the postmodification reaction yielding the telechelic polymers **1a**−**1d** as well as efficient reaction pathways for the complete attachment of nucleobase structures onto the PIB backbone together with the analysis of the end groups via NMR spectroscopy and MALDI.

Experimental Section

Instrumentation. NMR spectra were obtained from a 200 MHz Bruker AC200 spectrometer, a 400 MHz Bruker Avance DRX 400 and a 600 MHz Bruker DRX 600 in $CDCl_3$ (liquid NMR). GPC analysis was performed on a Hewlett-Packard Chemstation 1100 system using Styragel linear columns in THF at 40 °C. Polyisobutylene standards were used for conventional external calibration using a Waters RI 2410 refractive index detector. DSC-measurements were done on a Mettler DSC30 System TA4000. MALDI−TOF mass spectra were performed on a Micromass TofSpec2E time-of-flight mass spectrometer equipped with a nitrogen laser (λ = 337 nm, operated at 5 Hz) and a time-lag focusing unit. Ions were generated by irradiation just above the threshold laser power. The spectra were recorded in the reflectron mode with an acceleration voltage of 20 kV and externally calibrated with a suitable mixture of poly(ethylene glycol)s (PEG). Sample solutions were prepared by mixing a solution of dithranol in THF (c = 10 mg/mL), a solution of the analyte (c = 3 mg/mL), and a solution of CF3COOAg (AgTFA, c = 1 mg/mL) and CF3COONa (NaTFA, c = 1 mg/mL), respectively, in a ratio of 5:1:1 (v/v/v). Additionally, 5:1:1:0.1 dithranol−analyte−NaTFA−AgTFA mixtures were applied, and 0.5 μL of the mixture was deposited on the sample plate (stainless steel) and allowed to dry under air. The spectra of 100−150 shots were averaged to improve the signal-to-noise ratio.

Materials. All materials were obtained from Aldrich and used without further purification if not mentioned otherwise. 2,6-Diaminopyridine was recrystallized from boiling chloroform. Silylated nucleobases were prepared according to Griengl et al.[24a] 1-*tert*-Butyl-3,5-bis(1-chloro-1-methylethyl)benzene (DCCl) was obtained according to Faust et al.[21e] *N*-(6-Aminopyridine-2-yl)butyramide was obtained according to Lehn et al.[23] DMA (*N*,*N*-dimethylacetamide) was dried over calcium hydride and distilled in vacuo before use. *n*-Hexane was refluxed over concentrated H_2SO_4 for 48 h in order to remove olefins. The organic layer was washed with distilled water, dried with $MgSO_4$ and stored over CaH_2. It was distilled under a dry Ar atmosphere before use. THF was freshly distilled from potassium before use. CH_2Cl_2, $CHCl_3$, $C_2H_4Cl_2$, and methanol were dried and distilled over CaH_2 under dry argon. DMF was dried and distilled over BaO under dry argon. Isobutylene was dried by passing the gas through a column packed with potassium hydroxide.

Syntheses of Allyl-Terminated PIB's (2). A general method for synthesis of allyl-terminated PIB's is shown by the synthesis of allyl-terminated PIB with M_n = 2500 g mol^{-1} according to Ivan et al.[21b,f] Dichloromethane (160 mL), olefin-free *n*-hexane (160 mL), DMA (1.96 mL), and DCCl (3.05 g, 10.61 mmol) were added to a 1 L three-necked flask equipped with a septum, a mechanical stirrer, and a nitrogen inlet and cooled to −80 °C. Condensated isobutylene (14 g, 250 mmol) was charged into the reactor by a syringe. After 5 min of stirring, a prechilled solution of $TiCl_4$ (40.25 g, 212 mmol) and 2,6-di-*tert*-butylpyridine (0.2 mL) in methylenchloride (80 mL) and olefin-free *n*-hexane (200 mL) was transferred to the reactor by a transfer needle. The temperature was held at −80 °C during the whole polymerization procedure. After 10 min, a second addition of isobutylene (9.82 g, 175 mmol) followed. 20 min later, the polymerization was terminated by the addition of prechilled allyltrimethylsilane (6.7 g, 58.6 mmol). After 30 min, the mixture was poured into a vigorously stirred saturated aqueous $NaHCO_3$ solution and filtered through Hyflo. The organic layer was separated, washed 5 times with distilled water, dried over $MgSO_4$. The solvent was removed by rotary evaporator. Then, the polymer was redissolved in a small amount of *n*-hexane and precipitated 2 times into acetone in order to remove excess allyltrimethylsilane. Finally the colorless sticky polymer was dried under vacuum. Yield: 25.2 g (94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.79 (s, 12H), 0.83−1.50 (m, 433H), 1.54 (s, 4H), 1.83 (s, 4H), 2.01 (d, 4H), 5.00 (t, 4H), 5.83 (m, 2H), 7.17 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ(ppm) 28.70−31.60, 32.29, 34.75, 37.51−39.50, 50.29, 55.72, 58.00−60.00, 116.75, 120.06, 121.15, 136.08, 148.5, 148.93.

Syntheses of Hydroxy-Terminated PIB's (6). A general method for synthesis of hydroxy-terminated PIB's is shown

by the synthesis of hydroxyl-terminated PIB with $M_n = 2500$ g mol^{-1} according to a modified protocol of Ivan et al.[21c] Allyl-terminated PIB **2** (7.5 g, 3 mmol) was dissolved in THF (430 mL), freshly distilled over potassium. The solution was sparged with argon for 5 min. A 0.5 M 9-BBN-solution in THF (75 mL, 37.5 mmol) was added dropwise under dry argon atmosphere at room temperature. After 5 h of stirring the mixture was cooled to 0 °C and methanol (2.1 mL) and *m*-chloroperoxybenzoic acid (47 g, 0.19 mol) were added carefully. The reaction was allowed to react for 10−15 h, and then *n*-hexane (100 mL) and distilled water (100 mL) were added. The aqueous phase was saturated with potassium carbonate. The organic layer was washed five times with 50% aqueous methanol and five times with distilled water, separated, and dried with sodium sulfate. After filtration the solvent was evaporated and the product dried under vacuum at ambient temperature. Yield: 7.5 g (100%); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.79 (s, 12H), 0.83−1.67 (m, 424H), 1.83 (s, 4H), 3.62 (t, 4H $J = 6.9$ Hz), 7.17 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 27.75, 30.76−31.62, 32.28, 34.76, 37.81−38.93, 41.41, 55.57, 58.54−59.50, 63.96, 120.06, 121.15, 148.5, 148.93.

Syntheses of Telechelic PIB's 1a—1c. A general method for synthesis of nucleoside telechelic PIB's is shown by the synthesis of thymine−telechelic PIB **1a** ($M_n = 2700$ g mol^{-1}). Gaseous HCl was introduced as a slow stream for 1 h into a cold (0−4 °C) mixture of PIB−OH (**6**) (1.1 g, 0.4 mmol), paraformaldehyde (50 mg, 1.6 mmol), and dry calcium chloride (2 g, 18 mmol) in dry 1,2-dichlorethane (50 mL), while maintaining the internal temperature below 15 °C. The quantitative conversion to PIB−OCH_2Cl (polymer **7**) was proven by ^{1}H NMR spectroscopy. After 15 min flushing with nitrogen, the reaction mixture was filtered into a 100 mL round-bottom flask which contained the silylated thymine (8 mmol). The clear solution was stirred for 3 h at room temperature under an atmosphere of nitrogen. After being gently evaporated to dryness, the reaction mixture was hydrolyzed by heating in water (20 mL)/ethanol (20 mL) under reflux for 30 min and dried under vacuum again. To remove the excess of thymine the crude product was suspended in dry chloroform, filtered and evaporated to dryness. Pure **1a** was afforded by chromatography (SiO_2, $CHCl_3$:THF = 8:1). Yield: 0.98 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.79 (s, 12H), 0.92−1.61 (m, 539H), 1.83 (s, 4H), 1.95 (s, 6H), 3.49 (t, 4H $J = 6.6$ Hz), 5.12 (s, 4H), 7.13 (s, 2H), 7.17 (s, 3H), 8.05 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 12.36, 24.43, 28.67−31.60, 32.26, 34.72, 37.75−38.92, 41.55, 55.57, 58.53−59.50, 70.52, 77.05, 111.57, 120.05, 121.14, 138.84, 148.48, 148.92, 151.10, 163.97.

NMR Characterization of PIB 1b. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.79 (s, 12H), 0.88−1.61 (m, 437H), 1.83 (s, 4H), 3.50 (t, 4H $J = 6.6$ Hz), 5.15 (s, 4H), 5.78 (d, 2H $J = 7.8$ Hz), 7.16 (s, 3H), 7.31 (d, 2H $J = 7.8$ Hz), 8.3−9.0 (bs, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 24.42, 27.93−31.62, 32.26, 34.73, 37.32−38.93, 41.57, 56.60, 58.57−59.50, 70.70, 77.19, 103.11, 120.04, 121.14, 142.99, 148.48, 148.94, 151.06, 163.56.

NMR Characterization of PIB 1c. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.79 (s, 12H), 0.90−1.60 (m, 419H), 1.83 (s, 4H), 3.51 (t, 4H $J = 6.1$ Hz), 5.20 (s, 4H), 5.81 (bs, 6H), 7.17 (s, 3H), 7.41 (d, 2H $J = 6.8$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 24.51, 29.27−31.61, 32.25, 34.72, 37.25−38.92, 41.63, 55.62, 59.68−59.68, 70.50, 77.20, 95.52, 120.03, 121.12, 144.01, 148.47, 148.93, 156.34, 165.69.

NMR Characterization of PIB 7. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.79 (s, 12H), 0.95−1.50 (m, 426H), 1.83 (s, 4H), 3.65 (t, 4H $J = 6.6$ Hz), 5.51 (s, 4H), 7.17 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 23.92, 29.30−31.58, 32.23, 34.72, 37.72−38.90, 41.49, 55.54, 58.50−59.50, 71.53, 83.32, 120.03, 121.12, 148.47, 148.91.

Syntheses of Model Compounds 5a—5c. A general method for the synthesis of model compounds is shown by the synthesis of 1-dodecyloxymethyl-5-methyl-1*H*-pyrimidine-2,4-dione (**5a**). Gaseous HCl was introduced as a slow stream for 1 h into a cold (0−4 °C) mixture of dodecane-1-ol (**3**) (1 g, 5.37 mmol), paraformaldehyde (0.18 mg, 5.9 mmol), and dry calcium chloride (5 g, 45 mmol) in dry 1,2-dichlorethane (50 mL), maintaining the internal temperature below 15 °C. The quantitative conversion to 1-chloromethoxydodecane (**4**) was proved by ^{1}H NMR spectroscopy. After 15 min of flushing with nitrogen, the reaction mixture was filtered into a 100 mL round-bottom flask which contained the silylated thymine (5.37 mmol). The clear solution was stirred for 3 h at room temperature under nitrogen atmosphere. The volume of the reaction mixture was reduced to 20 mL at the rotary evaporator, 5 mL distilled water was added, and the reaction mixture was stirred for 5 min to hydrolyze the product. Finally the reaction mixture was evaporated to dryness and the raw product purified by chromatography (SiO_2, $CHCl_3$:THF = 60:1). Yield: 1.6 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.86 (t, 3H $J = 6.8$ Hz), 1.24 (s, 18H), 1.54 (m, 2H), 1.93 (s, 3H), 3.51 (t, 2H $J = 6.8$ Hz), 5.12 (s, 2H), 7.14 (s, 1H), 9.36 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 12.20, 13.97, 22.53, 25.81, 29.20, 29.23, 29.42−29.47, 29.51, 31.76, 69.41, 76.14, 111.45, 138.80, 151.44, 164.51.

NMR Characterization of 1-Dodecyloxymethyl-1*H*-pyrimidine-2,4-dione (5b). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.87 (t, 3H $J = 6.4$ Hz), 1.24 (s, 18H), 1.56 (m, 2H), 3.52 (t, 2H $J = 6.8$ Hz), 5.15 (s, 2H), 5.77 (d, 1H $J = 7.7$ Hz), 7.31 (d, 1H $J = 7.67$ Hz), 9.28 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 14.09, 22.65, 25.90, 29.29−29.61, 31.87, 69.76, 76.60, 103.08, 142.96, 151.07, 163.55.

NMR Characterization of 4-Amino-1-dodecyloxymethyl-1*H*-pyrimidin-2-one 5c. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (t, 3H $J = 5.9$ Hz), 1.25 (s, 18H), 1.55 (m, 2H), 3.53 (t, 2H $J = 6.4$ Hz), 5.20 (s, 2H), 5.80 (d, 3H $J = 7.0$ Hz), 7.39 (d, 1H $J = 7.0$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 14.12, 22.68, 25.97, 29.36−29.65, 31.91, 69.71, 76.48, 95.13, 144.31, 156.04, 165.29.

NMR Characterization of 1-Chloromethoxydodecane (4). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.87 (t, 3H $J = 5.6$ Hz), 1.25 (s, 18H), 1.60 (m, 2H), 3.66 (t, 2H $J = 6.7$ Hz), 5.49 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 14.04, 22.65, 25.92, 28.88, 29.28, 29.33, 29.51−29.62, 31.89, 70.62, 83.25.

1,6-Bis[3,5-bis(methoxycarbonyl)phenoxy]hexane (10). A mixture of 5-hydroxyisophthalic acid dimethyl ester (1.198 g, 5.7 mmol), 1,6-dibromohexane (**8**) (0.732 g, 3.0 mmol), potassium carbonate (1.330 g, 9.6 mmol), and 18-crown-6 (0.220 g, 0.8 mmol) in dry THF (25 mL) was refluxed for 48 h. The mixture was evaporated to dryness, dissolved in chloroform, and washed twice with water and once with brine. The organic layer was dried with magnesium sulfate, filtered, and evaporated to dryness. The crude product was purified by chromatography (SiO_2, hexane/ethyl acetate 6:1) in order to afford pure **10**. Yield: 1.182 g (78%). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.26 (s, 2H), 7.74 (s, 4H), 4.06 (t, 4H), 3.95 (s, 12H), 1.85 (m, 4H), 1.59 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 166.2, 159.1, 131.6, 122.8, 119.7, 68.3, 52.4, 29.0, 25.7.

1,12-Bis[3,5-bis(methoxycarbonyl)phenoxy]dodecane (11). Compound **11** was prepared analogous to product **10** using 1,12-dibromododecane (**9**) (0.656 g, 2.0 mmol) as starting material. Yield: 1.006 g (85%). ^{1}H NMR (200 MHz, $CDCl_3$): δ(ppm) 8.25 (s, 2H), 7.73 (s, 4H), 4.03 (t, 4H), 3.93 (s, 12H), 1.81 (m, 4H), 1.60−1.20 (m, 16H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 166.2, 159.2, 131.6, 122.7, 119.8, 68.6, 52.4, 29.5, 29.3, 29.0, 25.9.

1,6-Bis[3,5-bis(carboxy)phenoxy]hexane (12). Tetraester **10** (0.750 g, 1.5 mmol) was suspended in methanol (20 mL) and was heated to reflux. A solution of NaOH (0.216 g, 5.4 mmol) in water (1.3 mL) was added, and the solution was stirred at that temperature for 12 h. The mixture was evaporated to dryness, dissolved in water and treated with concentrated HCl. The precipitate was collected by filtration, washed twice with cold water and dried under vacuo to afford **12**. Yield: 0.588 (88%). ^{1}H NMR (200 MHz, DMSO): δ (ppm) 8.10 (s, 2H), 7.66 (s, 4H), 4.12 (t, 4H), 1.81 (m, 4H), 1.54 (m, 4H). ^{13}C NMR (50 MHz, DMSO): δ (ppm) 167.1, 159.0, 133.6, 122.5, 119.8, 68.3, 28.8, 25.5.

1,12-Bis[3,5-bis(carboxy)phenoxy]dodecane (13). Compound **13** was synthesized analogous to product **12** starting with tetraester **11** (0.701 g, 1.19 mmol). Yield: 0.525 (83%). ^{1}H NMR (200 MHz, DMSO): δ (ppm) 13.26 (s, 4H), 8.05 (s,

2H), 7.61 (s, 4H), 4.04 (t, 4H), 1.71 (m, 4H), 1.39 (m, 4H), 1.24 (m, 16H). ^{13}C NMR (50 MHz, DMSO): δ (ppm) 166.4, 158.7, 132.5, 122.0, 118.9, 68.0, 28.9, 28.6, 28.4, 25.35.

1,6-Bis[3,5-bis[6-(butyrylamino)pyridin-2-yl-carbamoyl]-phenoxy]hexane (14). Tetraacid **12** (0.230 g, 0.52 mmol) was suspended in thionyl chloride (10 mL), and a drop of dry DMF was added. The solution was heated to reflux and stirred for 18 h. The excess $SOCl_2$ was distilled off at normal pressure, and the residue was dried under high vacuum for 2 h. This tetraacid chloride was used without any further purification. The residue was dissolved in dry THF (2 mL) and injected into a previously prepared solution of *N*-(6-aminopyridin-2-yl)-butyramide (0.395 g, 2.20 mmol) and triethylamine (0.223 g, 2.20 mmol) in dry THF (10 mL) at 0 °C. The mixture was heated to room temperature and stirred for 1 h after which the solvent was removed under diminished pressure. The residue was digested in water at 40 °C for 30 min; the crude product was filtered and digested in methanol at 40 °C for another 30 min in order to afford **14**. Yield: 0.280 g (50%). ^{1}H NMR (400 MHz, DMSO): δ (ppm) 10.51 (s, 4H), 10.14 (s, 4H), 8.16 (s, 2H), 7.87 (m, 8H), 7.82 (t, 4H), 7.75 (s, 4H), 4.21 (t, 4H), 2.42 (t, 8H), 1.88 (m, 4H), 1.70−1.55 (m, 12H), 0.94 (t, 12H). ^{13}C NMR (50 MHz, DMSO): δ (ppm) 172.4, 165.3, 159.0, 150.9, 150.4, 140.4, 135.9, 120.0, 117.5, 110.9, 110.3, 68.4, 38.3, 28.9, 25.6, 18.8, 13.9.

1,12-Bis[3,5-bis[6-(butyrylamino)pyridin-2-yl-carbamoyl]phenoxy]dodecane (15). The synthesis was performed analogously to that of product **14** using tetraacid **13** (0.500 g, 0.95 mmol) as the starting material. The crude product was purified by chromatography (SiO_2, chloroform/methanol 30:1) in order to afford **15**. Yield: 0.798 g (72%). ^{1}H NMR (400 MHz, DMSO): δ (ppm) 10.51 (s, 4H), 10.14 (s, 4H), 8.15 (s, 2H), 7.87 (m, 8H), 7.82 (t, 4H), 7.73 (s, 4H), 4.16 (t, 4H), 2.42 (t, 8H), 1.82 (m, 4H), 1.64 (m, 8H), 1.48 (m, 4H), 1.4−1.3 (m, 12H), 0.94 (t, 12H). ^{13}C NMR (50 MHz, DMSO): δ (ppm) 171.9, 164.8, 158.6, 150.5, 150.0, 139.9, 133.5, 119.5, 117.1, 110.4, 109.9, 68.1, 38.0, 30.6, 29.0, 28.7, 28.5, 25.4, 18.3, 13.5.

Bromo-Terminated Telechelic PIB (17). The presented synthesis was accomplished for PIB with M_n = 10 000 (g mol^{-1}), for which the same reaction conditions can be applied as for M_n = 3000 (g mol^{-1}). To a mixture of hydroxy-terminated PIB **16** (9.33 g, 0.93 mmol) and CBr_4 (3.56 g, 10.73 mmol) in dry CH_2Cl_2 (250 mL) was added dropwise a solution of triphenylphosphine (2.45 g, 9.33 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C. The mixture was allowed to reach room temperature and was stirred for 12 h. The solvent was completely removed under vacuo, suspended in hexane, and filtered. The solvent was removed again, and the crude product was purified by chromatography (SiO2, hexane/ethyl acetate 50:1) to afford **17**. Yield: 8.79 g (94%). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 7.17 (s, 3H), 3.37 (t, 4H), 1.83 (m, 4H), 0.83−1.50 (m, 1580H), 0.79 (s, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): δ(ppm) 149.0, 148.5, 58.5−59.5, 55.7, 44.1, 38.8−37.8, 34.9, 32.3, 31.9−30.7, 29.1, 28.1, 24.2.

Bis[3,5-bis(methoxycarbonyl)phenoxy]-Terminated PIB (18). The presented synthesis was accomplished for PIB with M_n = 10 000 (g mol^{-1}), same reaction conditions can be applied for M_n = 3000 (g mol^{-1}). A mixture of bromo-terminated PIB **17** (4.82 g, 0.48 mmol), potassium carbonate (1.18 g, 8.68 mmol), 18-crown-6 (0.50 g, 1.89 mmol), and 5-hydroxyisophthalic acid dimethylester (2.03 g, 9.64 mmol) in dry THF (150 mL) was stirred under reflux for 3 d. THF was removed under low pressure, and the residue was suspended in hexane. The organic layer was washed twice with water and once with brine, dried over magnesium sulfate, filtered, and dried in vacuo. The crude product was purified by chromatography (SiO_2, hexane/ethyl acetate 40:1) in order to afford **18**. Yield: 4.09 g (85%). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.27 (s, 2H), 7.74 (s, 4H), 7.17 (s, 3H), 4.01 (t, 4H), 3.94 (s, 12H), 1.83 (m, 4H), 0.83−1.50 (m, 1530H), 0.79 (s, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 166.2, 159.2, 148.9, 148.5, 131.7, 122.8, 121.2, 120.1, 119.8, 69.4, 59.5−58.5, 55.5, 52.4, 41.5, 38.8−37.8, 34.8, 32.3, 31.9−30.7, 29.4, 24.2.

Bis[3,5-bis[6-aminopyridin-2-yl-carbamoyl]phenoxy]-Terminated PIB (19). The presented synthesis was accomplished for PIB with M_n = 10 000 (g mol^{-1}), for which the same reaction conditions can be applied as for M_n = 3000 (g mol^{-1}). A solution of 2,6-diaminopyridine (0.872 g, 8 mmol) in dry THF (150 mL) was prepared under argon atmosphere and cooled to −78 °C. A 2.5 M solution of buthyllithium in hexane (2.88 mL, 7.2 mmol) was added dropwise to this mixture and was stirred for 20 min. A mixture of **18** (0.400 g, 0.04 mmol) in dry THF was added slowly to the reaction, which was stirred for another 8 h at a constant temperature of −78 °C. The mixture was allowed to reach room temperature and was stirred at that temperature for 10 h. A solution of 1 M aqueous $NaHCO_3$ (40 mL) was added in order to quench the reaction and the mixture was distributed between chloroform and water. The aqueous layer was extracted three times with chloroform,and the combined organic layer was washed with brine, dried over magnesium sulfate, filtrated, and evaporated under vacuo. To obtain pure monoacylated PIB **19**, the crude product was precipitated twice from chlorofrom in methanol to afford **19**. Yield: 0.364 g (91%). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.76 (s, 4H), 7.89 (s, 2H), 7.68 (d, 8H), 7.57 (s, 4H), 7.45 (t, 4H), 7.18 (s, 3H), 6.25 (d, 4H), 4.51 (s, 8H), 3.93 (t, 4H), 1.83 (m, 4H), 1.55−0.83 (m, 1480H), 0.79 (s, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 164.5, 159.8, 157.2, 149.8, 148.9, 148.5, 140.1, 136.1, 121.1, 120.0, 117.1, 104.8, 103.7, 69.4, 59.5−58.5, 55.5, 52.4, 41.5, 38.8−37.8, 34.8, 31.9−30.7, 29.4, 24.2, 14.2.

Bis[3,5-bis[6-(butyrylamino)pyridin-2-yl-carbamoyl]-phenoxy]-Terminated PIB (1d). The presented synthesis was accomplished for PIB with M_n = 10 000 (g mol^{-1}); the same reaction conditions were applied for M_n = 3000 (g mol^{-1}). A solution of **19** (0.36 g, 0.036 mmol) and triethylamine (0.85 mL, 6 mmol) in dry THF (40 mL) was cooled to 0 °C, and a solution of butyryl chloride (0.32 mL, 3 mmol) in dry THF (5 mL) was added dropwise. The mixture was allowed to reach room temperature, at which it was stirred for another 2 h. The solvent was removed under high vacuo and the residue was suspended in chloroform. The organic layer was washed twice with a saturated $NaHCO_3$ solution and once with brine, dried over magnesium sulfate, filtered, and evaporated under diminished pressure. The product was precipitated three times from chloroform in methanol to afford pure title compound **1d**. Yield: 0.335 g (93%). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.56 (s, 4H), 8.10−7.85 (m, 14H), 7.73 (t, 4H), 7.62 (s, 4H), 7.18 (s, 3H), 4.01 (t, 4H), 2.37 (t, 8H), 1.90−1.65 (m, 12H), 0.83−1.50 (m, 1560H), 0.79 (s, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 171.6, 164.3, 160.0, 149.7, 149.3, 148.9, 148.5, 140.9, 136.0, 121.1, 120.0, 117.1, 110.1, 109.6, 69.4, 59.5−58.5, 55.5, 52.4, 41.5, 38.8−37.8, 34.8, 31.9−30.7, 29.4, 24.2, 14.2.

Results and Discussion.

Synthesis of PIB Telechelics with Nucleobase Moieties. The synthesis of polymers **1a**−**1c** starts with the corresponding telechelic hydroxyterminated PIB−OH (**2**) (M_n = 2500 (PD = 1.17)), prepared by cationic polymerization according to ref 21c) (Scheme 2). Initial attempts to use direct nucleophilic substitution reactions with silylated nucleobases (Vorbrüggen method[24] on halo-terminated PIB) were not successful because of the limited solubility of PIB in dipolar aprotic solvents. We therefore changed our synthetic strategy to the more activated chloromethyl ethers which are more prone to nucleophilic reactivity toward nucleobases such as thymine, uracil, and cytosine.[25] This strategy was tested using short chain models with alkyl moieties instead of PIB moieties (Scheme 2a). The transformation from the alcohol **3** into the chloromethyl ether **4** went cleanly in a variety of solvents including dichloromethane, chloroform and 1,2-dichloroethane by use of paraformaldehyde (trioxane). Critical for the avoidance of side reaction was to keep the temperature below 15 °C under a permanent stream of dry hydrogen chloride. The reaction was checked permanently by ^{1}H NMR spec-

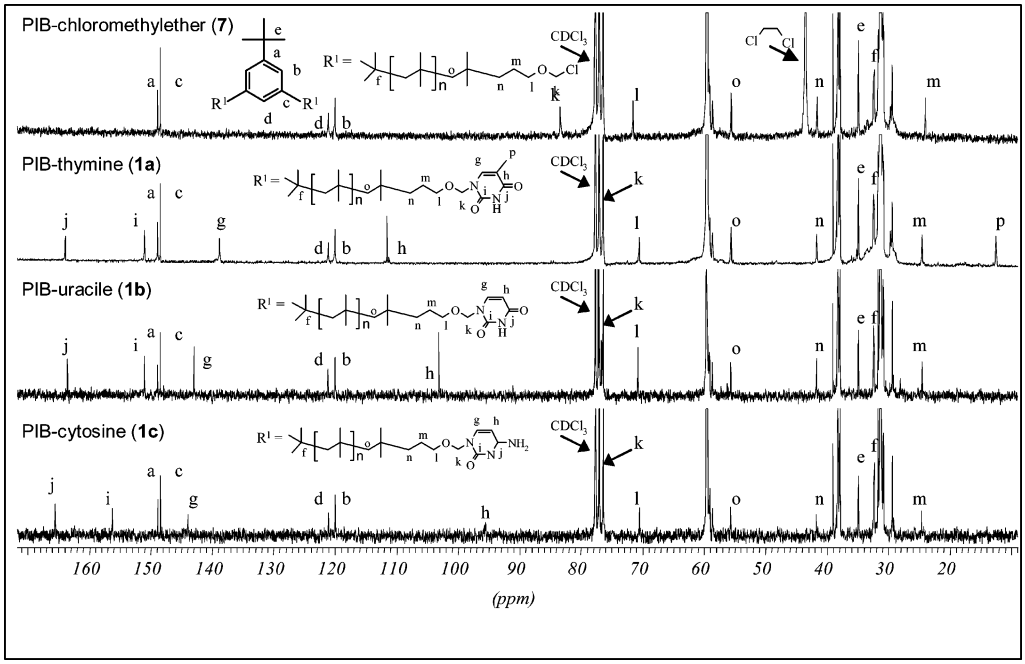
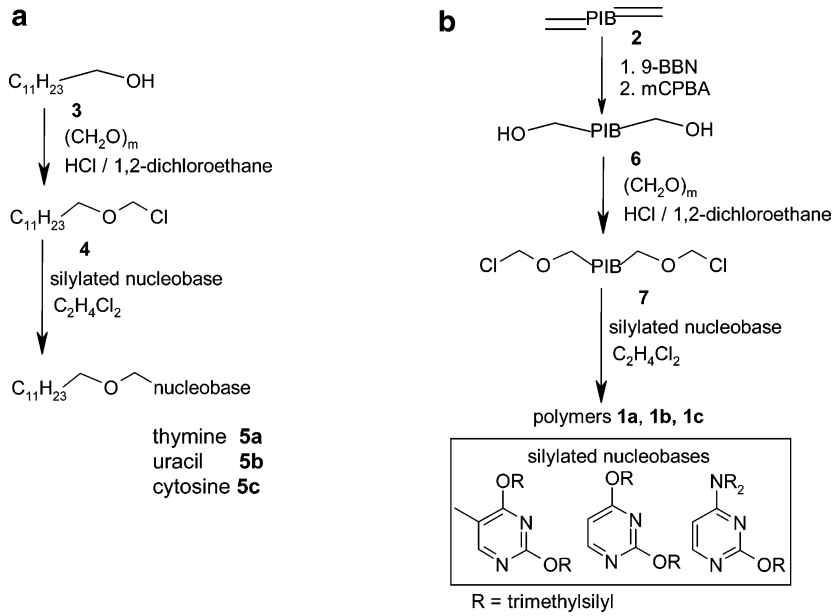


Figure 1. ^{13}C NMR spectra of polymers **7**, **1a**, **1b**, and **1c**.

Scheme 2



troscopy and found to be complete after 60 min. Shorter reaction times lead to the formation of side products, in particular the methylene-1,1-bis(alkyl ether) visible via resonances at 4.65 ppm (singlet, O−CH_2−O moiety) and 3.50 ppm (triplet, CH_2−O−CH_2−O−CH_2− moiety).[26] After evaporation of the solvent, the final chloromethyl ether **4** was obtained in quantitative yield. This can be transformed into the respective nucleobase-terminal methyl ethers by direct reactions with silylated nucleobases in 1,2-dichloroethane as solvent in quantitative yield. After quenching of the reaction with water (to destroy the excess of silylated nucleobase) and purification by chromatography over silica (which removes the excess nucleobase) the final products **5a**−**5c** are obtained in yields above 90%.

The reaction worked equally well when applied to PIB: thus the PIB−chloromethyl ether **7** was prepared directly by reaction of PIB−OH (**6**) with paraformaldehyde in dry dichloroethane and gaseous HCl. PIB−OH was obtained by a modified procedure from Ivan et al.[21c] via a hydroboration/oxidation strategy from the PIB−allyl **2**. To achieve homogeneous reaction conditions, we changed to *m*-chloroperoxybenoic acid instead of hydrogen peroxide as oxidant. During the formation of the chloromethyl ether **7** a reaction temperature below 15 °C and a permanent check of the reaction progress by NMR spectroscopy is required. The side reaction toward a bridged (or cyclic) methylene-1,1-bis(alkyl ether) was not observed by NMR spectroscopy, presumably due to the low concentration of the CH_2−OH end group. Subsequent reaction of the PIB−chloromethyl ether **7** with silylated nucleobases furnishes the final telechelic PIB **1a**−**1c** after column-chromatography in quantitative yield. The transformation efficiency is quantitative as judged via ^1H and ^{13}C NMR spectroscopy as shown in Figures 1 and 2. The chemical structure of the end

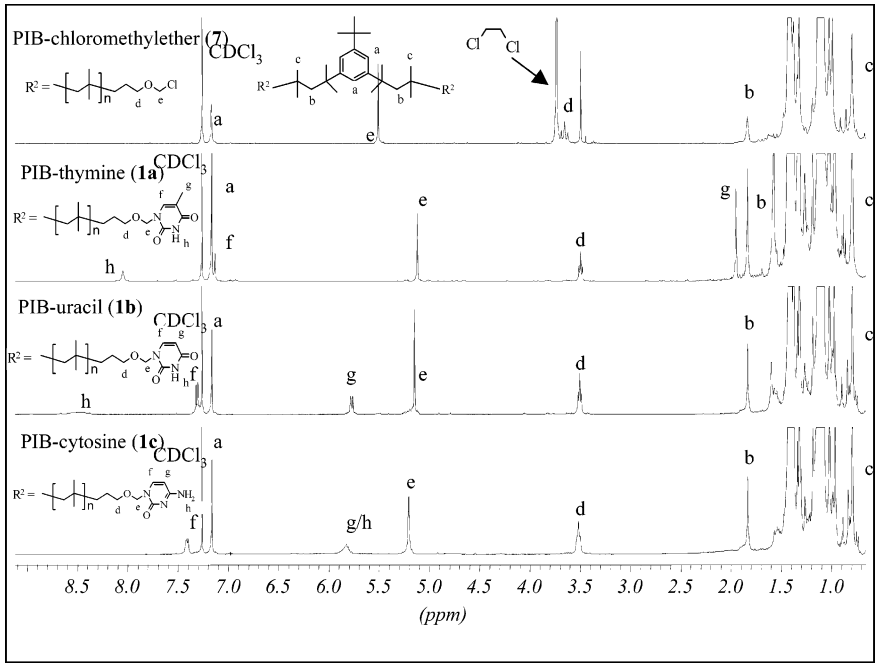


Figure 2. ^{1}H NMR spectra of polymers **7**, **1a**, **1b**, and **1c**.

Table 1. Molecular Weights and Molecular Weight Distributions of PIB Polymers

entry	polymer	$M_{n(theor)}$	$M_{n(GPC)}$	$M_w/M_{n(GPC)}$	$M_{n(MALDI)}$	$M_w/M_{n(MALDI)}$
1	**1a**	2700	2760	1.17	2189	1.11
2	**1b**	2850	3200	1.14	2483	1.05
3	**1c**	2700	2850	1.14	2207	1.08
4	**1d**	3000	3720	1.22	3539	1.03
		10 000	10 300	1.19	n.d.[a]	n.d.
5	**2**	2500	2650	1.17	2048	1.11
6	**6**	2500	2760	1.15	1994	1.09
7	**16**	10 000	10 100	1.2	n.d.	n.d.
8	**17**	10 000	10 100	1.20	n.d.	n.d.
9	**18**	10 000	10 800	1.17	n.d.	n.d.
10	**19**	3000	3740	1.23	3315	1.04
		10 000	10 200	1.15	n.d.	n.d.

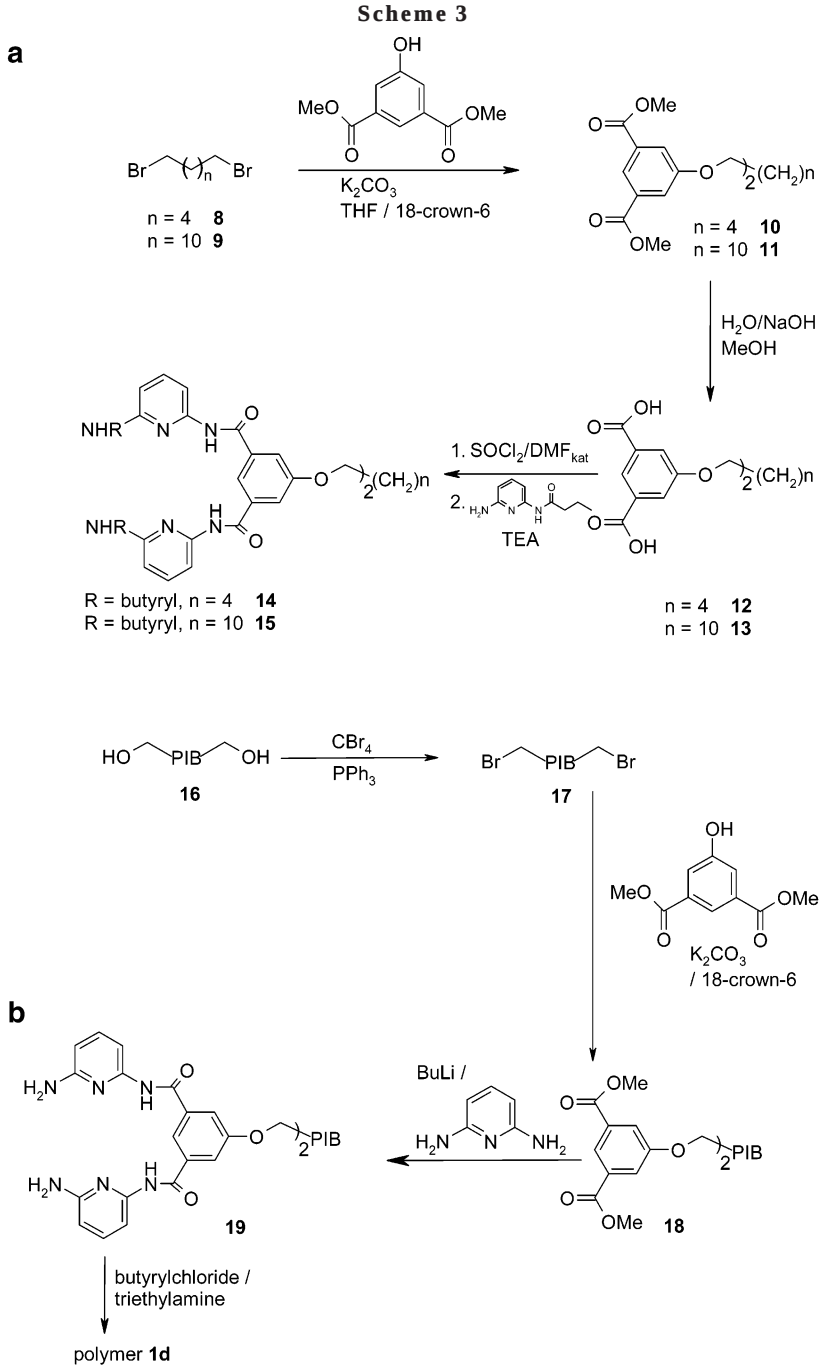
[a] n.d.: not determined.

groups can be assigned in the corresponding spectra clearly due to the presence of the nucleobase resonances. A critical point in this reaction is the molecular weight of the PIB: whereas, with molecular weights up to 3000 Da, the solubility of PIB in 1,2-dichloroethane is sufficient to promote the reaction between the chloromethyl ether **7** and the silylated nucleobase, at higher molecular weights (above 10 000), the solubility of PIB in the solvent is insufficient to achieve a complete reaction. Thus, this method proceeds well with low molecular weight PIB, but not with high molecular PIB. The use of alternative solvents (such as dichloromethane, chloroform, or tetrahydrofuran) did not lead to improved results.

Synthesis of PIB−Telechelics with Multiple Hydrogen-Bonding Moieties. Fixation of multiple hydrogen bonds onto the PIB is attractive, since the binding constant of this moiety is a factor 10^3 M^{-1} higher than those of the nucleobase moieties. This hydrogen bonding motive resembles those of a cleft and was introduced by Lehn et al.[23] representing strong binding toward barbituric acid and cyanuric acid derivatives. Initially we have investigated the synthesis of alkyl-type model systems in order to optimize the synthetic strategy to achieve 100% transformation efficiencies within nonpolymeric substrates (Scheme 3a). Thus, 1,6-dibromohexane (**8**) and 1,12-dibromododecane (**9**) were used as starting points of the nucleophilic substitution reaction with 5-hydroxyisophthalic acid dimethyl ester yielding the corresponding esters **10** and **11**. Dipolar aprotic solvents (such as *N*,*N*-dimethylformamide[23]), which are conventionally used for this type of reaction had to be avoided due to the poor solubility of PIB within these type of solvents. Instead, after optimization, the combination of K_2CO_3/18-crown-6 in tetrahydrofuran (THF) was successful in achieving a complete conversion without side reaction such as elimination reactions. Cleavage of the ester groups yielded the tetraacids **12** and **13**, which were readily converted into the corresponding tetraacid chlorides using thionyl chloride reaction with *N*-(6-aminopyridin-2-yl)butyramide and triethylamine[23] yielded the title compounds **14** and **15**.

The synthesis of the chelate-type PIB **1d** starts from the corresponding PIB−OH **16** (M_n = 10 100 (PD = 1.20) as well as a PIB with M_n = 3000 (PD = 1.22)which is converted to the dibromide PIB−Br **17** in quantitative yield using triphenylphosphine/CBr_4[27] (Scheme 3b). Analogous to the small molecular alkyl derivative **12** this can be quantitatively substituted with 5-hydroxyisophthalic acid dimethyl ester by a SN_2-type nucleophilic reaction in the presence of 18-crown-6 in tetrahydrofuran yielding the PIB−ester **18**. Reaction of the PIB−tetraester **18** with butyllithium/2,6-diaminopyridine furnishes PIB **19**, which can be transformed into

Scheme 3



the final chelate-type PIB **1d** by reaction with butyryl chloride in THF. The reactions steps proceed with yields above 95%, which is the detection limit of ^{1}H NMR spectroscopy for the higher molecular weight polymers (Figure 3).

A critical point within the synthetic pathway concerned the transformation of the PIB−phthalate **18** into the amine **19** via the lithiated 2,6-diaminopyridine. By use of very high excess of the nucleophilic reagents, dimerization into bridged PIB derivatives in the amount of approximately 15% was observed (Scheme 4). The formation of the dimerization product was proven by GPC-analysis clearly showing the product with the doubled molecular weight. This can be explained by an exchange reaction between the monolithium salt of 2,6-diaminopyridine with the already formed product **19**. Since the pK_a values of the amino groups are comparable, the high excess of 2,6-diaminopyridine/butyllithium favored the exchange reaction and thus the dimerization of the PIB chains. Experiments to verify these results via MALDI−TOF MS failed until this point, probably due to the low concentration. However, the side reaction could be diminished by use of a moderate excess of 2,6-diaminopyridine over butyllithium together with high dilution conditions of the reaction medium.

Structural Analysis by MALDI—TOF MS. Selected samples of the nucleoside telechelic PIB's **1a**−**1c** and the chelate-type PIB **1d** as well as the corresponding precursors **2**, **6**, and **19** were investigated by means of MALDI−TOF MS. Generally, it has to be mentioned that a rather strong influence of the end groups of the PIB's on the ionization behavior was observed. For polymers **2** and **6** the best spectra were obtained by ionization with silver ions (matrix: dithranol/AgTFA). The structure of the telechelic PIB's **1a** and

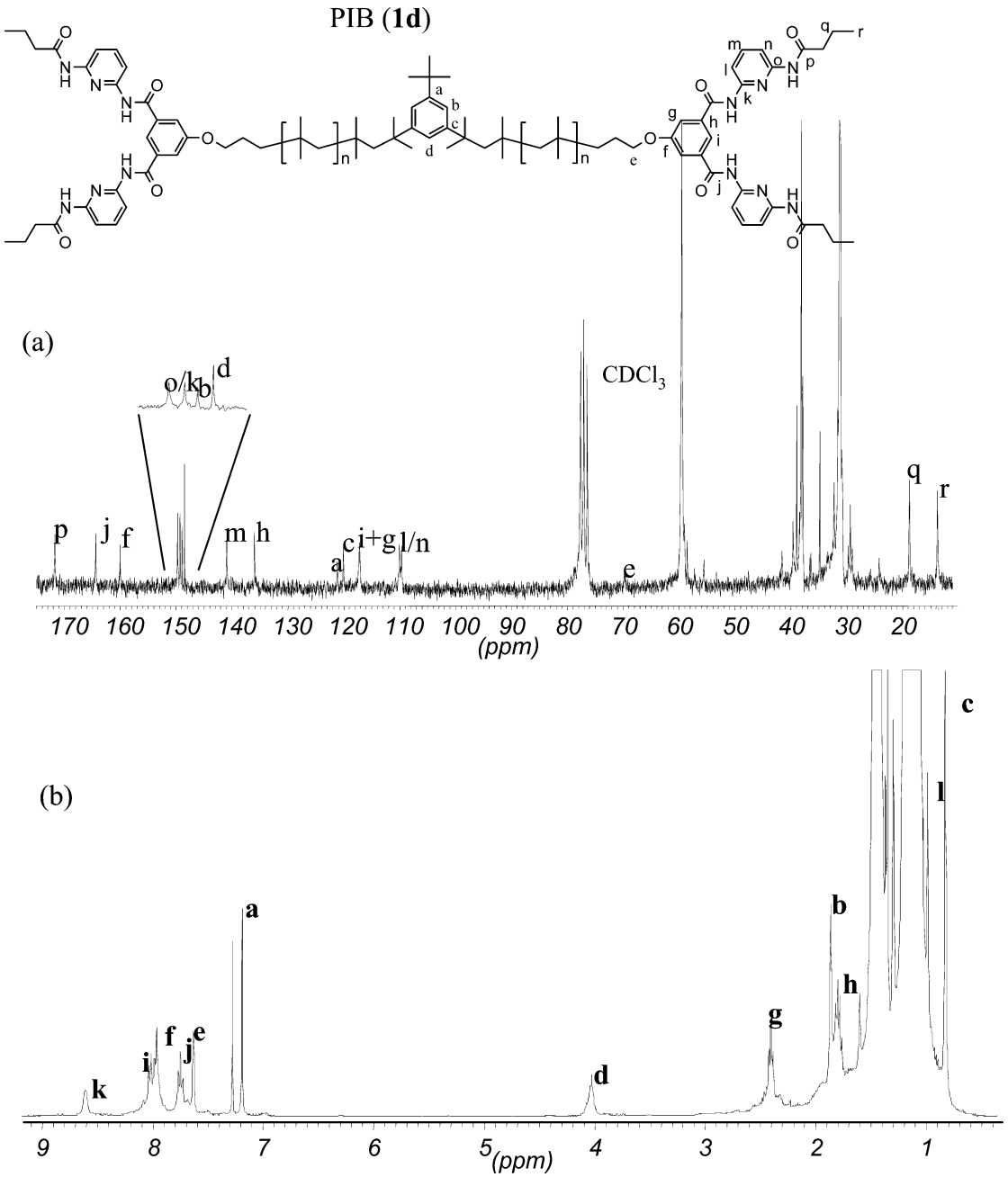


Figure 3. ^{1}H NMR (b) and ^{13}C NMR spectra (a) of polymer **1d**.

1b could be verified using dithranol/AgTFA/NaTFA as matrix (Figure 4). Both spectra show the expected ions $[M{\cdot}Ag]^+$ and $[M{\cdot}Na]^+$, respectively. In contrast to these results, an unusual behavior of the two polymers was detected when dithranol/AgTFA was applied. Figure 5 gives an expanded view of a corresponding spectrum of polymer **1a**. The spectrum shows only one important series of ions which were separated by 56 Da, the mass of the repeating unit. However, the *m*/*z* values of the observed signals do not correspond to pseudo-molecular ions $[M{\cdot}Ag]^+$ that were expected due to the addition of AgTFA. For example, polymer **1a** with a degree of polymerization *n* of 28 ionized by attachment of Ag^+ would have a monoisotopic mass of 2287.0 Da, a value where no significant signal was detected. Ionization of polymer **1a** with protons or sodium ions would lead to ions $[M{\cdot}H]^+$ and $[M{\cdot}Na]^+$, respectively, that have different masses too. It is important to note that comparable results were obtained for polymer **1b** when investigated from dithranol/AgTFA (Figure 5). Again the observed signals could not be assigned to simple pseudo-molecular ions like $[M{\cdot}Ag]^+$. But it is important to note that a mass difference of 28 Da was observed between corresponding signals in the two spectra of polymer **1a** and **1b**, respectively. This difference has to be observed due to the additional CH_3 groups of the thymine end groups of polymer **1a** in comparison to the uracile end groups of polymer **1b**. Consequently, an unusual behavior during the MALDI process was considered. On the basis of the observed isotope pattern, and the results of exact mass measurements where silver clusters (compare Figure 5) were used for internal calibration, the signals observed in these MALDI spectra of the polymers **1a** and **1b** are interpreted as ions containing three silver atoms. Assuming replacement of the acidic CO−N*H*-CO protons of the thymine or uracile groups by silver ions—e.g., during the sample preparation for MALDI or during the irradiation with laser light—and

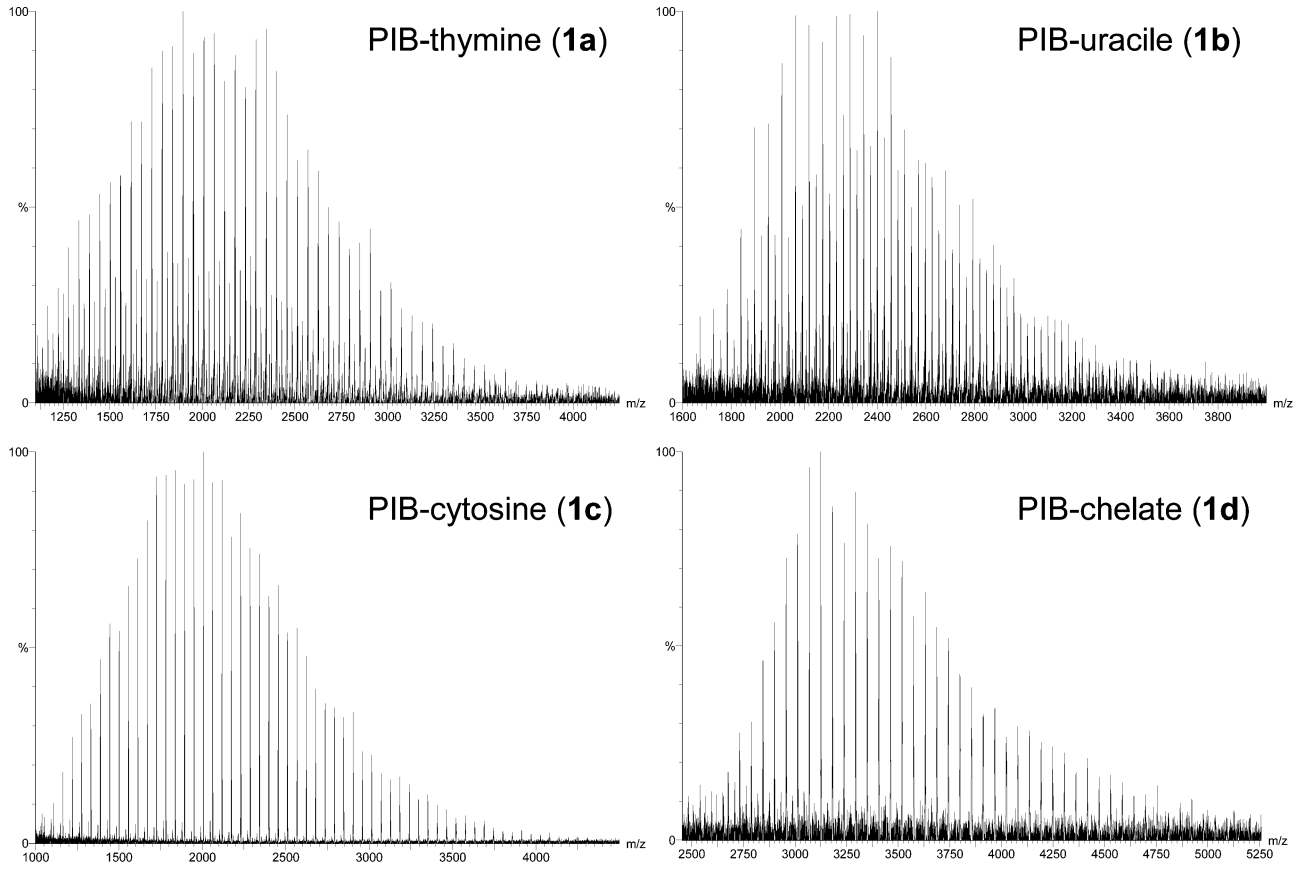
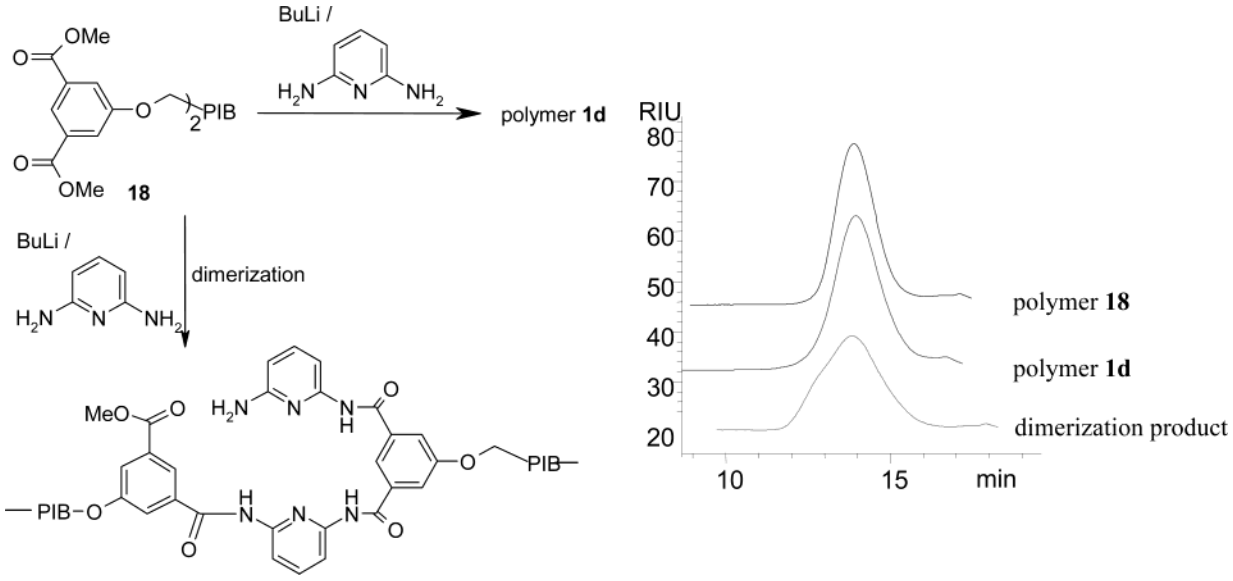


Figure 4. MALDI−TOF mass spectra of the telechelic PIB's **1a**, **1b** (matrix, dithranol/NaTFA/AgTFA; major series, $[M{\cdot}Ag]^+$; minor series, $[M{\cdot}Na]^+$), and **1c**, **1d** (matrix, dithranol/NaTFA; ions, $[M{\cdot}Na]^+$).

Scheme 4



subsequent ionization with an additional Ag^+ would lead to singly charged ions having masses that agree to the measured signals with errors <15 ppm. For example, a species $[C_{130}H_{240}N_4O_6Ag_2{\cdot}Ag]^+$ could be formed via this way from polymer **1a** with $n = 24$. The theoretical m/z value of the most intense peak of the isotope distribution of this species is 2278.579 Da, a value that agrees excellently with the signal at 2278.606 (Figure 5a). The interpretation is also supported by the observation, that this unusual behavior was not observed for polymer **1c**, a product with a very similar chemical structure of the end groups but without acidic protons. Furthermore, reduction of the silver concentration and simultaneous addition of NaTFA lead to suppression of the phenomenon as already shown with the spectra in Figure 4.

Ionization with sodium ions (matrix: dithranol/NaTFA) was found to be preferable for the products **1c**, **1d** and **19**. The MALDI spectra of the polymers **1c** and **1d** (Figure 4) showed the expected ions $[M{\cdot}Na]^+$.

The number-average molecular weights M_n and polydispersities PD (PD = M_w/M_n) calculated from the

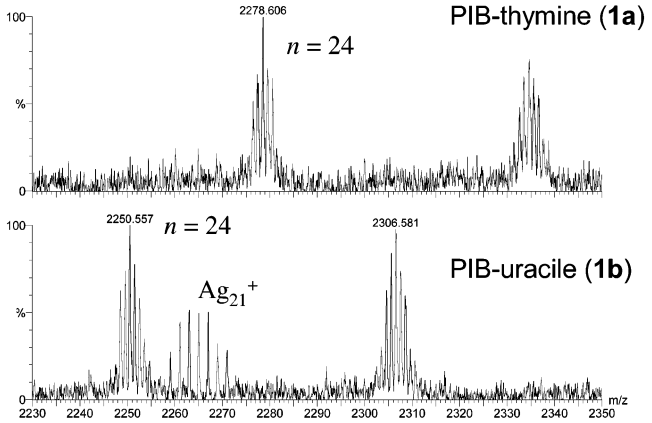


Figure 5. Expanded view of the MALDI−TOF mass spectra of the polymers **1a** and **1b** (matrix, dithranol/AgTFA; ions, $[(M - 2H + 2Ag)\cdot Ag]^+$; for discussion see text).

MALDI spectra correlated systematically with the results obtained by GPC (Table 1). In all cases the values of M_n calculated from the MALDI spectra were approximately 500−700 Da lower than those obtained by GPC. Possible reasons are for example the fact that the GPC was calibrated with polyisobutylene standards that do not contain the rigid central aromatic segment of the PIB's investigated in this work and the fact that the different end groups will have a significant influence on the hydrodynamic volumes too, especially since the molecular weight range of the products investigated here was only a few kilodaltons. Furthermore, it is well-known that mass discrimination during MALDI experiments can lead to somewhat lower values of M_n. Analysis of MALDI spectra that were acquired in the linear mode gave values of M_n that were approximately 100 Da higher than the reflectron data presented in Table 1.

However, the MALDI results obtained for different PIB's which were prepared from the same batch correlated satisfactory. For example, PIB−chelate **1d** ($M_{n,MALDI}$ = 3539) was synthesized from polymer **19** ($M_{n,MALDI}$ = 3315) (compare Scheme 3b). Thus, an increase of M_n of 224 Da was detected. The deviation from the theoretically predicted increase (280 Da) is acceptable.

Conclusion

We have demonstrated two highly efficient synthetic pathways for the preparation of telechelic hydrogen-bonded polyisobutylenes. Starting from hydroxy−telechelic polyisobutylenes (PIB−OH, **3**) the nucleoside telechelic PIB's **1a**−**1c** as well as the chelate-type PIB **1d**, with a multiple binding hydrogen motive, were prepared in quantitative yields and high efficiency. The identities of the products were characterized via ^{1}H NMR and ^{13}C NMR spectroscopy as well as MALDI. Altogether the synthesis of the telechelic PIB's **1a**−**1d** demonstrates an excellent tool for the construction of supramolecular polymers opening way to pseudo-block copolymers as described in a forthcoming publication.[22c]

Acknowledgment. We thank the Austrian Science Fund (FWF, Projects 14844-CHE and 13962-CHE) for financial support. Dr. H. P. Kählig is thanked for providing a 600 MHz ^{1}H NMR instrument.

Supporting Information Available: Figures showing NMR spectra of polymers **1a**, **1b**, **1c**, **1d**, **6**, **7**, **17**, **18**, and **19**, MALDI−TOF mass spectra of polymers **1a**, **1b**, **1c**, **1d**, **2**, **6**, and **19**, and DSC traces of polymers **1a**, **1b**, **1c**, and **6** as well as GPC traces of polymers **1a**, **1b**, **1c**, **1d**, **6**, and **17** and a comparision of GPC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA034924T