Synthesis and Characterization of Poly(phenylacetylenes) Featuring Activated Ester Side Groups

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ABSTRACT: Four monomers based on 4-ethynylbenzoic acid have been synthesized, one of those featuring an activated ester. With the metathesis catalytic system WCl_6/Ph_4Sn, these acetylenic monomers could successfully be polymerized yielding conjugated polymers with molecular weights of around 10,000 to 15,000 g/mol and molecular weight distributions $M_w/M_n \leq 2.1$. Also the copolymerization of phenylacetylene or methyl 4-ethynylbenzoate with pentafluorophenyl 4-ethynylbenzoate as reactive unit was conducted. Polymer analogous reactions of the reactive polymers and copolymers with amines have been investigated and it was found that poly(pentafluorophenyl 4-ethynylbenzoate) featured a significant reactivity, such that reactions proceeded quantitatively even with aromatic amines. Moreover the UV-Vis spectra of the activated ester based polymer before and after conversion with aliphatic amines showed a change, indicating an effect on the conjugated backbone of the polymers. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 211–224, 2011

KEYWORDS: activated ester; conjugated polymers; copolymerization; functionalization of polymers; metathesis; metathesis polymerization; substituted poly(phenylacetylene)s

INTRODUCTION The synthesis of conjugated polymers has gained a lot of attention in recent years due to their application in optoelectronic devices,[1–3] sensors[4–6] or gas separating membranes.[7–9] Polyacetylene is the simplest and best known conjugated polymer,[10–12] however, its instability and insolubility have limited its practical applications. Attachment of appropriate pendant groups or substituents to the polyacetylene backbone cannot only help to improve the processability and stability but also equip it with new functionalities. While the polyacetylene backbone with its conjugated double bonds is electronically conductive,[13] introduction of pendant functional groups may provide novel properties and interesting chemical characteristics to the polymers, which are absent in the parent form, for example, photo- and electroluminescence,[14,15] optical activity,[16–18] liquid christallinity[18–20] or anion sensing property.[21,22] Such multifunctional polymers have been receiving an increasing amount of attention in material and life science.

In general, functional polymers can be obtained by two different ways. The first and classical way is the polymerization of the corresponding functional monomers yielding polymers featuring the respective functional group. However, the preparation of the respective monomers and their polymerization is often difficult or even impossible, especially when highly complex chemical structures are required. An alternative route would be the synthesis of precursor polymers containing reactive units along its backbone. Polymer analogous reactions of these polymers would then easily lead to functional polymers. In the past, such postpolymerization reactions have been employed for various kinds of polymers and different reactive groups have proved to be useful.[23] However, only few examples on postpolymerization modifications of conjugated polymers are known from the literature.[24,25] As possible reactive groups for postpolymerization reactions activated esters proved to be extremely useful.[26] Activated ester based precursor polymers can be converted into the respective functional polymers by reaction with different nucleophiles, such as amines. The group of Theato as well as other groups have demonstrated the synthetic potential of polymeric activated esters in combination with controlled radical polymerization techniques.[27–30] Especially pentafluorophenyl (PFP) esters proved to be useful because they combine several synthetic advantages: (i) excellent solubility in common organic solvents, (ii) possibility to store PFP ester polymers for a long time without the potential risk of hydrolysis of the ester bond, (iii) quantitative and selective conversion with amines under mild conditions and (iv) easy analysis using ^{19}F NMR and IR spectroscopy.

So far, the research of activated ester based monomers focused mainly on vinylic systems. To the best of our

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knowledge, until now no investigation has been conducted to synthesize acetylenic monomers exhibiting an activated ester group. As such, we herein report on the synthesis of PFP ester monomers based on 4-ethynylbenzoic acid and its polymerization and copolymerization with phenylacetylene and methyl 4-ethynylbenzoate. Further, we investigated the polymer analogous conversion of these PFP ester based (co)polymers with aliphatic and aromatic amines as nucleophiles.

EXPERIMENTAL

Materials and Instruments

All reagents were obtained from Acros, Aldrich or Fluka and used as received unless stated differently. Toluene was distilled from sodium and triethylamine (NEt_3) from potassium hydroxide. Phenylacetylene **M1** was distilled under reduced pressure before use.

^{1}H- and ^{13}C-NMR spectra were recorded using a Bruker AC 300 instrument and chemical shifts relative to TMS are given in ppm. ^{19}F NMR data was obtained on a Bruker DRX 400. IR spectra were recorded on a Bruker Vector 22 FTIR Spectrometer. Mass spectra were obtained on a Finningan MAT 95 Mass Spectrometer. Size exclusion chromatography (SEC, GPC) was performed using a system from Jasco (PU-980 pump, RI-939 RI detector, UV-970 UV detector) and THF as the eluent at a flow rate of 1.0 mL min^{-1}. The number-average molecular weight and polydispersity of the polymers were calculated on the basis of a calibration with polystyrene.

Monomer Synthesis

Methyl 4-Bromobenzoate

To a mixture of 4-bromobenzoic acid (33.4 g, 166 mmol) and methanol (MeOH) (150 mL) conc. sulfuric acid (2.8 mL) under nitrogen atmosphere was added and heated to reflux. Under stirring the temperature was maintained for 24 h. After removing the solvent the obtained white solid was dissolved in diethyl ether and washed with water and then with 3% potassium carbonate solution until the aqueous phase remain basic and again with water until the aqueous phase remain neutral. The combined organic layer was dried with magnesium sulfate. After removal of the solvent the crude product was purified by recrystallization from MeOH to give methyl 4-bromobenzoate as white crystals.

Yield: 29.3 g (82%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.89 (s, 3H, CH_3), 7.56 (d, 2H, Ar), 7.88 (d, 2H, Ar). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 52.52 (COO*C*H$_3$), 127.89 (Ar), 129.00 (Ar), 131.03 (Ar), 131.67 (Ar), 166.30 (COO). FDMS (*m/z*, relative intensity): calcd for $C_8H_7O_2Br$, 215.04; found, 213.9 (100%), 214.9 (8%), 215.9 (97%), 216.9 (8%).

Methy 4-[(Trimethylsilyl)ethynyl]benzoate

A mixture of methyl 4-bromobenzoate (12.1 g, 56 mmol), ethynyltrimethylsilane (9.8 mL, 71 mmol), dichlorbis(triphenylphosphine)palladium (63 mg, 90 μmol), triphenylphosphine (183 mg, 698 μmol) and copper iodide (49 mg, 257 μmol) in NEt_3 (70 mL) was stirred under nitrogen atmosphere at 50 °C for 18 h. After cooling to room temperature the mixture was filtered to remove the insoluble triethylamine hydrobromide. The salt was washed with diethyl ether until the ether washing were clear. The combined filtrates were evaporated under reduced pressure to dryness. The solid obtained was dissolved in Et_2O and washed with water and then with 3% hydrochloric acid solution and again with water until the aqueous phase was neutral. The combined organic layers were dried with magnesium sulfate. After removing of the solvent the crude product was purified by column chromatography on silica gel with cyclohexane/ethylacetate (15/1, v/v) to give methyl 4-[(trimethylsilyl)ethynyl]-benzoate as pale yellow crystals.

Yield: 12.2 g (95%). FTIR (ATR, cm^{-1}): 2955 (CH_3), 2159 (C≡C), 1725(C=O). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.24 (s, 9H, Si(CH_3)$_3$), 3.89 (s, 3H, CH_3), 7.50 (d, 2H, Ar), 7.95 (d, 2H, Ar). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): −0.20 (Si(CH_3)$_3$), 52.18 (COO), 97.64 (C ≡C), 104.04 (C≡C), 127.73 (Ar), 129.65 (Ar), 131.83 (Ar), 166.45 (*C*OOCH$_3$). FDMS (*m/z*, relative intensity): calcd for $C_{13}H_{16}O_2Si$, 232.35; found, 232.0 (100%), 233.0 (18%), 234.1 (4%).

Methyl 4-Ethynylbenzoate (M2)

Methyl 4-[(trimethylsilyl)ethynyl]benzoate (10.5 g, 45 mmol) was mixed with potassium carbonate (3.5 g) in MeOH (100 mL). The mixture was degassed once and stirred under argon atmosphere for 4 h. The solution was concentrated under reduced pressure; thereby the heating band should not exceed 30 °C. To the residue was added dichloromethane and the mixture was washed with water. The aqueous phase was extracted with dichloromethane twice. The combined organic layer was dried with $MgSO_4$ and after removing of the solvent methyl 4-ethynylbenzoate was obtained as yellow crystals.

Yield: 5.9 g (64%). FTIR (ATR, cm^{-1}): 3239 (C≡CH), 2952 (CH_3), 2104 (C≡C), 1701 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 3.21 (s, 1H, HC≡C), 3.90 (s, 3H, CH_3), 7.53 (d, 2H, Ar), 7.97 (d, 2H, Ar). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 52.24 (CH_3), 80.06 (C≡C), 82.76 (C≡C), 126.71 (Ar), 129.42 (Ar), 130.09 (Ar), 132.04 (Ar), 166.37 (COO). FDMS (*m/z*, relative intensity): calcd for $C_{10}H_8O_2$, 160.17; found, 160.0 (100%), 161.0 (10%).

Ethyl 4-Bromobenzoate

To a mixture of 4-bromobenzoic acid (10.1 g, 50 mmol) and ethanol (50 mL) was conc. sulfuric acid (0.6 mL) under nitrogen atmosphere added and heated to reflux. Under stirring the temperature was maintained for 24 h. After removing the solvent the obtained liquid was diluted with diethyl ether and washed with water and then with 3% potassium carbonate solution until the aqueous phase remain basic and again with water until the aqueous phase remain neutral. The combined organic layers were dried with magnesium sulfate and after removing of the solvent ethyl 4-bromobenzoate was obtained as a colorless liquid.

Yield: 9.8 g (86%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.37 (t, 3H, CH_2CH_3), 4.35 (q, 2H, CH_2CH_3), 7.55 (d, 2H, Ar), 7.88 (d, 2H, Ar).

Ethyl 4-[(Trimethylsilyl)ethynyl]benzoate

A mixture of ethyl 4-bromobenzoate (9.8 g, 43 mmol), ethynyltrimethylsilane (7.8 mL, 56 mmol), dichlorbis(triphenylphosphine)palladium (43 mg, 61 μmol), triphenylphosphine (145 mg, 553 μmol) and copper iodide (40 mg, 210 μmol) in NEt_3 (50 mL) was stirred under nitrogen atmosphere at 50 °C for 18 h. After cooling to room temperature the mixture was filtered to remove the insoluble triethylamine hydrobromide. The salt was washed with diethyl ether until the ether washing were clear. The combined filtrates were evaporated under reduced pressure to dryness. The solid obtained was dissolved in diethyl ether and washed with water and then with 3% hydrochloric acid solution and again with water until the aqueous phase was neutral. The combined organic layers were dried with $MgSO_4$. After removing the solvent the crude product was purified by column chromatography on silica gel with dichloromethane/hexane (1/1, v/v) to give ethyl 4-[(trimethylsilyl)ethynyl]benzoate as a orange liquid.

Yield: 10.1 g (95%). FTIR (ATR, cm^{-1}): 2960 and 2902 (CH_3, CH_2), 2159 (C≡C), 1719 (s, C=O). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.24 (s, 9H, $Si(CH_3)_3$), 1.37 (t, 3H, CH_2CH_3), 4.35 (q, 2H, CH_2CH_3), 7.49 (d, 2H, Ar), 7.95 (d, 2H, Ar).

^{13}C NMR (300 MHz, $CDCl_3$, ppm): −0.20 ($Si(CH_3)_3$), 14.26 (CH_2CH_3), 61.08 (CH_2CH_3), 97.48 (C≡C), 104.11 (C≡C), 129.24 (Ar), 130.01 (Ar), 131.78 (Ar), 165.93 (COO). FDMS (*m/z*, relative intensity): calcd for $C_{14}H_{18}O_2Si$, 246.38; found, 246.0 (100%), 247.0 (17%), 238.0 (6%).

Ethyl 4-Ethynylbenzoate (M3)

Ethyl 4-[(trimethylsilyl)ethynyl]benzoate (8.5 g, 34 mmol) was mixed with potassium carbonate (3.5 g) in ethanol (100 mL). The mixture was degassed once and stirred under argon atmosphere for 4 h. The solution was concentrated under reduced pressure; thereby the heating bath should not exceed 30 °C. Dichloromethane was added to the residue and the mixture was washed with water. The aqueous phase was extracted with dichloromethane twice. The combined organic layers were dried with magnesium sulfate and after removing of the solvent ethyl 4-ethynylbenzoate was obtained as a red liquid.

Yield: 5.5 g (94%). FTIR (ATR, cm^{-1}): 3291 (C≡CH), 2982, 2936 (CH_3, CH_2), 2109 (C≡C), 1713 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.37 (t, 3H, CH_2CH_3), 3.21 (s, 1H, HC≡C), 4.36 (q, 2H, CH_2CH_3), 7.52 (d, 2H, Ar), 7.98 (d, 2H, Ar). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 13.92 (CH_2CH_3), 61.68 (CH_2CH_3), 79.94 (C≡C), 82.84 (C≡C), 126.04 (Ar), 129.39 (Ar), 130.61 (Ar), 132.26 (Ar), 165.91 (COO).

Methyl 4-(4-Methoxycarbonylphenyl)-2-methyl-3-butyn-2-ol

A mixture of methyl 4-bromobenzoate (17.9 g, 83 mmol), 2-methyl-3-butyn-2-ol (9.6 mL, 99 mmol), dichlorbis(triphenylphosphine)palladium (81 mg, 115 μmol), triphenylphosphine (235 mg, 896 μmol) and copper iodide (69 mg, 362 μmol) in NEt_3 (95 mL) was stirred under a nitrogen atmosphere at 50 °C for 18 h. After cooling to room temperature the mixture was filtered. The filter residue was washed with diethyl ether until the ether washing were clear. The combined filtrates were evaporated under reduced pressure to dryness. The obtained solid was dissolved in diethyl ether and washed with water and then with 3% hydrochloric acid solution and again with water until the aqueous phase was neutral. The combined organic layers were dried with magnesium sulfate. After removing the solvent the crude product was purified by recrystallization from toluene to give methyl 4-(4-methoxycarbonylphenyl)-2-methyl-3-butyn-2-ol as white crystals.

Yield: 14.6 g (81%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.60 (s, 6H, $(CH_3)_2C$), 2.19 (s, 1H, OH), 3.89 (s, 3H, CH_3), 7.44 (d, 2H, Ar), 7.95 (d, 2H, Ar).

Potassium 4-Ethynylbenzoate

To a solution of potassium hydroxide (12.2 g, 217 mmol) in 2-propanol (140 mL) were added methyl 4-(4-methoxycarbonylphenyl)-2-methyl-3-butyn-2-ol (14.6 g, 67 mmol) and the mixture was stirred at room temperature for 4 h. After filtration potassium 4-ethynylbenzoate was obtained as a white solid.

Yield 12.3 g (100%). FTIR (ATR, cm^{-1}): 3297 (HC≡C), 1666 (C=O), 1583 and 1539 (COO^-). ^{1}H NMR (300 MHz, MeOH-d_4, ppm): 7.42 (d, 2H, Ar), 7.87 (d, 2H, Ar). ^{13}C NMR (300 MHz, MeOH-d_4, ppm): 80.04 (C≡C), 83.83 (C≡C), 125.45 (Ar), 130.23 (Ar), 132.43 (Ar), 174.47 (COO^-). ESIMS (*m/z*, relative intensity): calcd for $C_9H_5O_2K$, 184.23; found, 145.1 (100%) $[M]^-$, 313.1 (90%) $[2M+Na]^-$, 329.0 (84%) $[2M+K]^-$.

4-Ethynyl Benzoyl Chloride

A solution of potassium 4-ethynylbenzoate (13.4 g, 73 mmol) in chloroform (80 mL) was stirred under a nitrogen atmosphere at 0 °C, following thionyl chloride (20.0 mL, 276 mmol) was added gradually. Then three drops of DMF were added and the mixture was stirred at room temperature for 4 h. The resulting orange solution was evaporated under reduced pressure to dryness. The 4-ethynyl benzoyl chloride was extracted from the solid with dichloromethane. Because of the sensitivity of 4-ethynyl benzoyl chloride against humidity the yield of the reaction was not determined and the obtained orange solution of 4-ethynyl benzoyl chloride in dichloromethane was directly used for the next conversion.

FTIR (ATR, cm^{-1}): 3264 (HC≡C), 2110 (C≡C), 1772 and 1730 (C=O). ^{1}H NMR (300 MHz, Aceton-d_6, ppm): 4.09 (s, 1H, HC≡C), 7.72 (d, 2H, Ar), 8.14 (d, 2H, Ar). ^{13}C NMR (300 MHz, Aceton-d_6, ppm): 82.60 (C≡C), 84.31 (C≡C), 130.39 (Ar), 132.04 (Ar), 133.38 (Ar), 133.43 (Ar), 164.83 (COCl). FDMS (*m/z*, relative intensity): calcd for H_5OCl, 164.56; found, 164.0 (100%), 165.0 (4%), 166.0 (25%).

Pentafluorophenyl 4-Ethynylbenzoate (M4)

To a solution of pentafluorophenol (4.2 g, 23 mmol) in dichloromethane (150 mL) was added the solution of 4-ethynyl benzoyl chloride in dichloromethane gradually under an argon atmosphere at 0 °C. The mixture was stirred at room temperature for 12 h. The mixture was washed with water three times and the combined organic layers were

dried with magnesium sulfate. The crude product was purified by column chromatography on silica gel with hexane/toluene (4/1, v/v) to give pentafluorophenyl 4-ethynylbenzoate as white crystals.

Yield: 4.6 g (68%). FTIR (ATR, cm^{-1}): 3271 (HC≡C), 1754 (C=O), 1518 (C—F). ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.31 (s, 1H, HC≡C), 7.63 (d, 2H, Ar), 8.14 (d, 2H, Ar). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 81.38 (C≡C), 82.25 (C≡C), 126.81 (Ar), 128.74 (Ar), 130.50 (Ar), 132.40 (Ar), 136.31 (Ar—F), 137.98 (Ar—F), 139.66 (Ar—F), 141.47 (Ar—F), 142.92 (Ar—F), 161.94 (COO). ^{19}F NMR (400 MHz, $CDCl_3$, ppm): −152.78 (d, 2F), −158.02 (t, 1F), −162.53 (t, 2F). FDMS (*m/z*, relative intensity): calcd for $C_{15}H_5O_2F_5$, found, 311.9 (100%), 312.9 (13%), 314.0 (1%). Anal. calcd for $C_{15}H_5O_2F_5$: C, 57.71%; H 1.61%. Found: C, 58.06%; H 1.50%.

Polymerization

General Procedure

All polymerization reactions and manipulations of the monosubstituted phenylacetylenes **M1**-**M4** were carried out under an argon atmosphere using Schlenk techniques in a vacuum line system or in an inert-atmosphere glovebox, except of the purification of the polymers, which were done in an open atmosphere. A typical polymerization was conducted similar to the procedures reported in the literature[24] as follows. Into a dry 20 mL Schlenk flask a solution of the respective monomer (1 eq.) in toluene was added. The catalyst solution was prepared in another dry Schlenk flask by dissolving WCl_6 (0.01 eq.) and $SnPh_4$ (0.015 eq.) in toluene. The mixtures were degassed by three freeze-pump-thaw cycles. The two flasks were refilled with argon and aged at 80 °C for 15 min. The monomer solution was then transferred to the catalyst solution using a hypodermic syringe. The reaction mixture was stirred at 80 °C for 24 h and then cooled to room temperature. Polymer formed was isolated by precipitation into a large amount of MeOH, centrifuged and dried under vacuum.

Poly(phenylacetylene) (P1)

According to the general procedure the polymerization of **M1** (410 mg, 4.0 mmol) was conducted using tungstenhexachloride (WCl_6) (16 mg, 410 μmol) and tetraphenyltin ($SnPh_4$) (27 mg, 63 μmol) in toluene (4 mL) to give **P1** as orange powder.

Yield: 310 mg (76%). M_n = 12,310 g/mol, M_w/M_n = 1.31. ^1H NMR (300 MHz, $CDCl_3$, ppm): 6.98 (br s, 6H, HC=C, Ar).

Poly(methyl 4-ethynylbenzoate) (P2)

According to the general procedure the polymerization of **M2** (680 mg, 4.2 mmol) was conducted using WCl_6 (16 mg, 41 μmol) and $SnPh_4$ (27 mg, 63 μmol) in toluene (4 mL) to give **P2** as orange powder.

Yield: 540 mg (79%). M_n 15,090 g/mol, M_w/M_n = 1.42. ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.88 (s, 3H, CH_3), 6.56 (br s, 3H, HC=C, Ar), 7.60 (br s, 2H, Ar).

Poly(ethyl 4-ethynylbenzoate) (P3)

According to the general procedure the polymerization of **M3** (700 mg, 4.0 mmol) was conducted using WCl_6 (16 mg, 41 μmol) and $SnPh_4$ (27 mg, 63 μmol) in toluene (4 mL) to give **P3** as orange powder.

Yield: 150 mg (21%). M_n = 13,720 g/mol, M_w/M_n = 1.41. ^1H NMR (300 MHz, $CDCl_3$, ppm): 1.30 (s, 3H, CH_2CH_3), 4.29 (s, 2H, CH_2CH_3), 6.43 (br s, 3H, HC=C, Ar), 7.62 (br s, 2H, Ar).

Poly(pentafluorophenyl 4-ethynylbenzoate) (P4)

According to the general procedure the polymerization of **M4** (970 mg, 3.1 mmol) was conducted using WCl_6 (16 mg, 41 μmol) and $SnPh_4$ (23 mg, 54 μmol) in toluene (4 mL) to give **P4** as orange powder.

Yield: 480 mg (49%). M_n = 10,610 g/mol, M_w/M_n = 2.09. FTIR (ATR, cm^{-1}): 1765 (C=O), 1522 (C—F). ^1H NMR (300 MHz, $CDCl_3$, ppm): 6.91, 7.96 (br s, 5H, HC=C, Ar). ^{19}F NMR (400 MHz, $CDCl_3$, ppm): −152.97 (s, 2F), −157.13 (s, 1F), −162.10 (s, 2F).

Poly(phenylacetylene-co-pentafluorophenyl 4-ethynylbenzoate) (P1/4)

According to the general procedure the copolymerization of **M1** (112 mg, 1.1 mol) with **M4** (342 mg, 1.1 mmol) was conducted using WCl_6 (8 mg, 19 μmol) and $SnPh_4$ (10 mg, 22 μmol) in toluene (4 mL) to give **P1/4** as orange powder.

Yield: 364 mg (77%). M_n = 27,350 g/mol, M_w/M_n = 1.54. FTIR (ATR): ν (cm^{-1}) = 1761 (C=O), 1520 (C—F). ^1H NMR (300 MHz, $CDCl_3$, ppm): 6.97, 7.78 (br s, 11H, HC=C, Ar). ^{19}F NMR (400 MHz, $CDCl_3$, ppm): −152.64 (s, 2F), −157.78 (s, 1F), −162.32 (s, 2F).

Poly(methyl 4-ethynylbenzoate-co-pentafluorophenyl 4-ethynylbenzoate) (P2/4a)

According to the general procedure the copolymerization of **M2** (460 mg, 2.9mol) with **M4** (101 mg, 0.3 mmol) was conducted using WCl_6 (10 mg, 25 μmol) and $SnPh_4$ (18 mg, 42 μmol) in toluene (3 mL) to give **P2/4a** as orange powder.

Yield: 150 mg (27%). M_n = 19,030 g/mol, M_w/M_n = 1.45. FTIR (ATR, cm^{-1}): 1762 (C=OC_6F_5), 1718 (C=OCH_3), 1521 (s, C—F). ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.82 (s, 3H, CH_3), 6.42, 7.48 (br s, 10H, HC=C, Ar).

Poly(methyl 4-ethynylbenzoate-co-pentafluorophenyl 4-ethynylbenzoate) (P2/4b)

According to the general procedure the copolymerization of **M2** (273 mg, 1.7mol) with **M4** (206 mg, 0.7 mmol) was conducted using WCl_6 (12 mg, 30 μmol) and $SnPh_4$ (14 mg, 33 μmol) in toluene (3 mL) to give **P2/4b** as orange powder.

Yield: 360 mg (75%). M_n = 19,330 g/mol, M_w/M_n = 1.47. FTIR (ATR, cm^{-1}): 1763 (C=OC_6F_5), 1722 (C=OCH_3), 1520 (s, C—F). ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.88 (s, 3H, CH_3), 6.48, 7.55 (br s, 10H, HC=C, Ar).

Poly(methyl 4-ethynylbenzoate-co-pentafluorophenyl 4-ethynylbenzoate) (P2/4c)

According to the general procedure the copolymerization of **M2** (181 mg, 1.1mol) with **M4** (354 mg, 1.1 mmol) was conducted using WCl_6 (8 mg, 19 μmol) and $SnPh_4$ (10 mg, 22 μmol) in toluene (4 mL) to give **P2/4c** as orange powder.

Yield: 398 mg (74%). M_n = 26,760 g/mol, M_w/M_n = 1.87. FTIR (ATR, cm^{-1}): 1763 (C=OOC_6F_5), 1726 (C=$OOCH_3$), 1521 (s, C—F). ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.85 (s, 3H, CH_3), 6.69, 7.73 (br s, 10H, HC=C, Ar). ^{19}F NMR (400 MHz, $CDCl_3$, ppm): −152.75 (s, 2F), −157.65 (s, 1F), −162.14 (s, 2F).

Poly(methyl 4-ethynylbenzoate-co-pentafluorophenyl 4-ethynylbenzoate) (P2/4d)

According to the general procedure the copolymerization of **M2** (88 mg, 0.5mol) with **M4** (406 mg, 1.3 mmol) was conducted using WCl_6 (15 mg, 38 μmol) and $SnPh_4$ (19 mg, 44 μmol) in toluene (3 mL) to give **P2/4d** as orange powder.

Yield: 376 mg (76%). M_n = 20,030 g/mol, M_w/M_n = 1.35. FTIR (ATR, cm^{-1}): 1763 (C=OOC_6F_5), 1725 (C=$OOCH_3$), 1519 (s, C—F). ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.77 (s, 1H, CH_3), 6.63, 7.73 (br s, 10H, HC=C, Ar).

Poly(methyl 4-ethynylbenzoate-co-pentafluorophenyl 4-ethynylbenzoate) (P2/4e)

According to the general procedure the copolymerization of **M2** (31 mg, 0.2mol) with **M4** (524 mg, 1.7 mmol) was conducted using WCl_6 (15 mg, 38 μmol) and $SnPh_4$ (16 mg, 37 μmol) in toluene (3 mL) to give **P2/4e** as orange powder.

Yield: 398 mg (72%). M_n = 12,790 g/mol, M_w/M_n = 1.39. FTIR (ATR, cm^{-1}): 1763 (C=OOC_6F_5), 1727 (C=$OOCH_3$), 1519 (s, C—F). ^1H NMR (300 MHz, $CDCl_3$, ppm): 3.72 (s, 0.5H, CH_3), 6.62, 7.80 (br s, 10H, HC=C, Ar).

Fractionated Precipitation of Poly(phenylacetylene) (P1)

P1 (70 mg, 5.7 μmol) was dissolved in 1.5 mL THF. Under stirring MeOH was added until polymer began to precipitate. The precipitated polymer fraction was separated from the polymer solution by centrifugation. Precipitation was then continued by further addition of MeOH (∼2 mL) and the process was continued for three times. The rest of the solution was finally evaporated to dryness. All fractions were dried under vacuum to yield **P1a**, **P1b**, **P1c**, **P1d** and **P1e** as orange powders. **P1a**: yield 35 mg, M_n = 14,700 g/mol, M_w/M_n = 1.23. **P1b**: yield 9 mg, M_n = 6800 g/mol, M_w/M_n = 1.18. **P1c**: yield 3 mg, M_n = 3800 g/mol, M_w/M_n = 1.15. **P1d**: yield 3 mg, M_n = 2400 g/mol, M_w/M_n = 1.11. **P1a**: yield 8 mg, M_n = 600 g/mol, M_w/M_n = 1.8.

Fractionated Precipitation of Poly(pentafluorophenyl 4-ethynylbenzoate) (P4)

P4 (50 mg, 4.7 μmol) was dissolved in 1.0 mL THF and the fractionated precipitation was induced by addition of MeOH following the procedure above. All fractions were dried under vacuum to yield **P4a**, **P4b**, **P4c**, **P4d** and **P4e** as orange powders. **P4a**: yield 18 mg, M_n = 13,000 g/mol, M_w/M_n = 1.29. **P4b**: yield 13 mg, M_n = 10,100 g/mol, M_w/M_n = 1.13. **P4c**: yield 4 mg, M_n = 7100 g/mol, M_w/M_n = 1.09. **P4d**: yield 3 mg, M_n = 4600 g/mol, M_w/M_n = 1.14. **P4a**: yield 4 mg, M_n = 3100 g/mol, M_w/M_n = 1.13.

Polymer Analogous Reaction

General Procedure

Polymers and copolymers of **M4** were converted with different amines according to the same general procedure: To a solution of the polymer (1eq.) in chloroform was added first NEt_3 (1.05eq. related to the monomer units) then the corresponding amine (1.10eq. related to the monomer units). The mixture was stirred for the indicated time at the indicated temperature. The organic layer was washed with water and the resulting polymers were purified by precipitation into a large amount of cyclohexane (**P4_N1-3**) or *n*-hexane (**P4_N4-6, P1/4_N1, P2/4c_N1**), centrifuged and dried under vacuum.

Poly(N-hexyl 4-ethynylbenzamide) (P4_N1)

According to the general procedure of the polymer analogous reaction **P4** (33 mg, 103 μmol), NEt_3 (0.03 mL, 216 μmol) and hexylamine (0.02 mL, 152 μmol) in chloroform (3 mL) were stirred for 12 h at room temperature to yield **P4_N1** as an orange powder.

Yield: 23 mg (95%). M_n = 6240 g/mol, M_w/M_n = 1.39. FTIR (ATR, cm^{-1}): 3293 (N—H), 2955 and 2927 and 2856 (CH_3, CH_2), 1637and 1541 (C=ONH). ^1H NMR (300 MHz, $CDCl_3$, ppm): 0.86 (s, 3H, CH_3), 1.28 (s, 6H, CH_2), 1.60 (s, 2H, CH_2), 3.34 (s, 2H, CH_2NH), 7.11 (br s, 5H, HC=C, Ar).

Poly(phenylacetylene-co-N-hexyl 4-ethynylbenzamide) (P1/4_N1)

According to the general procedure of the polymer analogous reaction **P1/4** (45 mg, 144 μmol), NEt_3 (0.03 mL, 216 μmol) and hexylamine (0.02 mL, 152 μmol) in chloroform (3 mL) were stirred for 12 h at room temperature to yield **P1/4_N1** as an orange powder.

Yield: 26 mg (91%). M_n = 19,300 g/mol, M_w/M_n = 1.50 FTIR (ATR, cm^{-1}) = 3355 (N—H), 2956 and 2926 and 2858 (CH_3, CH_2), 1637 and 1541 (C=ONH). ^1H NMR (300 MHz, CD_2Cl_2, ppm): 0.85 (s, 3H, CH_3), 1.26 (s, 6H, CH_2), 1.56 (s, 2H, CH_2), 3.35 (s, 2H, CH_2NH), 7.03 (br s, 11H, HC=C, Ar).

Poly(methyl 4-ethynylbenzoate-co-N-hexyl 4-ethynylbenzamide) (P2/4c_N1)

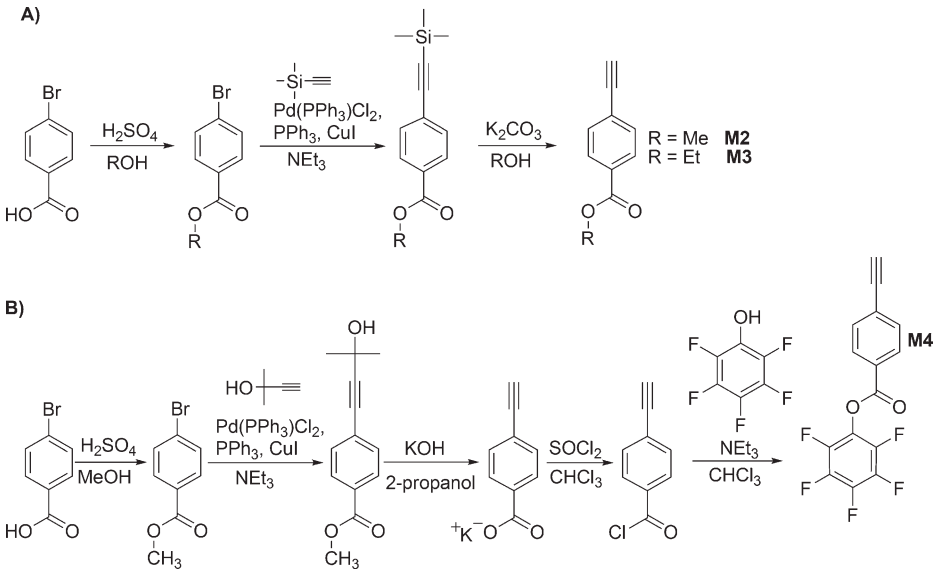
According to the general procedure of the polymer analogous reaction **P2/4c** (41 mg, 131 μmol), NEt_3 (0.03 mL, 216 μmol) and hexylamine (0.02 mL, 152 μmol) in chloroform (3 mL) were stirred for 12 h at room temperature to yield **P2/4c_N1** as an orange powder.

Yield: 24 mg (88%). M_n = 14,440 g/mol, M_w/M_n = 1.40. FTIR (ATR, cm^{-1}) = 3328 (N—H), 2952 and 2931 and 2858 (CH_3, CH_2), 1723 (C=O), 1640 and 1540 (C=ONH). ^1H NMR (300 MHz, CD_2Cl_2, ppm): 0.88 (s, 3H, CH_3), 1.30 (s, 6H, CH_2), 1.58 (s, 2H, CH_2), 3.39 (s, 2H, CH_2NH), 3.85 (s, 3H, $COOCH_3$), 7.59 (br s, 10H, HC=C, Ar).

Poly(N-isopropyl 4-ethynylbenzamide) (P4_N2)

According to the general procedure of the polymer analogous reaction **P4** (36 mg, 115 μmol), NEt_3 (0.03 mL, 216 μmol) and isopropylamine (0.02 mL, 233 μmol) in chloroform (3 mL) were stirred for 12 h at room temperature to yield **P4_N2** as an orange powder.

Yield: 21 mg (96%). M_n = 6170 g/mol, M_w/M_n = 1.35. FTIR (ATR, cm^{-1}): 3299 (N—H), 2972 and 2934 and 2874 (CH_3, CH), 1636 and 1536 (C=ONH). ^1H NMR (300 MHz, $CDCl_3$,



SCHEME 1 Three-step synthesis of methyl 4-ethynylbenzoate **M2** and ethyl 4-ethynylbenzoate **M3** (A) and five-step synthesis of pentafluorphenol 4-ethynylbenzoate **M4** (B).

ppm): 1.24 (s, 6H, CH_3), 4.20 (s, 1H, CH), 7.35 (br s, 5H, HC=C, Ar).

Poly(*N,N*-dibutyl 4-ethynylbenzamide) (P4_N3)

According to the general procedure of the polymer analogous reaction **P4** (39 mg, 155 μmol), NEt_3 (0.03 mL, 216 μmol) and dibutylamine (0.03 mL, 177 μmol) in chloroform (3 mL) were stirred for 12 h at room temperature to yield **P4_N3** as an orange powder.

Yield: 32 mg (80%). M_n = 6620 g/mol, M_w/M_n = 1.69. FTIR (ATR, cm^{-1}) = 2957 and 2930 and 2871 (CH_3, CH_2), 1631 (C=ONH). ^1H NMR (300 MHz, $CDCl_3$, ppm): 0.92 (s, 10H, CH_3, CH_2), 1.33 (s, 4H, CH_2), 3.29 (s, 4H, CH_2NH), 7.03 (br s, 5H, HC=C, Ar).

Poly(N-phenyl 4-ethynylbenzamide) (P4_N4)

According to the general procedure of the polymer analogous reaction **P4** (26 mg, 83 μmol), NEt_3 (0.02 mL, 144 μmol) and aniline (0.01 mL, 110 μmol) in chloroform (3 mL) were stirred for 7d at 50 °C to yield **P4_N4** as a red powder.

Yield: 18 mg (99%). M_n = 5210 g/mol, M_w/M_n = 1.91. FTIR (ATR, cm^{-1}) = 1717 and 1669 (C=ONH). ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.09, 7.30, 7.70 (br s, 10H, HC=C, Ar).

Poly(N-(N′,N′-dimethyl-p-pheny) 4-ethynylbenzamide) (P4_N5)

According to the general procedure of the polymer analogous reaction **P4** (24 mg, 77 μmol), NEt_3 (0.02 mL, 144 μmol) and *N′,N′*-dimethyl-*p*-phenylenediamine (11 mg, 81 μmol) in chloroform (3 mL) were stirred for 7d at 50 °C to yield **P4_N5** as a purple powder.

Yield: 20 mg (98%). M_n = 5170 g/mol, M_w/M_n = 1.37. FTIR (ATR, cm^{-1}): 3297 (N—H), 2921 (CH_3), 1713 and 1642 (C=ONH). ^1H NMR (300 MHz, $CDCl_3$, ppm) = 2.91 (s, 6H, CH_3), 6.69, 7.53 (br s, 9H, HC=C, Ar).

Poly(N-(p-nitrophenyl) 4-ethynylbenzamide) (P4_N6)

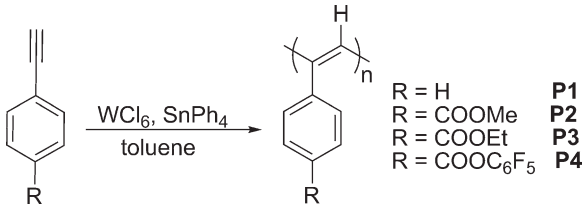
According to the general procedure of the polymer analogous reaction **P4** (28 mg, 90 μmol), NEt_3 (0.02 mL, 144 μmol) and 4-nitroaniline (15 mg, 109 μmol) in chloroform (3 mL) were stirred for 7d at 50 °C to yield **P4_N6** as a yellow powder.

Yield: 14 mg (58%). M_n = 6530 g/mol, M_w/M_n = 1.62. FTIR (ATR, cm^{-1}): 3361 (CH_3), 1760 (C=O), 1714, 1630 (C=ONH), 1521 (C—F), 1505, 1293 (NO_2). ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.09, 7.30, 7.70 (br s, 9H, HC=C, Ar).

RESULTS AND DISCUSSION

Monomer Synthesis

In this study four different monomers featuring a polymerizable triple bond were investigated. Phenylacetylene **M1** is commercially available and was only distilled under reduced pressure before use. The three other monomers were all based on 4-ethynylbenzoic acid and had to be synthesized. Our synthetic routes to these three monomers started from 4-bromobenzoic acid and are presented in Scheme 1. The two monomers, methyl 4-ethynylbenzoate (**M2**) and ethyl 4-ethynylbenzoate (**M3**), were synthesized in a three-step reaction following standard reaction conditions with an overall yield higher than 60%, as described in the following [see Scheme 1(A)]. First an esterification under general conditions of 4-bromobenzoic acid with the corresponding alcohol resulted in methyl 4-bromobenzoate or ethyl 4-bromobenzoate, which were both purified by recrystallization. In the second step the triple bond was incorporated by a Sonogashira reaction in a modified procedure from the literature.[31] Trimethylsilylacetylene as a coupling agent was converted with the alkyl 4-bromobenzoate in the presence of Pd(0) complex, copper iodide, triphenylphosphine and dry triethylamine (NEt_3). Differing from the literature trimethylsilylacetylene was used as a coupling agent instead of 2-methyl-3-butyn-2-ol and only dry NEt_3 was used as the solvent instead of a mixture of dry NEt_3 and pyridine. The resulting methyl 4-[(trimethylsilyl)ethynyl]benzoate and ethyl 4-[(trimethylsilyl)ethynyl]benzoate were purified by column chromatography. In the last step, the protecting group of the



SCHEME 2 Polymerization of monosubstituted phenylacetylenes **M1–M4**.

triple bond was removed to yield **M2** and **M3**, respectively.[32] It is worthwhile to mention that potassium carbonate as the applied base was just basic enough to remove the trimethylsilyl group but not basic enough to cleave the ester bond. Both monomers have been characterized by FTIR spectroscopy, ^{1}H NMR and ^{13}C NMR spectroscopy, and **M2** was also analyzed by mass spectrometry.

Pentafluorophenyl 2-ethynylbenzoate (**M4**) was synthesized in a five-step reaction as shown in Scheme 1(B). Starting from 4-bromobenzoic acid, the first step was to protect the acid group prior introduction of the triple bond via a Sonogashira reaction similar to the synthesis of **M2** and **M3**. However, as a coupling agent 2-methyl-3-butyn-2-ol was used instead of trimethylsilylacetylene. The resulting methyl 4-(4-methoxycarbonylphenyl)-2-methyl-3-butyn-2-ol was purified by recrystallization. Because 2-methyl-3-butin-2-ol was used, a stronger base was needed for deprotection of the triple bond. Hence, potassium hydroxide was used as a base, which resulted thereby not only in deprotection of the triple bond but also in cleavage of the ester bond yielding potassium 4-ethynylbenzoate, similar to the reaction described in the literature.[33] To obtain the activated pentafluorophenyl ester, the potassium carboxylate was first converted into the acid chloride by reaction with thionyl chloride and a very small amount of DMF as a catalyst to yield 4-ethynyl benzoyl chloride.[33] Finally, an esterification of the acid chloride with pentafluorophenol (PFP) in the presence of NEt_3 as base was performed. The resulting monomer **M4** was purified by column chromatography and characterized by FTIR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectroscopy, mass spectrometry and elemental analysis. Similar to vinylic activated ester monomers,[34] **M4** exhibited an excellent solubility in many organic solvents such as chloroform, dichloromethane, toluene, THF, diethyl ether and benzene. One of the synthetic advantages of **M4** is that ^{19}F NMR spectroscopy can easily be applied, which enables a direct analysis. The ^{19}F NMR spectrum of **M4** showed three signals at −152.8 ppm, −158.0 ppm and −162.5 ppm that can be assigned to the PFP ester (see Supporting Information). Those signals were clearly shifted compared to the signals obtained for free pentafluorophenol, which appear at −163.9 ppm, −164.2 ppm and −168.7 ppm, respectively, thereby indicating the successful synthesis and purification of **M4**.

Polymerization

Next, the polymerization and copolymerization of the four acetylenic monomers **M1** to **M4** was investigated. Following the reports of the group of Tang, we investigated the polymerization of acetylenic monomers utilizing a tungsten catalyst.[24] The polymerization of the monomers was carried out in solution of dry toluene at 80 °C for 24 hours using the metathesis catalyst tungsten hexachloride (WCl_6) with tetraphenyltin ($SnPh_4$) as a cocatalyst, as shown in Scheme 2. The catalyst is very sensitive to moisture as well as oxygen and therefore all polymerizations had to be carried out under inert gas atmosphere. The results of the polymerizations are summarized in Table 1. After the polymerization, all polymers remained soluble in solution and could be isolated by precipitation into methanol. While the polymerization of **M1** and **M2** could be conducted in good yields of almost up to 80%, polymerization of **M3** resulted in polymer **P3** only in moderate yields of slightly more than 20%. The polymerization of **M4** resulted in the activated ester polymer **P4** with acceptable yields of around 50%. Polymers **P1** to **P3** had molecular weights between 12.000 and 15.000 g/mol with molecular weight distributions varying between 1.3 and 1.4. In contrast, polymer **P4** resulted in a broader molecular weight distribution ($M_w/M_n < 2.1$), likely due to the presence of the activated ester.

All polymers were characterized by NMR spectroscopy. Exemplary the ^{1}H NMR spectra of **M2** is shown in the Supporting Information and showed peaks of the proton of the triple bound at 3.21 ppm, of the methylester at 3.90 ppm and of the protons of the phenyl ring at 7.53 and 7.97 ppm. In the ^{1}H NMR spectra of **P2** (see Supporting Information) the signal related to the methyl ester is remaining at 3.89 but the signal of the triple bond completely vanished. The signals of the aromatic and vinylic protons appeared as overlaid broad peaks at 5–8 ppm. The ^{1}H NMR -spectra of all the prepared polymers show only one broad peak at the range of 5–8

TABLE 1 Polymerization of Substituted Phenylacetylenes **M1–M4**[a]

		Polymer		
Polymer	Monomer (mol %)	Yield (%)[b]	M_n (g/mol)[c]	M_w/M_n[c]
P1	**M1**[d]	76	12,300	1.31
P2	**M2**[d]	79	15,100	1.42
P3	**M3**[d]	21	13,700	1.41
P4	**M4**[d]	49	10,600	2.09
P1/4	**M1/M4 (1/1)**[e]	77	27,400	1.54
P2/4a	**M2/M4 (9/1)**[e]	27	19,030	1.45
P2/4b	**M2/M4 (7/3)**[e]	75	19,330	1.47
P2/4c	**M2/M4 (5/5)**[e]	74	26,760	1.87
P2/4d	**M2/M4 (3/7)**[e]	76	20,030	1.35
P24e	**M2/M4 (9/1)**[e]	72	12,790	1.39

[a] In toluene, 80 °C, 24 h.
[b] After precipitation in MeOH.
[c] Determination by GPC in THF on the basis of polystyrene calibration.
[d] $[M]_0/[W] = 100$.
[e] $[M]_0/W = 50$.

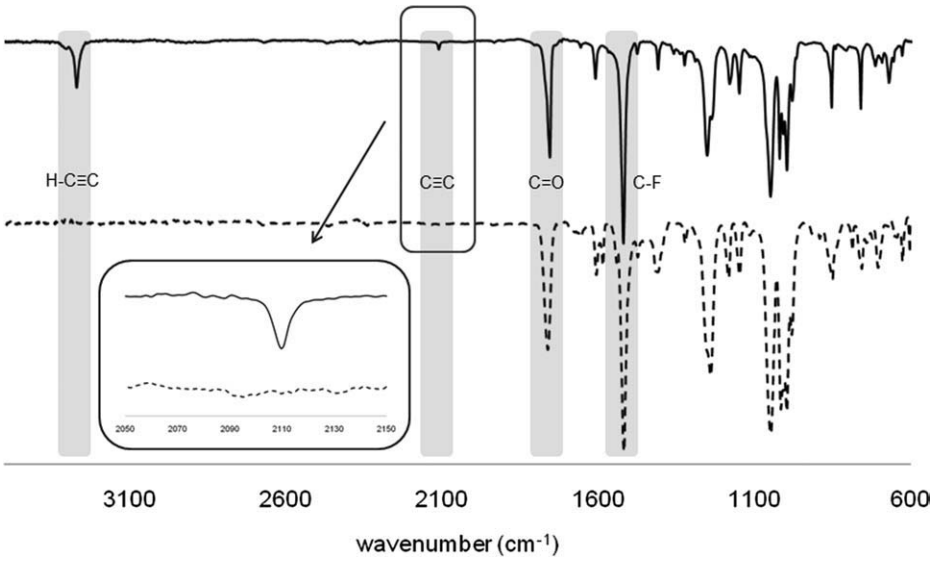


FIGURE 1 FTIR spectra of **M4** (continuous line) and **P4** (dashed line) showing the characteristic bands of the active ester in both spectra and the disappearance of the characteristic band of the triple bond in the polymer in comparison to the monomer.

ppm related to the aromatic and vinylic protons of the polymer backbone, indicating that the polymers are not stereo regular in the main chain configuration.[35]

Besides the homopolymers **P1**–**P4**, also copolymers were synthesized. Due to the low yields of **P3**, only the synthesis of copolymers of **M1** and **M2** with **M4** was investigated. The copolymers could be obtained in good yields of around 75% and as shown in Table 1, the copolymers were obtained with reasonable molecular weights and moderate molecular weight distributions ($M_w/M_n < 1.9$). All the synthesized homo- and copolymers showed an excellent solubility in many organic solvents such as chloroform, dichloromethane, THF and toluene and were characterized by FTIR, ^{1}H NMR spectroscopy and gel permeation chromatography (GPC).

The motivation of the present study is the preparation of reactive polyacetylenes that can be utilized in a postpolymerization functionalization. As such, **P4** and its copolymers were analyzed in respect to their reactive pentafluorophenyl ester group. The FTIR spectra of **M4** and **P4** are shown in Figure 1. Both spectra show the characteristic band of the C=O bond of the PFP ester at 1760 cm^{-1} and the band of the aromatic pentafluorophenyl group at 1520 cm^{-1}. The characteristic bands of the C≡C bond at 2100 cm^{-1} and of the H—C≡ bond at 3270 cm^{-1} are clearly observed in the FT IR spectrum of **M4**. After polymerization the respective bands of the acteylenic group at 2100 cm^{-1} and 3270 cm^{-1} were not present in the FT IR spectrum of **P4** anymore, indicating that the triple bound was indeed consumed during the polymerization. Additionally the homopolymer and the copolymers containing the activated ester moiety **P4**, **P1/4** and **P2/4c** were analyzed by ^{19}F NMR spectroscopy. Figure 2 compares the ^{19}F NMR spectrum of **P4** with the ^{19}F NMR spectra of the polymers from vinylic PFP based monomers poly(pentafluorophenyl acrylate) (PPFPA) and poly(pentafluorophenyl 4-vinylbenzoate) (PPFPVB). All spectra show three broad signals with a 2:1:2 integral ratio and these signals correspond to signals expected for the three chemically

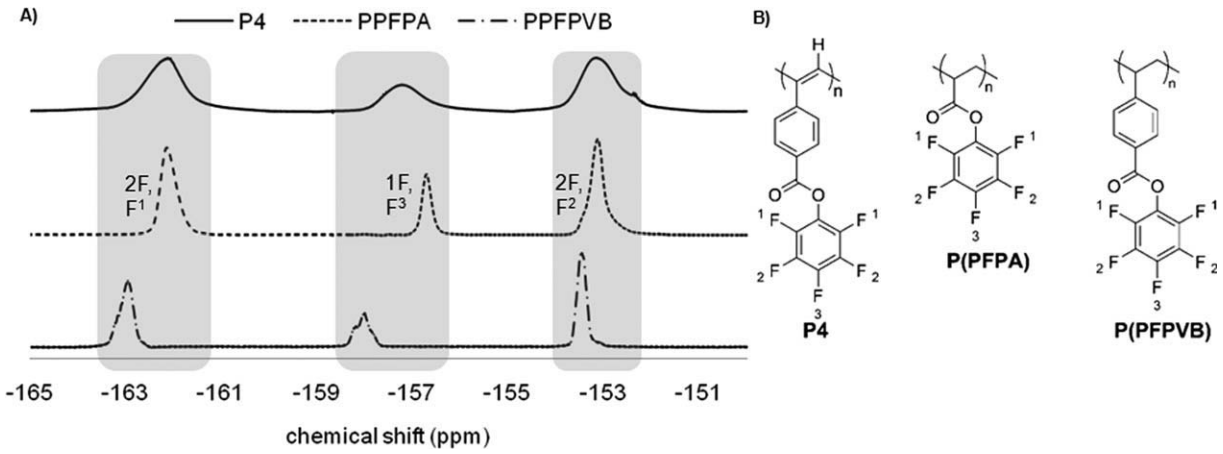


FIGURE 2 ^{19}F NMR spectra of **P4**, poly(pentafluorphenolacrylate) and poly(pentafluorphenol 4-vinylbenzoate) (A) and the corresponding chemical formulas (B).

TABLE 2 Ratio of Copolymers P2/4a-e

Polymer	Monomer (mol %)	Ratio[a] (mol %)	M(M2)	M(M4)	m(M2)	m(M4)
P2/4a	**M2/M4 (90/10)**	**M2/M4 (88/12)**	0.90	0.10	0.88	0.12
P2/4b	**M2/M4 (70/30)**	**M2/M4 (69/31)**	0.70	0.30	0.69	0.31
P2/4c	**M2/M4 (50/50)**	**M2/M4 (46/54)**	0.50	0.50	0.46	0.54
P2/4d	**M2/M4 (30/70)**	**M2/M4 (31/69)**	0.30	0.70	0.31	0.69
P2/4e	**M2/M4 (10/90)**	**M2/M4 (13/87)**	0.10	0.90	0.13	0.87

[a] Determination by integration of the carbonyl band of the active ester and the methyl ester in the IR spectra.

different fluorine atoms for the PFP ester. Noteworthy, no monomeric or free pentafluorophenol signals could be detected.

The copolymerization behavior of **M2** with **M4** was analyzed a bit more in detail. The copolymerization of **M2** with **M4** was studied for molar fractions of **M4** [**M**(**M4**)] ranging from 0.9 to 0.1 in the feed. The molar fractions of **M4** incorporated in the polymer [**m**(**M4**)] were obtained by IR-spectroscopy analysis. In the IR-spectra the ratio of the integrated values of the two C=O bands of the polymers, the PFP-ester carbonyl band at 1760 cm^{-1} (indicative for the fraction of **M4**) and the methyl ester carbonyl band at 1700 cm^{-1} (indicative for the fraction of **M2**), were compared. The calculated molar fractions of the monomer feed and incorporated molar fractions in the polymers are shown in Table 2 and the plot of the mole fraction of **M4** in feed [**M**(**M4**)] versus that of **M4** in the copolymer [**m**(**M4**)] is shown in the Supporting Information (Fig. S5). The monomer reactivity ratios for the copolymerization of **M2** with **M4** were further determined from the monomer feed ratios and the copolymer composition, following the Fineman-Ross method.[36] According to the Fineman-Ross method, the monomer reactivity ratios can be obtained as follows:

$$(f-1)/F = -r_2(f/F^2) + r_1 \quad (1)$$

with

$$F = \mathrm{M}(\mathbf{M2})/\mathrm{M}(\mathbf{M4}) \quad \text{and} \quad f = \mathrm{m}(\mathbf{M2})/\mathrm{m}(\mathbf{M4}) \quad (2)$$

with r_1 and r_2 being the values corresponding to monomer reactivity ratios, and F is the monomer molar composition in the feed and f is the copolymer molar composition, respectively. Plotting (f-1/F) as ordinate and f/F^2 as abscissa results in a straight line whose slope is minus r_2 and whose intercept is r_1. The corresponding graphical plot and the linear fit are given in the Supporting Information (Fig. S5). The values of $r_1 = 0.67$ and $r_2 = 0.69$ are smaller than 1, which indicates that the system copolymerizes statistically. Also the copolymer composition in dependence of the time was determined. For that a copolymerization of **M2** and **M4** with molar fraction of the feed 0.60 [**M**(**M2**)] and 0.40 [**M**(**M4**)] was conducted and samples of the polymerization solution after certain times were taken, the polymers were isolated by precipitation in MeOH and the composition of the copolymers were calculated by IR-spectroscopy by comparing the ratio of the integrated values of the two C=O bands of the two respective repeating units. The results are summarized in Table 3. The first sample was taken directly after injection of the monomer solution into the catalyst solution and the sample contained only a very small amount of polymer with very low molecular weight. Thus no polymer could be precipitated in MeOH from this sample. From all samples taken thereafter the composition of the copolymers remained constant with polymerization time, see graphical plot of the molar fraction of **M4** versus polymerization time in the Supporting Information (Fig. S5). This result also indicates a statistical copolymerization behavior of **M2** and **M4**.

To obtain polymer samples with a narrower polydispersity, a fractionated precipitation of the conjugated polymers was realized. The results of the fractionated precipitation of **P1** and **P4** are presented in Table 4 and the respective GPC curves of the fractions of **P4** are shown in Figure 3. As a result, polymer fractions with a narrow M_w/M_n were obtained, with the major fraction of 43% having a M_n = 13,000 g/mol and a $M_w/M_n = 1.29$.

Polymer Analogous Reaction

The PFP ester based polymer **P4** obtained by metathesis polymerization was converted into functional polymers by a polymer analogous reaction with various amines according to Scheme 3. For this reaction the polymer had been

TABLE 3 Copolymer Composition in Dependence of the Polymerization Time of a Molar Fraction of the Feed of **M**(**M2**) = 0.60 and **M**(**M4**) = 0.40

Sample	Time (min)	M(M2)[a]	M(M4)[a]
1	0	**0.61**	**0.39**
2	30	**0.60**	**0.40**
3	60	**0.57**	**0.43**
4	180	**0.56**	**0.44**
5	420	**0.60**	**0.30**
6	1200	**0.61**	**0.39**

[a] Determination by integration of the carbonyl band of the active ester and the methyl ester in the IR spectra.

TABLE 4 Fractionated Precipitation of the Polymers **P1** and **P4**[a]

	Fraction	Amount (mg)	M_n (g/mol)[b]	M_w/M_n[b]
Polymer **P1**	**P1a**	35	14,700	1.23
	P1b	9	6,800	1.18
	P1c	3	3,800	1.15
	P1d	3	2,400	1,11
	P1e[c]	8	600	1.80
	P1a	35	14,700	1.23
Polymer **P4**	**P4a**	18	13,000	1.29
	P4b	13	10,100	1.13
	P4c	4	7,100	1.09
	P4d	3	4,600	1.14
	P4e[c]	4	3,100	1.13

[a] Precipitation from THF in MeOH.
[b] Determination by GPC in THF on the basis of polystyrene calibration.
[c] MeOH soluble part.

dissolved in chloroform and a slight excess of amine (1.1 eq.) and NEt_3 (1.05 eq.) as an auxiliary base were added. The resulting polymers were isolated by precipitation into a large amount of cyclohexane or *n*-hexane and the dried polymer samples were analyzed by FTIR, ^{1}H NMR and GPC. The reaction conditions and the results are listed in Table 5. As expected, the aliphatic amines showed a higher reactivity compared to the aromatic amines, which is due to the fact that aromatic amines are poorer nucleophiles with regard to aliphatic amines. For aliphatic primary and secondary amines a quantitative conversion was achieved after stirring for 12 h at 25 °C, while aromatic amines showed no complete conversion under the same reaction conditions. However, after increasing the reaction time and temperature to stirring for 6d at 45 °C, a quantitative conversion of **P4** could even be achieved with aromatic amines. Only the reaction with 4-nitroaniline proceeded not quantitatively (conversion 86%) because of the deactivating effect of the para-substituted nitro group on the nucleophilicity of the amine. As an example the FTIR spectra and the GPC traces of **P4** before conversion and the resulting polymer after conversion with hexylamine **P4N1** are shown in Figure 4. Because in a polymer analogous reaction with hexylamine the heavier PFP unit is converted to a hexylamide unit the molecular weight of the polymer should decrease. As such, in the GPC a shift of the elution volume to higher values, equivalent to smaller molecular weights, was observed. Also the polydispersity of the polymer after conversion with hexylamine decreases, indicated by the smaller elution curve of **P4N1** compared to **P4**. This is the case because of the different solubility of the polymer before and after conversion with hexylamine in the precipitation solvent. **P4** was precipitated in MeOH and it is likely that a small amount of the polymer with low molecular weight remained in solution, thereby resulting in a narrow molecular weight distribution for the precipitated fraction. **P4N1** possess a different polarity compared to **P4** and therefore it was necessary to precipitate the polymer into cyclohexane. But also in cyclohexane only the polymer fraction with a high molecular weight precipitated and a larger amount of the polymer remained in solution compared to **P4**. Clearly, in the FTIR spectra a complete conversion could be concluded. The characteristic bands of the PFP ester at 1760 cm^{-1} of the C=O bond and at 1520 cm^{-1} of the aromatic C—F bond completely vanished after the reaction with hexylamine and in exchange the amide band at 1640 cm^{-1} and 1540 cm^{-1} could be detected. Further, the N—H band at 3300 cm^{-1} appeared, indicating the formation of a primary amide group, as expected for the reaction with the primary amine hexylamine. When comparing the reaction of different polymers exhibiting a pentafluorophenyl activated ester (**P4**, poly(pentafluorophenyl acrylate) (PPFPA) and poly(pentafluorophenyl 4-vinyl benzoate) (PPFPVB) with aromatic amines only **P4** and PPFPVB showed a sufficient reactivity, resulting in a quantitative reaction. Noteworthy, PPFPA showed only 14% conversion with aniline,[27] while **P4** and PPFPVB[34] reacted quantitative with aniline. This can be

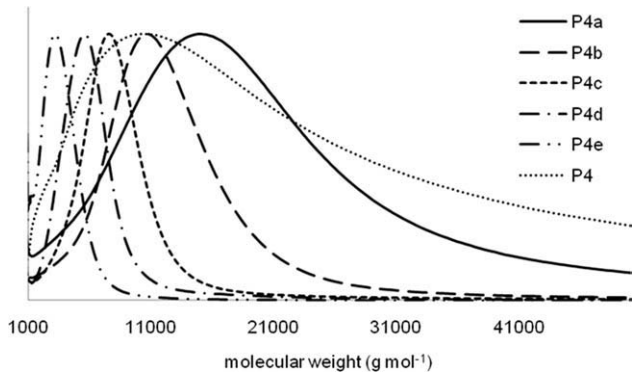
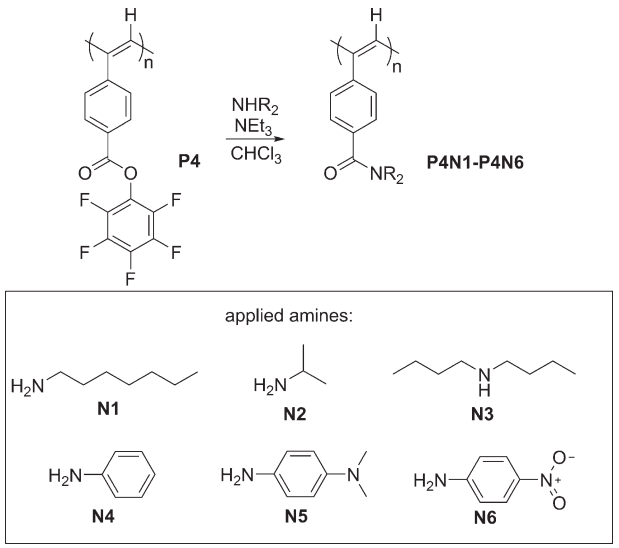


FIGURE 3 Gel permeation chromatograms of the fractionated precipitation of **P4**.



SCHEME 3 Polymer analogous reaction of poly(phenylacetylene) functionalized with active ester **P4** with amines and the chemical structures of the applied amines **N1–N6**.

TABLE 5 Polymer Analogous Reaction of **P4** with Amines **N1–N6**[a]

Polymer	Amine	Time	Temperature (°C)	Conversion (%)[b]	Polymer M_n (g/mol)[c]	Polymer M_w/M_n[c]
P4N1	**N1**	12 h	20	100	6,200	1.39
P4N2	**N2**	12 h	20	100	6,200	1.35
P4N3	**N3**	12 h	20	100	6,600	1.69
P4N4a	**N4**	12 h	20	0	–	–
P4N4b	**N4**	6 d	20	24	–	–
P4N4c	**N4**	6 d	45	100	5,200	1.91
P4N5	**N5**	6 d	45	100	5,200	1.37
P4N6	**N6**	6 d	45	86	6,500	1.62

[a] In $CHCl_3$ with NEt_3 as base.
[b] Determination by comparison of the characteristic band in the IR spectra of the active ester moiety in **P4** and **P4N1-6**.
[c] Determination by GPC in THF on the basis of polystyrene calibration.

attributed to the increased reactivity of the benzoic acid based pentafluorophenyl ester, making these polymers superior to the PPFPA.

Of course, the PFP ester unit in the copolymers can also react selectively with amines. Therefore **P1/4** and **P2/4c** were converted with hexylamine and the results of the polymer analogous reaction are presented in Table 6. Exemplary, the FTIR spectra of **P2/4c** before conversion with hexylamine and the resulting polymer after conversion with hexylamine (**P2/4cN1)** are shown in Figure 5. The characteristic bands of the PFP ester at 1760 cm^{-1} of the C=O bond and at 1520 cm^{-1} of the aromatic C—F bond completely vanished after the reaction with hexylamine, but the C=O band of the methyl ester at 1720 cm^{-1} is detected in both spectra. Furthermore, the amide band at 1640 cm^{-1} and 1540 $cm^{-1}$and the N—H band at 3300 cm^{-1} can be detected in **P2/4cN1**, indicating the successful and quantitative conversion of the activated ester into the amide.

An equimolar feed ratio of both monomers was used for the copolymer synthesis of **P1/4** and **P2/4c**. The exact incorporation ratio was measured by ^1H NMR spectroscopy of the copolymers after the conversion with hexylamine by comparing the integrals of the aliphatic protons of the hexylamine moiety, which should direct correspond to the previous PFP ester moieties, and the aromatic protons of the polymer backbone (see Supporting Information). The results are summarized in Table 6. As a result, it could be calculated that both monomers were incorporated into the copolymers with almost the same probabilities of about 50%, thereby confirming the statistical copolymerization behavior.

Polymer analogous reaction of **P4** or its copolymers led easily to functional conjugated polymers. This synthetic route provides several benefits. For example, polymers, which cannot be prepared by direct polymerization of the respective monomers, may be obtained by attachment of appropriate functional groups to the conjugated backbone if they feature an amine group. As a consequence polymers with new functionalities can be synthesized from a reactive precursor polyacetylene. Full exploration of these synthetic possibilities is beyond the scope of the present study, however, a selected number of experiments are provided to indicate exemplary

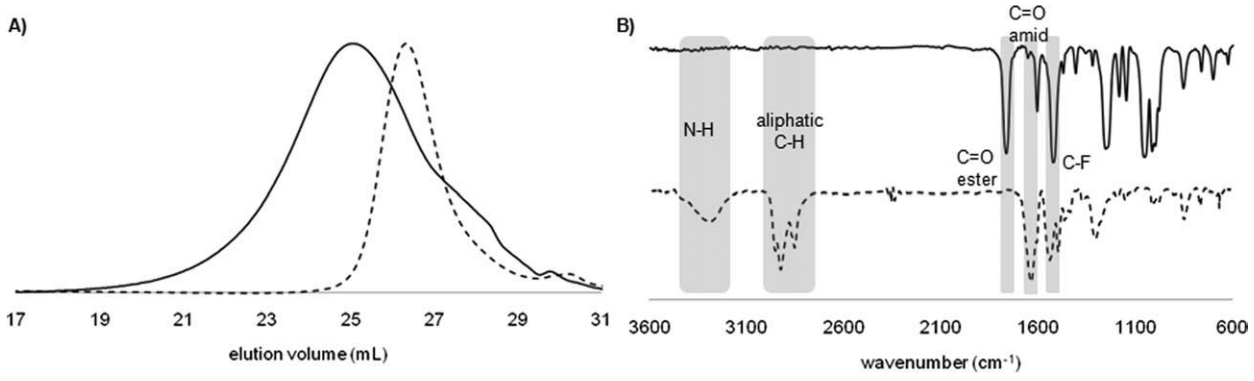


FIGURE 4 Gel permeation chromatograms (A) showing the shift of the molecular weight and FTIR spectra (B) showing the disappearance of the characteristic active ester bands after conversion with amines (B) of **P4** (continuous line) and **P4N1** (dashed line).

TABLE 6 Polymer Analogous Reaction of Copolymers **P1/4** and **P2/4c** with Hexylamine **N1**[a]

				Polymer	
Polymer	Monomer (mol %)	Ratio (mol %)[b]	Conversion (%)[c]	M_n (g/mol)[d]	M_w/M_n[d]
P1/4N1	**M1/M4 (50:50)**	**M1/M4 (45:55)**	100	19,300	1.50
P2/4cN1	**M2/M4 (50:50)**	**M2/M4 (49:51)**	100	14,400	1.40

[a] In $CHCl_3$ with NEt_3 as base, 12 h, 20 °C.
[b] Determination by ^1H NMR spectroscopy.
[c] Determination by comparison of the characteristic band in the IR spectra of the active ester moiety in **P1/4**, **P2/4c** and **P1/4N1**, **P2/4cN1**.
[d] Determination by GPC in THF on the basis of polystyrene calibration.

the potential applications, which may be realized utilizing the developed polyacetylenes featuring PFP activated ester moieties.

Ultraviolet-Visible (UV-Vis) Spectra

Essentially, most properties of polyacetylenes can be related to their conjugated polymer backbone. As such, in a first instance the investigation of the absorption properties of PFP based conjugated polymers and its derivates after conversion with amines was worthwhile to be conducted. Figure 6 summaries the normalized UV-Vis spectra of **P4** before and after conversion with different amines. All UV-Vis spectra were recorded in chloroform at 25 °C. The spectra of **P4** showed a shoulder between 550 nm and 350 nm that can be attributed to the conjugated backbone of the polymer in agreement with the literature.[37,38] After the polymer analogous reaction of **P4** with amines the ester bond is replaced by an amide bond. It is known from the literature that the amide bond possess a partial character of a double bond and as a result the conjugated system of the polymer backbone should extend above the amide bond. This effect was recently shown by Kilbinger and coworkers for conjugated thiophene amide polymers.[39] Thus, depending on the electronic nature of the amine used for the reaction with **P4**, an influence on the conjugation of the backbone of the resulting polymer can be expected.

When **P4** was converted with aromatic amines, no dramatic changes in the UV-Vis spectra could be observed. The conversion of **P4** with aniline, an unsubstituted aromatic amine, yielding **P4N4c**, did not lead to considerable changes in the UV-Vis spectrum. Also the conversion of **P4** with the substituted aromatic amines *p*-nitro aniline (**N6**) containing electron withdrawing or *N′*,*N′*-dimethyl-*p*-phenylenediamine (**N5**) containing electron donating groups resulted in no significant variation in the UV-Vis spectra of the conjugated backbone. Only after conversion of **P4** with *p*-nitro aniline (**N6**) a new strong peak in the UV-Vis spectra at 350 nm appeared that can be attributed to the nitro group, as can been seen in Figure 6. But after conversion with aliphatic amines the absorption of the conjugated backbone was shifted to lower wavelength ($\Delta\lambda > -50$ nm). Exemplary the UV-Vis spectra of **P4N1** and **P4N3** are shown in Figure 6. These promising results clearly demonstrate the influence of the side group functionality on the absorption properties of the polymer backbone and hence its electronic properties. These results are in agreement with the generally accepted theory that the side groups of polyacetylenes induce a better solubility but at the same time perturb the conformation of the backbone.[40] As hardly no effect on the UV-Vis spectra of the polymers after conversion with aromatic amines was observed, it may be hypothesized that their steric requirements are similar to the pentafluorophenyl substituent. Only the polymers obtained after reaction with aliphatic amines showed a change in the UV-Vis spectra, indicating a variation in the steric requirements of the side groups thereby influencing the backbone conformation. Obviously more amines should

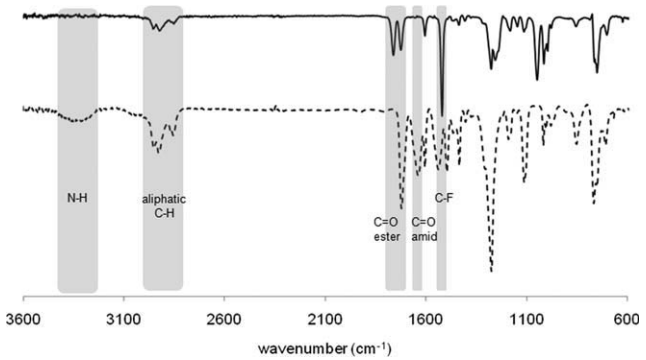


FIGURE 5 FTIR spectra of **P2/4c** (continuous line) and **P2/4cN1** (dashed line) showing the selective conversion of the active ester moiety in comparison to the methyl ester.

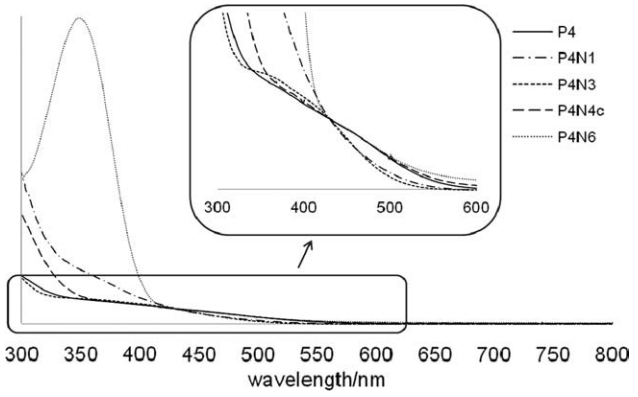


FIGURE 6 UV-Vis spectra of **P4** before and after conversion with amines in chloroform at 25 °C.

be tested to fully understand the influence of side groups onto the conjugated polymer backbone. However, it can be concluded that the polymer analogous reactions utilizing polyacetylenenes with activated ester side groups represent an ideal platform to investigate these structure-property relationships. Because a polymer analogous reaction does not alter the degree of polymerization, the influence of only sterical and chemical changes of the side groups can be studied. The respective experiments along with a detailed characterization of the optical and electronic properties are in progress and the results will be published in future.

CONCLUSIONS

In summary, three ester monomers derived from 4-ethynylbenzoic acid had been synthesized. One of them was an activated ester based monomer. Further, the polymerization of phenyalcetylene and these monomers yielding the respective polymers **P1** to **P4** was investigated. With a metathesis catalyst not only the homopolymers but also the copolymers **P1/4** and **P2/4a** to **P2/4e** of the active ester based monomer **M4** could be obtained. All polymers were soluble in common organic solvents. Polymer analogous reaction of polymers **P4**, **P1/4** and **P2/4c** with various amines have been investigated and it was found that these polymers exhibit a high reactivity toward amines. Even the reaction with aromatic amines occurred quantitatively. Hence, poly(pentafluorophenyl 4-ethynylbenzoate) **P4** is considered as a new valuable reactive precursor polymer for the synthesis of multifunctional polymers as it combines a superb solubility and reactivity. Moreover the UV-Vis spectra of **P4** before and after conversion with amines were measured. By reaction of **P4** with aromatic amines with either electron withdrawing or donating groups, the UV-Vis spectra of the polymers changed.

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