Synthesis and properties of novel poly(*p*-xylylene)s with aliphatic substituents

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Abstract: Poly(*p*-xylylene)s (PPX) with aliphatic substituents at the alpha position were synthesized by chemical vapor deposition (CVD) via vapor phase pyrolysis of α -chloro-1,4-xylenes, or by base-induced dehydrohalogenation of α -chloro-1,4-xylenes (Gilch route). These PPXs are soluble under ambient conditions in organic solvents. The glass transition temperature of the *tert*-butyl substituted PPX is remarkably high. Good thermal stability under nitrogen was observed for the trifluoromethyl substituted PPX. A functionalized compound suitable for polymer analogous reactions is the norbornenyl substituted PPX.

Introduction

PPX (trade name parylene N) represents an important class of aromatic polyhydrocarbons, which gains increasing significance due to many promising properties for a variety of applications. PPXs can be synthesized by CVD without action of any solvent or by solution based chemistry involving a variety of different C-C bond forming reactions [1,2]. Efficient CVD routes to PPXs are based upon vapor phase pyrolysis of [2.2]paracyclophanes [3] or diesters of α,α' -dihydroxy-1,4-xylene [4], α,α' -dibromo-1,4-xylenes in the presence of Zn/Cu [5], or α -bromo-1,4-xylenes [6] at reduced pressure. In a recent contribution, Lahann et al. expanded the vapor phase pyrolysis of paracyclophanes to functionalized PPXs [7,8]. The so-called Gilch route yields high molecular weight PPXs by solution-based chemistry if the resulting PPX derivatives are organosoluble under ambient conditions. The choice of the synthetic route for realization of a particular PPX derivative depends on several key issues, including synthetic access to starting materials which has prevented up to now the realization of many PPX derivatives and with that the exploitation of the full potential of this promising class of polymers. It should be noted here that the term starting material as precursor has been coined instead of monomers since the actual monomers, quinodimethanes, are formed *in situ* from the starting material, independently from the nature of the polyreaction. It should also be stated that it is not clear yet whether the polyreaction of quinodimethanes is a true polymerization or a polyrecombination reaction. As long as this is the case, it is most accurate to refer to a polyreaction.

To the best of our knowledge, PPXs with alkyl substituents in the alpha position are only known for methyl substituted PPXs which were obtained by reaction of *p*-diiso-

propylbenzene with peroxides [9]. Therefore we report here on the synthesis of PPXs with aliphatic substituents at the α -position either by CVD or by the Gilch route. These new PPX derivatives offer improved features or novel perspectives.

Experimental part

Materials

All reactions were carried under inert gas atmosphere. All solvents were dried and distilled prior to use by standard technologies.

Measurements

IR spectroscopy was performed using a Perkin Elmer FT-IR 1600 (KBr pellets). ^1H NMR spectra (300 MHz), ^{13}C NMR spectra (75 MHz) and COSY spectra were recorded on a Bruker AC 300. The COSY experiments were performed in the conventional manner using 180 time increments, each of 1K points, over a 8.414 ppm spectral window. The f1 time domain data were zero filled to a 1K x 0.256K matrix, and both directions were multiplied by an unshifted sine-bell function before Fourier transformation. ^{19}F NMR spectra (188 MHz) were recorded on a Bruker AC 200. Differential scanning calorimetry (DSC) measurements were performed by means of a Mettler DSC 20 in standard aluminium pans with a heating rate of 10 K/min. Gel permeation chromatography (GPC) was performed with tetrahydrofuran (THF) as solvent and a set of 5 μm mixed bead columns (PSS) and a Viscotek detector. GPC molecular weight analysis was performed by universal calibration versus polystyrene standards. Intrinsic viscosity ($[\eta]$) was obtained from GPC analysis using a viscodetector and universal calibration.

Synthesis of 2,2,2-trifluoro-1-(4-methylphenyl)ethan-1-one, **3**

A three-necked flask equipped with stirring bar, reflux condenser and a dropping funnel was charged with 6.07 g of Mg (250 mmol) and 30 ml of THF. 42.75 g of **1** (250 mmol) was dissolved in 80 ml of THF and added dropwise to the Mg slurry. The reaction was stirred and heated to reflux for another hour after completion of addition. After cooling of the reaction mixture to 20°C, 11.04 g of trifluoroacetic acid (100 mmol) dissolved in 90 ml of THF was added dropwise. After completion of addition, the reaction mixture was heated to reflux for 2 h. The reaction mixture was quenched after cooling by addition of 200 ml of saturated NH_4Cl solution. The mixture was extracted with diethyl ether and the combined organic extracts were dried over Na_2SO_4 . **3** was isolated by fractionated vacuum distillation; b.p. 35 - 40°C, 1 mbar. Yield 10.34 g (55 mmol), 55% (based on trifluoroacetic acid).

IR (KBr, cm^{-1}): 3044 m; 2928 m; 1713 s; 1607 s; 1568 w; 1514 w; 1338 m; 1177 s; 939 s; 835 s; 752 s.

^1H NMR (CDCl_3 , δ in ppm): 2.44 (s, 3 H, $-\text{C}(1)\text{H}_3$); 7.33 (d, $J = 7.8$ Hz, 2 H, $\text{Ar}(\text{C}3)\text{H}$); 7.96 (d, $J = 7.8$ Hz, 2 H, $\text{Ar}(\text{C}4)\text{H}$).

^{13}C NMR (CDCl_3 , δ in ppm): 21.5 ($-\text{CH}_3$); 116.8 (q, $^1J = 290$ Hz, $-\text{CF}_3$); 127.4 (ArC); 129.7 (ArC); 130.1 (ArC); 147.0 (ArC); 179.9 (q, $^2J = 35$ Hz, $-\text{C}(\text{O})-\text{CF}_3$).

Synthesis of 2,2-dimethyl-1-(4-methylphenyl)propan-1-ol, **4a**

A three-necked flask equipped with stirring bar, reflux condenser and a dropping funnel was charged with 2.79 g of Mg (115 mmol) and 30 ml of THF. 18.80 g of **1** (110 mmol) was dissolved in 80 ml of THF and added dropwise to the Mg slurry. After completion of addition, the reaction was stirred and heated to reflux for another hour. After cooling of the reaction mixture to 20°C, 7.90 g of **2a** (92 mmol) dissolved in 90 ml of THF was added dropwise. After completion of addition, the reaction mixture was heated to reflux for 2 h. After cooling, the reaction mixture was quenched by addition of 200 ml of saturated NH₄Cl solution. The mixture was extracted with diethyl ether and the combined organic extracts were dried over Na₂SO₄. **4a** was isolated by fractionated vacuum distillation; b.p. 80 - 85°C, 1 mbar. Yield 13.30 g (75 mmol), 81% (based on **2a**).

IR (KBr, cm⁻¹): 3437 m; 3020 w; 2953 m; 2868 m; 1911 w; 1614 w; 1514 m; 1479 s; 1362 s; 1179 m; 1051 s; 1007 s; 820 m; 760 s.

¹H NMR (CDCl₃, δ in ppm): 0.88 (s, 9 H, -C(C(7)H₃)₃); 2.31 (s, 3 H, -C(1)H₃); 4.27 (s, 1 H, -OH); 7.07 (d, *J* = 8 Hz, 2 H, Ar(C3)H); 7.17 (d, *J* = 8.1 Hz, 2 H, Ar(C4)H).

¹³C NMR (CDCl₃, δ in ppm): 21.1 (-C(CH₃)); 25.9 (-C(CH₃)); 35.5 (-CH₃); 82.2 (-CH(OH)-); 127.5 (ArC); 128.2 (ArC); 136.7 (ArC); 139.3 (ArC).

Synthesis of bicyclo[2.2.1]hept-5-en-2-yl(4-methylphenyl)methan-1-ol, **4b**

The synthesis of **4b** was performed as described for **4a**; b.p. 135°C, 0.8 mbar. Yield 22.00 g (102 mmol), 93% (based on **2b**).

IR (KBr, cm⁻¹): 3366 s; 3055 s; 2960 s; 2868 s; 1902 w; 1614 w; 1513 s; 1446 m; 1335 s; 1069 m; 1015 s; 884 s; 718 s.

¹H NMR (CDCl₃, δ in ppm): 0.4 - 3.2 (m, 11 H, aliph. C(1,7,8,9,12,13)H); 3.7 - 4.2 (two t (diastereoisomers), 1H, C(6)H); 5.8 - 6.1 (m, 2 H, vinyl. C(10,11)H); 6.9 - 7.2 (m, 4 H, Ar(3,4)H).

¹³C NMR (CDCl₃, δ in ppm): (aliph. C:) 21.1; 29.3; 30.0; 30.2; 30.8; 41.8; 42.1; 42.2; 42.8; 43.6; 44.2; 44.3; 44.6; 45.1; 45.4; 46.5; 46.9; 47.8; 49.2; 49.6; (-CH(OH)-): 78.1; 78.7; 79.0; 79.5; (ArC:) 126.3; 126.5; 126.9; 129.0; 129.0; 132.3; 132.7; 137.1; 137.7; 140.2; 141.5.

Synthesis of 2,2,2-trifluoro-1-(4-methylphenyl)ethan-1-ol, **4c**

To a stirred solution of **3** (9.40 g; 50 mmol) in 50 ml of THF was added in 3 portions 0.76 g (20 mmol; 1.6 eq) of sodium borohydride at room temperature. The solution was refluxed for 3 h, cooled to room temperature and stirred overnight. After adding carefully 20 ml of hydrochloric acid (2 M) the solution was poured into diethyl ether (100 ml). The aqueous phase was extracted twice with 50 ml of diethyl ether. The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and dried in vacuum. The resulting yellow oil was purified by fractionated distillation; b.p. 55°C, 1 mbar. Yield 7.60 g (40 mmol), 80% (based on **3**).

IR (KBr, cm⁻¹): 3381 s; 3035 m; 2928 m; 1710 w; 1615 w; 1516 m; 1269 m; 1171 s; 1128 s; 1071 m; 807 s; 696 m.

^1H NMR (CDCl_3 , δ in ppm): 2.25 (s, 3 H, $-\text{C}(1)\text{H}_3$); 2.90 (s, 1 H, $-\text{C}(6)\text{H}(\text{OH})-$); 4.78 (q, $^3J = 12$ Hz, 1 H, $-\text{C}(7)\text{H}-\text{CF}_3$); 7.08 (d, $^3J = 8.1$ Hz, 2 H, $\text{Ar}(\text{C}3)\text{H}$); 7.22 (d, $^3J = 8.0$ Hz, 2 H, $\text{Ar}(\text{C}4)\text{H}$).

^{13}C NMR (CDCl_3 , δ in ppm): 21.6 ($-\text{CH}_3$); 73.1 (q, $J = 32$ Hz; $-\text{CH}(\text{OH})-$); 124.7 (q, $^1J = 280$ Hz; $-\text{CF}_3$); 127.8 (ArC); 129.8 (ArC); 131.4 (ArC); 140.0 (ArC).

Synthesis of 4-(1-chloro-2,2-dimethylpropyl)-1-methylbenzene, **5a**

A flask with stirring bar, reflux condenser and dropping funnel was charged with 11.17 g of SOCl_2 (94 mmol; 1.3 eq), 0.1 ml of pyridine, and 100 ml of toluene. 12.84 g of **4a** (72 mmol) was dissolved in 80 ml of toluene and added dropwise at 20°C to the reaction mixture. After completion of the addition, the mixture was heated to reflux for 3 h. The reaction was cooled to 20°C and quenched by addition of 50 ml of water. 60 ml of *tert*-butyl methyl ether was added to the reaction mixture. This mixture was extracted with saturated aq. Na_2HCO_3 solution and finally with water. After separation of organic and aqueous phases, **5a** was isolated by fractionated vacuum distillation; b.p. $72 - 75^\circ\text{C}$, 1 mbar. Yield 10.55 g (54 mmol), 75% (based on **4a**).

IR (KBr, cm^{-1}): 3024 m; 2972 s; 2869 m; 1911 w; 1613 w; 1513 s; 1479 m; 1365 s; 1255 m; 1174 m; 1021 w; 820 s; 762 s.

^1H NMR (CDCl_3 , δ in ppm): 1.00 (s, 9 H, $-\text{C}(\text{C}(7)\text{H}_3)_3$); 2.32 (s, 3 H, $-\text{C}(1)\text{H}_3$); 4.68 (s, 1 H, $-\text{C}(6)\text{HCl}-$); 7.09 (d, $J = 8.1$ Hz, 2 H, $\text{Ar}(\text{C}3)\text{H}$); 7.22 (d, $J = 7.6$ Hz, 2 H, $\text{Ar}(\text{C}4)\text{H}$).

^{13}C NMR (CDCl_3 , δ in ppm): 21.2 ($-\text{C}(\text{CH}_3)_3$); 27.0 ($-\text{C}(\text{CH}_3)_3$); 74.6 ($-\text{CHCl}-$); 128.4 (ArC); 128.6 (ArC); 136.8 (ArC); 137.6 (ArC).

Synthesis of 4-(bicyclo[2.2.1]hept-5-en-2-ylchloromethyl)-1-methylbenzene, **5b**

The synthesis of **5b** was performed as described for **5a**. b.p. $108 - 110^\circ\text{C}$, 0.2 mbar. Yield 20.00 g (86 mmol), 86% (based on **4b**).

IR (KBr, cm^{-1}): 3054 s; 2972 s; 2869 s; 1901 w; 1614; w; 1513 w; 1446 m; 1336 m; 1255 w; 1020 w; 819 m; 719 m.

^1H NMR (CDCl_3 , δ in ppm): 0.3 - 3.2 (m, 10 H, aliph. $\text{C}(1,7,8,9,12,13)\text{H}$); 4.0 - 4.4 (m, 1 H, $-\text{C}(6)\text{HCl}-$); 5.6 - 6.1 (m, 2 H, vinyl. $\text{C}(10,11)\text{H}$); 6.9 - 7.1 (m, 4 H, $\text{Ar}(3,4)\text{H}$).

^{13}C NMR (CDCl_3 , δ in ppm): 21.0; 31.9; 32.4; 32.5; 33.4; 42.0; 42.3; 42.7; 42.9; 45.0; 45.1; 45.5; 45.7; 47.6; 48.3; 48.8; 49.1; 49.9; ($-\text{CHCl}-$) 67.8; 68.5; 69.4; 69.9; (ArC); 126.9; 127.1; 127.3; 127.5; 128.6; 128.9; 131.2; 132.3; 136.2; 136.5; 137.0; 137.5; 137.7; 137.8; 138.4; 138.6.

Synthesis of 4-(1-chloro-2,2,2-trifluoroethyl)-1-methylbenzene, **5c**

The synthesis of **5c** was performed as described for **5a**. m.p. $60 - 62^\circ\text{C}$. Yield 5.40 g (26 mmol), 74% (based on **5c**).

IR (KBr, cm^{-1}): 2977 s; 2869 s; 1495 s; 1548 m; 1174 m; 1069 s; 911 m; 732 m.

^1H NMR (CDCl_3 , δ in ppm): 2.36 (s; 3 H, $\text{C}(1)\underline{\text{H}}_3$); 5.07 (q, $^3J = 7.1$ Hz, 1 H, $-\text{C}(6)\underline{\text{H}}\text{Cl}-$); 7.20 (d, $^3J = 8.1$ Hz, 2 H, $\text{Ar}(\text{C}3/\text{C}4)\underline{\text{H}}$).

^{13}C NMR (CDCl_3 , δ in ppm): 21.1 ($-\underline{\text{C}}\text{H}_3$); 58.7 (q, $^3J = 37.5$ Hz, $-\underline{\text{C}}\text{HCl}-$), 122.2 (q, $^3J = 277$ Hz, $-\underline{\text{C}}\text{F}_3$); 128.6 ($\text{Ar}\underline{\text{C}}$); 129.5 ($\text{Ar}\underline{\text{C}}$); 129.8 (q, $J = 7$ Hz, $\text{Ar}\underline{\text{C}}$); 140.3 ($\text{Ar}\underline{\text{C}}$).

*Synthesis of poly(*t*-butyl-1,4-xylylene) (6a) by the Gilch route*

A flask equipped with stirring bar, reflux condenser and septum was charged with 6.73 g of potassium butanoate (60 mmol) suspended in 300 ml of THF. This mixture was degassed and heated to reflux. 5.90 g of **5a** dissolved in 25 ml of THF was injected rapidly to the reaction mixture. Heating was continued for 2 h. Pouring into methanol quenched the hot reaction mixture. The polymer was isolated by filtration and was purified by repeated washing with water and methanol. Further purification was accomplished through reprecipitation from chloroform followed by drying in vacuum at 60°C. Yield: 1.90 g (11.8 mmol), 40%.

$T_g = 177^\circ\text{C}$, $M_n = 27\,500$, $M_w = 56\,900$, $[\eta] = 0.26$ dl/g.

IR (KBr, cm^{-1}): 3044 m; 2951 s; 2968 m; 1512 m; 1477 m; 1393 m; 1365 s; 1226 w; 1102 w; 1020 w; 820 w; 571 m.

^1H NMR (CDCl_3 , δ in ppm): 0.87 (s, 9 H, $-\text{C}(\underline{\text{C}}\text{H}_3)_3$); 2.36 ppm (s, 1 H, $-\underline{\text{C}}\text{H}_2-$); 2.72 (s, 1 H, $-\underline{\text{C}}\text{H}_2-$); 3.17 (s, 1 H, $-\underline{\text{C}}\text{H}(\text{Ar})-$); 6.5 - 6.8 (m, 4 H, $\text{Ar}\underline{\text{H}}$).

^{13}C NMR (CDCl_3 , δ in ppm): 28.5 ($-\text{C}(\underline{\text{C}}\text{H}_3)_3$); 34.1 ($-\underline{\text{C}}\text{H}_2-\text{CHAr}-$); 36.3 ($-\underline{\text{C}}(\text{CH}_3)_3$); 58.6 ($-\underline{\text{C}}\text{H}(\text{Ar})-\text{CH}_2$); 127.7 ($\text{Ar}\underline{\text{C}}$); 129.0 ($\text{Ar}\underline{\text{C}}$); 139.4 ($\text{Ar}\underline{\text{C}}$).

Synthesis of poly(norbornenyl-1,4-xylylene) (6b) by the Gilch route

The polyreaction was performed as described for **6a**. Yield: 0.55 g (2.8 mmol), 28%.

$T_g = 136^\circ\text{C}$, $M_n = 17\,000$, $M_w = 50\,600$, $[\eta] = 0.17$ dl/g.

IR (KBr, cm^{-1}): 3051 w; 2932 s; 2861 s; 1654 w; 1510 s; 1443 m; 1417 w; 1337 m; 1252 w; 1103 m; 1019 w; 964 m; 833 w; 718 s.

^1H NMR (CDCl_3 , δ in ppm): 0.4 - 3.2 (m; 10 H; aliph. $\underline{\text{H}}$); 5.7 - 7.9 (m; 11 H; $\text{Ar}\underline{\text{H}}$ und vinyl.- $\underline{\text{H}}$).

^{13}C NMR (CDCl_3 , δ in ppm): (aliph. $\underline{\text{C}}$): 31.9; 32.7; 33.4; 35.7; 36.5; 37.6; 38.1; 39.1; 39.3; 40.1; 41.4; 41.8; 42.2; 42.5; 42.9; 44.7; 45.0; 45.4; 45.7; 46.6; 47.4; 49.2; 49.4; 52.4; 53.1; 54.4; (vinyl. and $\text{Ar}\underline{\text{C}}$): 125.3; 125.8; 127.4; 127.9; 128.3; 128.5; 128.6; 128.8; 129.0; 129.2; 129.5; 130.6; 131.8; 132.6; 133.7; 133.9; 134.6; 134.8; 135.3; 136.7; 136.8; 137.3; 137.9; 138.2; 139.6; 139.9; 141.5; 141.9.

Synthesis of poly(trifluoromethyl-1,4-xylylene) (6c) by CVD

The quartz boat in the vaporization zone of the preheated (800°C) pyrolysis apparatus (see ref. [10]) was charged under argon atmosphere with 1.89 g of **5c** (7.2 mmol). The apparatus was evacuated and the pressure was kept between 0.2 - 0.4 mbar. Films of **6c** were formed at the glass walls of the tube behind the pyrolysis

zone above the cooling trap. The product was dissolved in THF and reprecipitated in methanol and dried in vacuum at 80°C. Yield: 0.60 g (3.5 mmol), 70%.

$T_g = 89^\circ\text{C}$, $M_n = 14\,000$, $M_w = 83\,2300$, $[\eta] = 0.85\text{ dl/g}$.

IR (KBr, cm^{-1}): 3036 m; 2964 m; 1514 m; 1376 s; 1171 s; 1328 s; 1020 w; 863 w; 805 m; 682 w.

^1H NMR (CDCl_3 , δ in ppm): 2.86 (s, 1 H, $-\text{CH}(\text{Ar})-$); 3.16 (s, 1 H, $-\text{CH}_2-$); 3.21 (s, 1 H, $-\text{CH}_2-$); 3, 67 (d, $-\text{ArCH}_2-\text{CH}_2\text{Ar}-$); 6.6 - 6.9 (s, 4 H, ArH).

^{13}C NMR (CDCl_3 , δ in ppm): 35.2 ($-\text{CH}_2-$); 51.6 (m; $-\text{CH}(\text{CF}_3)-$); 127.5 (q, $^1J = 280\text{ Hz}$, $-\text{CF}_3$); 128.8 (ArC); 128.9 (ArC); 132.3 (ArC); 137.4 (ArC).

^{19}F NMR (CDCl_3 , δ in ppm): -69.76 ($-\text{CF}_3$).

Results and discussion

Synthesis of starting materials

The starting materials (**5**) are based on α -substituted xylenes, which were obtained by chlorination of corresponding alcohols **4** by thionyl chloride in the presence of pyridine (Scheme 1) [9]. **4** was synthesized either by reaction of *p*-tolyl bromide (**1**) with Mg and subsequent reaction with functionalized aldehydes (**2**) or by reduction of **3** (Scheme 1). Starting materials **5a** - **c** were obtained in overall yields of 61% for **5a**, 69% for **5b**, and 32% for **5c** and were characterized by IR and NMR analysis. Four different diastereoisomers are possible from each of these starting materials as shown in Scheme 2 for **4b**. Therefore, a complex splitting pattern was obtained in ^1H NMR spectra with many overlapping peaks for the monomers as shown in Fig. 1 for **4b** and **5b**. The peak positions could not be assigned with certainty in ^1H NMR spectra just based on only 1D NMR measurements. Therefore, 2D COSY measurements were done for the correct assignment of peak positions in ^1H NMR. The representative COSY NMR of **4b** is shown in Fig. 1. The four peaks obtained in the region 5.6 - 6.1 ppm are assigned to vinylic hydrogens 10 and 11 (exo + endo diastereoisomers) based on the observation of ^1H - ^1H cross peaks of proton10 with protons 11 and 9 and that of proton11 with protons 12 and 10 as marked in the COSY NMR spectrum (Fig. 2). Similarly, the unambiguity in the peak assignments in ^1H NMR is confirmed from the COSY spectrum, and the detail assignments of the cross peaks are given in Fig. 2. Although, with ^1H NMR and COSY experiments, the differentiation could not be made between the protons of different diastereoisomers, the peak positions could be assigned with certainty.

Polymer synthesis

6a and **6b** were obtained by the Gilch route with **5a** and **5b**. **6c** was obtained by CVD via vapor phase pyrolysis of **5c** (Scheme 1). It should be mentioned that the conversion of **5c** under the conditions of the Gilch route did not result in PPX which is most likely due to the competition of nucleophilic displacement of the chlorine substituents by the *tert*-butyl ether group of t-BuOK. On the other hand the CVD route using **5a** and **5b** did not result in PPXs which is most likely due to the undesired decomposition of these alkyl substituted starting materials under pyrolysis conditions. However, **6a** was obtained from **5a** via the Gilch route in a yield of 85%. In contrast,

6b was obtained only in a yield of 26% via the Gilch route which can be speculatively attributed to steric effects of the lateral norbornene substituent in α -position. **6c** was obtained by the CVD route in a yield of 63%. In general, polymers **6** were soluble and fusible under feasible conditions, which allowed characterization by standard analytical techniques and processing from the melt or solution state. Molecular weight analysis was performed by GPC using universal calibration, which yielded molecular weights in close agreement with absolute molecular weights obtained by light scattering [10,11]. The molecular weight of **6a** was $M_n = 27\,500$ g/mol and the polydispersity was $M_w/M_n = 2.1$. Molecular weight of **6b** was in a similar range ($M_n = 17\,000$ g/mol) with a somewhat higher polydispersity ($M_w/M_n = 3.0$). In contrast, the polydispersity of **6c** prepared by CVD was much higher ($M_w/M_n = 59$) with $M_n = 14\,000$ g/mol. Enhanced polydispersities were observed for related CVD poly-reactions, which is most likely due to the heterogeneous nature of the reaction and to experimental deviations (e.g. control of the rate of vaporization of starting materials, contact times in pyrolysis zone, rate of monomer deposition) [12]. Nevertheless, molecular weights of **6a** - **c** were high enough for the formation of solution-cast free-standing films which is an important criterion for application related issues.

Scheme 1. Synthesis of starting materials and of polymers

Scheme 2. Different possible diastereoisomers

Fig. 1. ^1H NMR spectrum of (a) **4b**, (b) **5b**

Fig. 2. COSY NMR spectrum of **4b**

The thermal properties of **6a** - **c** are quite different. 5% weight loss of **6a** occurred under nitrogen atmosphere (heating rate 20 K/min) at 367°C, 5% weight loss of **6b** was observed at 436°C, and for **6c** even at 444°C, which is closest to the thermal stability of unsubstituted PPX (5% weight loss by TGA, heating rate 20 K/min, at 488°C). A similar stabilizing effect of CF₃ groups was observed before for 4-CF₃-phenyl substituted PPXs [12].

The glass transition temperatures (T_g) of **6a** - **c** were obtained by DSC measurement from second heating runs (heating and cooling runs with 10 K/min between 50 and 300°C). T_g of **6a** was 177°C which is high in comparison to **6b** (T_g = 136°C) and **6c** (T_g = 89°C). Indeed, T_g of **6a** is even higher than T_g 's of a variety of PPX derivatives with phenyl substituents in α position or as lateral substituents on the phenylene moiety [6,12,13]. Formation of isotropic melts was observed for **6a** - **6c** by hot-stage microscopy about 20 – 30 K above T_g (from DSC). DSC analysis of **6a** - **c** showed no endothermal signals in this temperature range which is a clear indication that as-polymerized **6a** - **c** were amorphous.

Conclusions

Starting materials for the synthesis of α -alkyl substituted PPXs can be synthesized in good to moderate yield by a two-step procedure. The choice of the synthetic route, either the CVD route or the Gilch route, depends to a large extent on the nature of the starting material. Three examples of PPXs with alkyl-substituents in α -position were presented, which have their own merits. The *tert*-butyl-substituted PPX **6a**

presents a high glass transition temperature. The norbornenyl-substituted PPX **6b** is a PPX derivate which opens perspectives for further chemical modifications due to its olefinic functionality. The CF₃-substituted PPX **6c** represents a promising aliphatic PPX derivative with remarkable thermal stability.

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