# Synthesis of Telechelic Poly(*p*-benzamide)s

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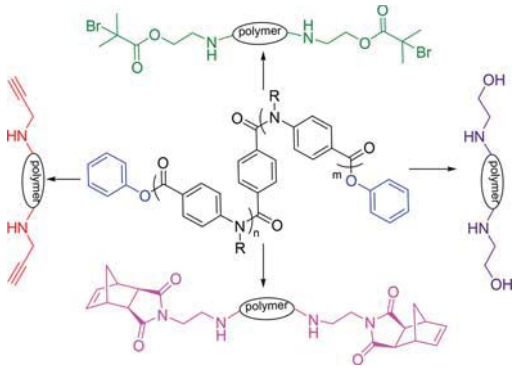
Supporting Information

**ABSTRACT:** Well-defined telechelic poly(benzamide)s were synthesized by chain-growth polycondensation of phenyl-4-amino benzoate and pentafluorophenyl-4-amino benzoate derivatives with a bifunctional initiator in the presence of LiTMP as base. The polymerization was carried out at −70 °C to prevent self-initiated polymerization. To confirm the control over molecular weight, different defined molecular weight polymers were synthesized and analyzed by GPC. Taking advantage of the labile ester end groups of these poly(benzamide)s, we carried out postpolymerization modifications to introduce different end functional groups such as alkyne, amine, alcohol, alkyl halide, and olefin suitable for different types of postpolymerization reactions. Successful end group modification was confirmed by $^{1}$H NMR spectroscopy and isotopically resolved MALDI-ToF mass spectrometry.




## INTRODUCTION

Polycondensation is an important method for the synthesis of commercial polymers such as polyamides and polyesters. Conventional polycondensations proceed in a step-growth manner with broad polydispersities, and control over the molecular weight can often be difficult.[1−3] Yokozawa et al. developed a polycondensation method using a chain-growth mechanism to synthesize well-defined aromatic polyamides with narrow polydispersity.[4−8] Many other well-defined polymers with narrow polydispersity have also been synthesized using chain-growth polycondensation mechanisms such as polyesters,[9,10] polyethers,[11−13] poly(ether sulfone)s,[14] polythiophenes,[15−17] polyphenylenes,[18] and polyfluorenes.[19]

The strategy used here for the synthesis of poly(benzamide)s relies on polymer end groups being more reactive than the monomer itself resulting in a kinetically controlled living chain-growth polymerization. Because of good control over the polydispersity and the molecular weight, a number of different polymer architectures have previously been reported using well-defined poly(benzamide)s. Block copolymers between polyaramides and different monomers polymerized by ATRP and RAFT were investigated using chain-growth polycondensation.[20,21] Graft copolymers were prepared by radical polymerization of styrene and a styryl monomer attached to poly(benzamide)s yielding polystyrenes grafted with poly(benzamide)s. Poly(benzamide)s carrying poly(tetrahydrofuran) grafts were synthesized from a 4-aminobenzoate macromonomer via chain-growth polycondensation.[22,23] Aramide star polymers were synthesized by either the core-first or the arm-first method.[24−26] Hyperbranched aromatic polyamides were synthesized via convergent chain-growth polycondensations of $AB_2$ monomers.[27−30]

Additionally, telechelic aromatic polyamides were prepared to make di- and triblock copolymers of polyamides and poly(tetrahydrofuran).[31] The well-defined poly(benzamide)s were used as macromonomers or macroinitiators in ATRP, RAFT, and other copolymerization methods to obtain di- and triblock copolymers.[32,33] Yokozawa et al. synthesized a triblock PEG−poly(*p*-benzamide)−PEG copolymer using a bifunctional initiator and replacing the terminal ester end groups of the polyamide with commercial PEG monomethyl ether via transesterification.[34]

Here, we report the synthesis of well-defined telechelic aromatic polyamides using a bifunctional initiator and a variety of monomers using the chain-growth polycondensation method. Two monomers, phenyl-4-(*N*-ethylhexylamino)benzoate carrying a solubilizing side chain on the amide nitrogen atom and phenyl-4-(*N*-dimethoxybenzylamino)benzoate carrying an N-protective group, were synthesized. The telechelic polymer prepared possesses two phenyl esters as the reactive end groups which are easily modifiable in one step to a variety of functional end groups. We present different postpolymerization modifications to functionalize the polymer chain ends. This is an efficient and mild approach to functionalize poly(benzamide)s in few straightforward steps. The functional end groups can allow subsequent postpolymerization modifications or copolymerization reactions to synthesize a wide range of copolymer architectures.

## EXPERIMENTAL SECTION

**Materials and Instrumentation.** Matrix-assisted laser desorption and ionization (MALDI) mass spectra were recorded on a Bruker ultrafleXtreme and electrospray ionization (ESI) mass spectra on a Bruker-Ion Trap MS esquire HCT mass spectrometer. Standard $^{1}$H, $^{13}$C, and $^{19}$F nuclear magnetic resonance spectra were recorded either on a Bruker Avance III 300 at a frequency of 300 and 75 MHz or at 400 MHz

($^1$H), 100 MHz ($^{13}$C), and 376 MHz ($^{19}$F) on a Bruker DPX 400 spectrometer. All NMR signals were referenced internally to residual solvent signals. Gel permeation chromatography (GPC) in THF was used. The instrument is an automated Viscotek GPCmax VE-2001 with a set of two Viscotek T6000 M linear columns (300 × 8 mm, 5 $\mu$m particle size). Signal detection occurred by use of a Viscotek Smartline 2600 UV detector (set to 254 nm wavelengths) and a Vicotek VE 3580 RI detector (refractive index). Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo STAR system at a heating rate of 10 °C/min. For differential scanning calorimetry (DSC) analysis, a Mettler-Toledo STAR system differential scanning calorimeter was utilized, and samples were heated and cooled with a rate of 10 °C/min. Solvents of analytical grade were purchased from Sigma-Aldrich, Honeywell, Fisher Scientific, Acros Organics, and Fluka and were used without further purification. Deuterated solvents ($CDCl_3$, DMSO-$d_6$, and DCM-$d_2$) were purchased from Cambridge Isotope Laboratories, Inc., or ARMAR AG. Solvents of technical grade were purified by distillation, if necessary. THF (extra dry) was purchased from Sigma-Aldrich. All chemicals were purchased from Acros Organics, Sigma-Aldrich, or Alfa Aesar and used as received.

**4-((2-Ethylhexyl)amino)benzoic Acid (1a).** 4-Aminobenzoic acid (10 g, 73 mmol) and 2-ethylhexanal (10.3 g, 82.2 mmol) were dissolved in 175 mL of DCM and 20 mL of acetic acid (365 mmol) and stirred for 1 h at room temperature. $NaBH(CH_3COO)_3$ (30.94 g, 146 mmol) was added to the solution portion by portion. The solution stirred for a further 12 h. The reaction was quenched with sodium bicarbonate and extracted three times with DCM. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure The product was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent to obtain a yellow oil (14.7 g, 81%). $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$, ppm: 0.83−0.90 (m, 6 H), 1.20−1.39 (m, 9 H), 1.53 (d, $J$ = 5.59 Hz, 1 H), 2.95 (t, $J$ = 5.82 Hz, 2 H), 6.33 (t, $J$ = 5.32 Hz, 1 H), 6.57 (d, $J$ = 8.89 Hz, 2 H), 7.67 (d, $J$ = 8.71 Hz, 2 H).

**4-((2,4-Dimethoxybenzyl)amino)benzoic Acid (1b).** 4-Aminobenzoic acid (10 g, 73 mmol) and 2,4-dimethoxybenzaldehyde (13.34, 80.3 mmol) were dissolved in 175 mL of DCM and 20 mL of acetic acid (365 mmol) and stirred for 1 h at room temperature. $NaBH(CH_3COO)_3$ (30.94 g, 146 mmol) was added to the solution portion by portion. The solution was stirred for a further 12 h. The reaction was quenched with sodium bicarbonate and extracted three times with DCM. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The white solid was obtained without purification (20 g, 94.5%). $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$, ppm: 3.63 (s, 3 H), 3.78 (s, 3 H), 4.25 (d, $J$ = 6.05 Hz, 2 H), 6.56 (m, $J$ = 8.80 Hz, 2 H), 6.72−6.88 (m, 3 H), 6.88−6.98 (m, 1 H), 7.64 (m, $J$ = 8.80 Hz, 2 H).

**General Synthesis Procedure for Pentafluorophenyl Ester M1 and M2.** The acid (1 equiv), DMAP (0.1 equiv), and pentafluorophenol (1.1 equiv) were dissolved in dry DCM. DCC (1.2 equiv) was added to solution at 0 °C for 5 min and then allowed to warm up to room temperature for 12 h.

**Phenyl 4-((2-Ethylhexyl)amino)benzoate (M3).** 4-((2-Ethylhexyl)amino)benzoic acid (5 g, 20 mmol), DMAP (0.24 g, 2 mmol), and phenol (4.42 g, 24 mmol) were dissolved in dry DCM. DCC (5 g, 24 mmol) was added to the stirred solution at 0 °C. The solution was stirred at 0 °C for 5 min and then allowed to warm up to room temperature for 12 h. The suspension was filtered, and the solvent was removed under reduced pressure. The residue was dissolved in DCM and washed with sodium bicarbonate. The organic layer was dried over magnesium sulfate, and the solvent was removed. The product was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent to obtain a yellow oil (5.2 g, 79%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$, ppm: 0.81−0.92 (m, 6 H), 1.23−1.41 (m, 8 H), 1.51−1.61 (m, 1 H), 3.01 (t, $J$ = 5.99 Hz, 2 H), 6.62−6.71 (m, 3 H), 7.19 (dd, $J$ = 8.44, 0.98 Hz, 2 H), 7.23−7.29 (m, 1 H), 7.40−7.47 (m, 2 H), 7.83 (d, $J$ = 8.93 Hz, 2 H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$, ppm: 10.58 (s, 1 C), 13.89 (s, 1 C), 20.76 (s, 1 C), 23.68 (s, 1 C), 28.30 (s, 1 C), 30.43 (s, 1 C), 37.99 (s, 1 C), 45.58 (s, 1 C), 110.87 (s, 1 C), 114.05 (s, 1 C), 121.75 (s, 1 C), 121.98 (s, 1 C), 125.37 (s, 1 C), 125.72 (s, 1 C), 129.35 (s, 1 C), 129.42 (s, 1 C), 131.74 (s, 1 C), 150.46 (s, 1 C), 151.00 (s, 1 C), 153.75 (s, 1 C), 164.66 (s, 1 C), 169.25 (s, 1 C).

**Phenyl 4-((2,4-Dimethoxybenzyl)amino)benzoate (M4).** 4-((2,4-Dimethoxybenzyl)amino)benzoic acid (7 g, 24 mmol), DMAP (0.3 g, 2.4 mmol), and phenol (2.5 g, 26.4 mmol) were dissolved in dry DCM. DCC (6 g, 28.8 mmol) was added to the stirred solution at 0 °C. The solution was stirred at 0 °C for 5 min and then allowed to warm up to room temperature for 12 h. The suspension was filtered, and the solvent was removed under reduced pressure. The product was recrystallized from ethyl acetate to give colorless crystals (7.23 g, 83%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$, ppm: 3.74 (s, 3 H), 3.83 (s, 3 H), 4.23 (d, $J$ = 5.75 Hz, 2 H), 6.48 (dd, $J$ = 8.31, 2.32 Hz, 1 H), 6.58 (d, $J$ = 2.45 Hz, 1 H), 6.65 (m, $J$ = 8.93 Hz, 2 H), 7.03 (t, $J$ = 5.75 Hz, 1 H), 7.12 (d, $J$ = 8.31 Hz, 1 H), 7.16−7.21 (m, 2 H), 7.23−7.29 (m, 1 H), 7.39−7.46 (m, 2 H), 7.81 (m, $J$ = 8.93 Hz, 2 H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$, ppm: 40.68 (s, 1 C), 55.38 (s, 1 C), 55.64 (s, 1 C), 98.58 (s, 1 C), 104.63 (s, 1 C), 111.44 (s, 1 C), 114.70 (s, 1 C), 118.54 (s, 1 C), 122.26 (s, 2 C), 125.60 (s, 1 C), 129.00 (s, 3 C), 129.57 (s, 1 C), 131.90 (s, 2 C), 151.22 (s, 1 C), 153.62 (s, 1 C), 158.11 (s, 1 C), 159.99 (s, 1 C), 164.78 (s, 1 C).

**2-((*tert*-Butoxycarbonyl)amino)ethyl 2-Bromo-2-methylpropanoate.** To the solution of ethanolamine (5 g, 82 mmol) in dry DCM was added di-*tert*-butyl dicarbonate (19.65 g, 9 mmol) dropwise at 0 °C and then allowed to warm up to room temperature for 12 h. Triethylamine (12.4 g, 12.27 mmol) was added to the solution, and $\alpha$-bromoisobutyryl bromide (20.68 g, 9 mmol) was added to reaction mixture dropwise at 0 °C. The solution was stirred at room temperature for 5 h. The salt was filtered off, and the filtrate was extracted three times with water. The organic layer was dried over magnesium sulfate and evaporated. The resulting t-Boc-aminoethyl 2-bromoisobutyrate was dissolved in DCM/TFA (1:1) and stirred at room temperature for 4 h. The solvent was evaporated under reduced pressure to yield 2-aminoethyl 2-bromoisobutyrate trifluoroacetate as a white solid (23.54 g, 88%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ ppm 1.92 (s, 6 H), 3.15 (br s, 2 H), 4.16−4.40 (t, 2 H), 8.18 (br s, 3 H).

**Exo-*N*-(2-Aminoethyl)-5-norbornene-2,3-dicarboximide.** To freshly distilled ethylenediamine (3.84 g, 64 mmol) a solution of *exo*-carbic anhydride (2 g, 8 mmol) in toluene (50 mL) was added dropwise over 1 h under mechanical stirring. The mixture was held under Dean−Stark conditions overnight. Before the solvent as well residual ethylenediamine was removed via distillation. Purification was achieved by column chromatography with dichloromethane:methanol (10:1) as eluent (1.15 g, 71%). $^1$H NMR (300 MHz, chloroform-d) $\delta$, ppm: 1.21 (br s, 2 H), 1.32 (d, $J$ = 9.81 Hz, 1 H), 1.42−1.55 (m, 1 H), 2.66 (t, 2 H), 2.79−2.93 (m, 2 H), 3.15−3.28 (m, 2 H), 3.51 (td, $J$ = 6.37, 2.38 Hz, 2 H), 6.18−6.36 (m, 2 H).

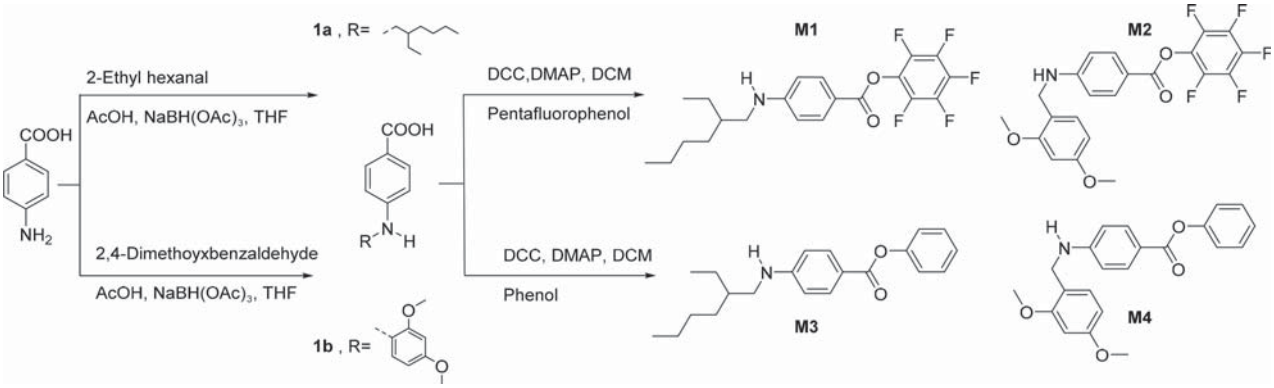
**General Procedure for Polymerization.** Monomer (12 equiv) and diphenyl benzoate as an initiator (1 equiv) were dissolved in dry THF. The reaction mixture was cooled to −70 °C. LiTMP (14.4 equiv) was dissolved in dry THF and added dropwise to the reaction solution. The solution was stirred at −70 °C for 12 h. The reaction was quenched with excess of dissolved phenol in THF at −70 °C, warmed up to room temperature, and then extracted with DCM. The organic layer was dried over magnesium sulfate, and the solvent evaporated under reduced pressure. **P2** and **P4** were precipitated in ethanol (83%). **P1** and **P3** were purified by recycling GPC.

**General Procedure for End-Functionalized Modifications of Polymer.** Polymer (1 equiv) and functionalized amine (30 equiv) were dissolved in acetonitrile. The solution was stirred at 80 °C for 12 h. The solution was extracted with DCM and dried over magnesium sulfate, and the solvent evaporated under reduced pressure.

## RESULTS AND DISCUSSION

The polycondensations described by Yokozawa et al. proceed in a chain-growth polymerization manner if the monomer reacts selectively with polymer chain ends.[30] To achieve this, an activated monomer first reacts with an initiator by means of a reactive site that increases the reactivity of the propagating polymer end group, and therefore the next monomer reacts with the propagating chain end rather than another monomer. The direct polymerization of primary amines within aromatic amino acid

**Scheme 1. Synthesis of Monomers M1−M4**




ester monomers is difficult with this method, as the resulting polyamides will be easily deprotonated to give insoluble polyanionic amides (the acidity of the obtained secondary amide during the polymerization is higher than that of the primary amine of the monomer). In addition to a reduced solubility, the deprotonated amide would also deactivate the terminal ester site due to a strong electron-donating ability, thereby slowing down the polymerization. Therefore, all monomers were secondary amines substituted by *N*-alkyl or *N*-alkoxybenzyl protecting groups.

N-substituted monomers were synthesized in two steps as shown in Scheme 1. Reductive alkylation of 4-aminobenzoic using 2-ethylhexanal gave 4-((2-ethylhexyl)amino)benzoic acid (**1a**, 81%). Using the same substrate and 2,4-dimethoxybenzeldahyde in a reductive alkylation gave 4-((2,4-dimethoxybenzyl)amino) benzoic acid (**1b**, 94.5%). Steglich esterification of **1a** and **1b** with pentafluorophenol yielded the corresponding ester monomers **M1** (88% yield) and **M2** (79% yield), respectively. Esterification with phenol yielded the monomers **M3** (79% yield, from **1a**) and **M4** (83% yield, from **1b**).

To obtain a telechelic polymer chain, we used diphenyl terephthalate as a bifunctional initiator. Either a phenyl or pentafluorophenyl ester would constitute the end groups of the telechelic polyaramid depending on which monomer **M1**−**M4** was employed. The possibility of postfunctionalization would depend on the reactivity of the ester end group toward nucleophiles. We therefore decided to investigate the more reactive monomers **M1** and **M2** carrying pentafluorophenyl esters first.

To synthesize the diester telechelic poly(benzamide), a LiTMP (lithium 2,2,6,6-tetramethylpiperidide) solution in THF was added to the diphenyl terephthalate initiator and monomer **M1** in dry THF at −70 °C. As shown in Table 1 (entries **P1**, **P1a**, and **P1b**), different molecular weight polymers could be synthesized by variation of the monomer:initiator ratio via this method. All polymers showed narrow molecular weight dispersities by GPC (THF) (Figure 1). To prove that the polymerization occurred in a living manner, a linear correlation between molecular weight and monomer:initiator ratio was obtained (see Supporting Information Figure S15). MALDI-ToF mass spectrometry revealed three different distributions belonging to telechelic polymers with either two pentafluorophenyl ester end groups, one phenyl ester and one

**Table 1. Results for the Polymerization of Different Monomers**

| entry | monomer | LiTMP (equiv) | $M_{n(theo)}$ | $M_n$[a] (g/mol) | $M_w$ (g/mol) | $Đ$[a] |
|---|---|---|---|---|---|---|
| **P1** | **M1** | 1.2 | 2800 | 2900 | 3050 | 1.07 |
| **P1a** | **M1** | 1.2 | 5700 | 6000 | 6770 | 1.14 |
| **P1b** | **M1** | 1.2 | 12000 | 11000 | 12400 | 1.12 |
| **P2** | **M2** | 1.2 | 2700 | 2900 | 3110 | 1.07 |
| **P3** | **M3** | 1.2 | 2800 | 2900 | 3120 | 1.08 |
| **P4** | **M4** | 1.2 | 2700 | 3100 | 3290 | 1.06 |

[a]Determined by GPC (THF) relative to polystyrene standards.

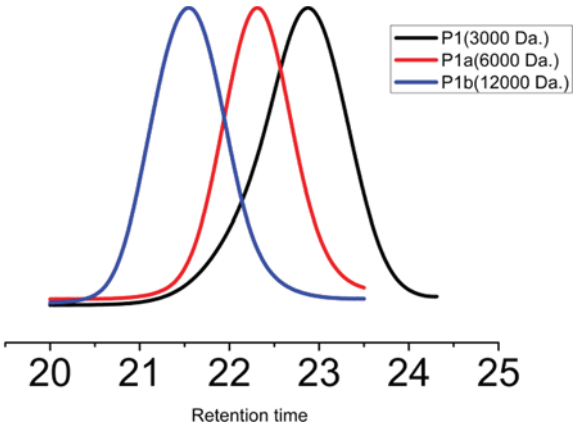



**Figure 1.** THF GPC elugram of the bifunctional initiated polymers using **M1** monomer.

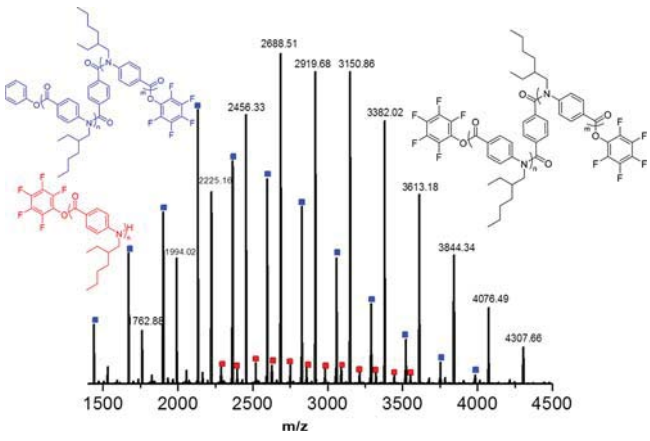



**Figure 2.** MALDI-ToF mass spectrum of the bifunctionally initiated ethylhexyl polymer **P1** as $Ag^+$ adduct (matrix: DCTB). Main distribution shows PFP ester as an end group (black). The blue distribution corresponds to one PFP ester and one phenolester. The red distribution corresponds to a self-initiated polymer.

**Scheme 2. Chain Growth Polycondensation of M3 or M4 with a Bifunctional Initiator Results in Functionalizable Telechelic Polymers P3 and P4**

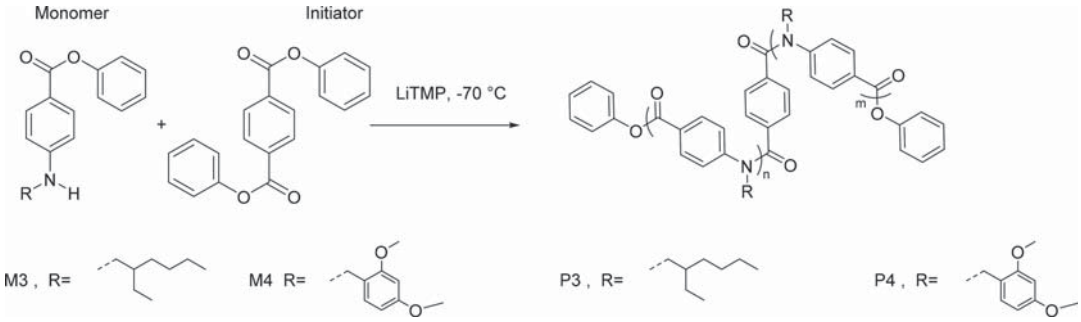



**Table 2. GPC (THF) Data of the Functionalized Polymers**

| reactive polymer | modified polymer | $M_n$[a] (g/mol) before modification | $M_n$[a] (g/mol) after modification | $Đ$ after modification[a] |
|---|---|---|---|---|
| **P3** | **P5** | 2800 | 2900 | 1.07 |
| **P4** | **P6** | 3100 | 2700 | 1.05 |
| **P4** | **P7** | 3100 | 2700 | 1.08 |
| **P3** | **P8** | 2900 | 2600 | 1.06 |
| **P3** | **P9** | 2900 | 2800 | 1.06 |

[a]Determined by GPC (THF) relative to polystyrene standards.

pentafluorophenyl ester end group, and also a small amount of self-initiated polymer carrying one pentafluorophenyl ester end group (Figure 2). This investigation proved the lability of the pentafluorophenyl ester end group, which was most likely replaced by the phenolate ion of the diphenyl terephthalate initiator. The presence of self-initiated polymer also shows the high reactivity of the pentafluorophenyl ester monomers. The monomer **M2** carrying an N-protective DMB group was also polymerized (Table 1) under the same conditions as **P1**.

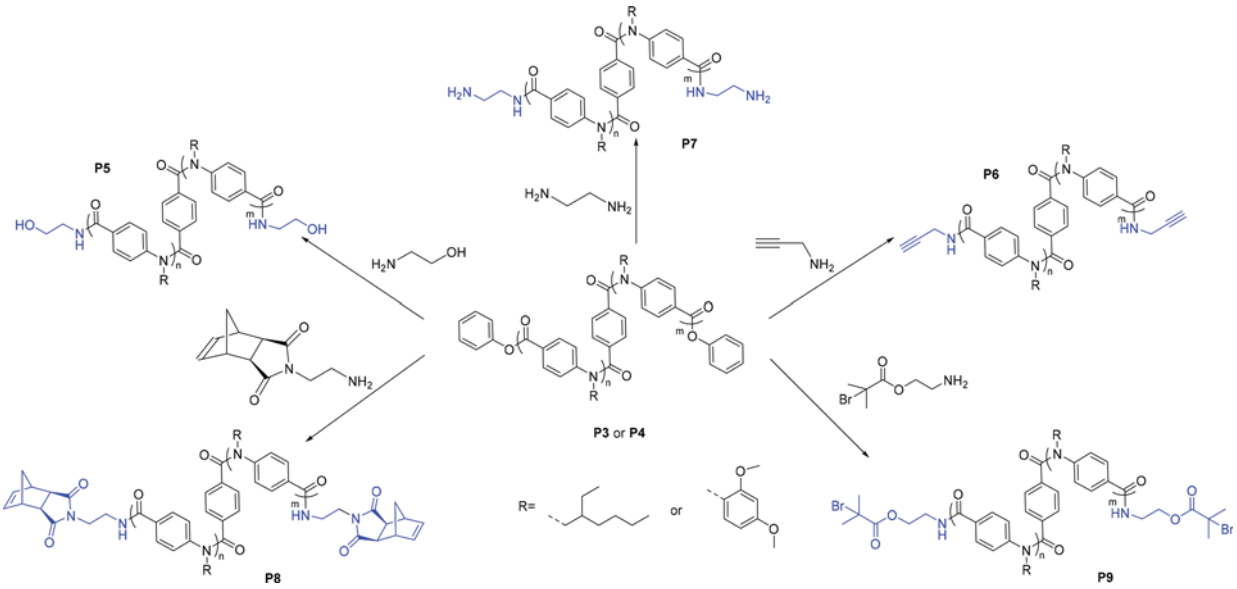
Nonetheless, the postpolymerization modification was examined with polymer **P1** and excess of ethanolamine (20 equiv) in acetonitrile at 80 °C for 12 h. MALDI-ToF mass spectrometry confirmed full conversion of both the phenolate and the pentafluorophenolate ester end group to the amide of ethanolamine (see Figure S20). As the phenolate ester was easily replaced by ethanolamine in a postpolymerization reaction, we next investigated phenyl ester monomers **M3** and **M4** in the synthesis of telechelic poly(benzamides).

A phenolate monomer (**M3** or **M4**) and the diphenyl terephthalate initiator were dissolved in dry THF at −70 °C, and a solution of LiTMP in THF was added and stirred for 12 h and then quenched with a phenol solution in THF (Scheme 2). THF GPC data show the control over the molecular weight with narrow polydispersity for both polymers **P3** and **P4** (Table 1). The MALDI-ToF spectrum exclusively showed phenolate end groups (see Figure S21). As expected, TGA analysis of both polymers proved the thermal stability of the materials (see Figures S16 and S17).

Telechelic aramide polymers were obtained by reacting the polymers with different functional amines in acetonitrile at 80 °C for 12 h. GPC (THF) data before and after postpolymerization modification showed no difference in molecular weight, thereby indicating that no cleavage of the amide bonds in the polymer chain due to transamidation had occurred (Table 2).

Different functional groups were chosen for postpolymerization modification such as propargylamine, ethylendiamine, ethanolamine, *exo-N*-(2-aminoethyl)-5-norbornene-2,3-dicarboximide, and 2-aminoethyl 2-bromo-2-methylpropanoate (Scheme 3). These telechelic aramide polymers are currently being investigated for the synthesis of ABA triblock copolymer synthesis via atom transfer radical polymerization (ATRP), click reactions,

**Scheme 3. Postpolymerization Modification of P3 and P4**



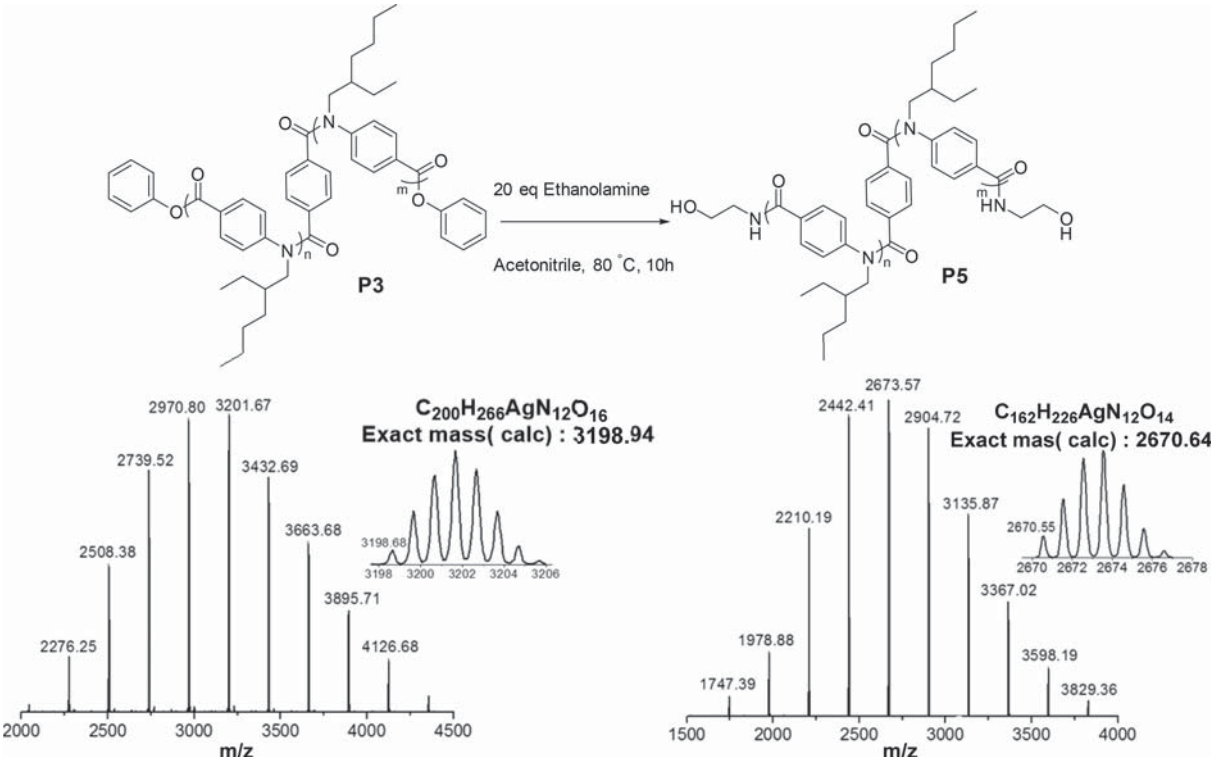



**Figure 3.** Left: MALDI-ToF mass spectrum of the bifunctional-initiated ethylhexyl polymer **P3** as an $Ag^+$ adduct. Right: MALDI-ToF mass spectrum of the modified bifunctional-initiated ethylhexyl polymer **P5** as an $Ag^+$ adduct. The insets show the most intense peak of the distribution isotopically resolved.

as diol components for polyurethane syntheses, or the preparation of cross-linked networks via the olefin metathesis reaction. Such materials might furthermore prove to be useful as shape persistent end-functional rodlike building blocks in particular after cleavage of the *N*-dimethoxybenzyl protective group. of polymer **P4**.

All postpolymerization end-group modified polymers **P5**−**P9** (Table 2 and Scheme 3) were characterized by GPC (THF) and MALDI-ToF mass spectrometry (see Supporting Information).

Figure 3 shows the MALDI-ToF mass spectrum of polymer **P3** (before) and polymer **P5** (after end-group modification with ethanolamine) as an example illustrating the clean end-group conversion feasible with the method described here.

From these results, we propose phenyl esters as excellent leaving groups for the synthesis of poly(benzamide)s via chain-growth polycondensation using LiTMP as a non-nucleophilic base and for postpolymerization end-group modification using derivatives of aliphatic amines. For monomers carrying N-protected secondary amine groups this method represents a facile route to end-functional shape-persistent building blocks for the construction of supramolecular architectures. For alkyl chain N-substituted amine monomers this method opens a pathway to soluble macromonomers that can be utilized in subsequent step-growth polymerization processes.[35−39] These end-functional polymers are currently investigated as macromonomers in step-growth polymerizations in our group.

## CONCLUSION

Here we presented the synthesis of end-functional telechelic poly(benzamide)s. Phenyl or pentafluorophenyl end groups could easily be modified with a range of suitable aliphatic amines allowing us the introduction of alcohol, alkyne, alkyl bromide, amine, or norbornene end groups. The poly(benzamide)s were *N*-alkyl or *N*-dimethoxybenzyl substituted to either ensure excellent organo-solubility or provide the possibility of later N-deprotection. The latter would result in the synthesis of rigid-rod-like shape persistent telechelic polymers. Such materials could be useful supramolecular building blocks for the construction of nanoscale architectures. The *N*-alkyl chains carrying soluble telechelic polybenzamide, on the other hand, are good macromonomer candidates for incorporation into step-growth polymers such as polyesters, polyamides, or polyurethanes.

All polymers were fully characterized before and after end-group modification by GPC and isotopically resolved MALDI-ToF spectrometry.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b00587.

$^1$H and $^{13}$C NMR spectra and MALDI ToF MS (PDF)

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### Notes

The authors declare no competing financial interest.

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