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Poly(*p*-xylylene) and Its Derivatives by Chemical Vapor Deposition: Synthesis, Mechanism, and Structure

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ABSTRACT: Poly(*p*-xylylene) (PPX) and its derivatives were prepared by vapor-phase pyrolysis and subsequent chemical vapor deposition (CVD) of the pyrolysis products. Readily available esters of α,α′-dihydroxy-*p*-xylylenes were utilized as starting materials. Mechanistical studies prove that 1,4-quinodimethane is formed by pyrolysis of diesters. The PPXs obtained compare well to PPXs obtained by the classical route using [2.2]paracyclophanes. ^{13}C CP-MAS NMR spectroscopy indicates that the arrangement of substituents along the polymer main chain is controlled by the size of substituents.

Introduction

Poly(*p*-xylyene) (PPX) and some of its derivatives are produced commercially following a procedure by Gorham,[1] the so-called vapor coating process. According to this process, [2.2]paracyclophane is pyrolyzed in the vapor phase followed by condensation of the pyrolysis products on cold substrates and simultaneous polyreaction forming solvent and pinhole-free films. It is remarkable that even sensitive substrates can be coated with PPX films since the coating conditions are mild and in particular solvent-free. Due its chemical resistance and electrical properties, PPX serves as an encapsulant for the preservation of corrosion-sensitive substrates and as an electrical insulator.[2] The preparation of PPXs with tailor-made properties is necessary in order to fully exploit the versatility of the preparation of PPXs by the vapor coating process for advanced applications, for example, as encapsulents for biomaterials, as light-emitting diodes, as low dielectric constant material for microelectronic devices, or as a mass-sensitive layer in gas sensors.

The synthesis of PPX derivatives is limited by the availability of paracyclophanes and the vaporizability of substituted paracyclophanes. Most of the research on the synthesis of PPX and its derivatives by CVD is focused on synthetic routes with *p*-xylenes or paracyclophanes as starting materials.[3,4] Moore et al. replaced paracyclophanes by α,α′-dihalogeno-*p*-xylylenes which can be utilized for the synthesis of PPX by pyrolytic metal induced dehalogenation reactions.[5] In a previous communication we have presented a synthetic route to PPX involving oxalic esters of α,α′-dihydroxy-*p*-xylylene as replacement for paracyclophanes.[6,7] The advantage of this route is good access to the starting materials (this also applies to Moore's route). Limitations are lower polymer yields compared to the paracyclophane route. The scope of this contribution is the presentation of detailed investigations of an ester route to PPX and its derivatives. Particular focus is on the choice of the starting materials for the polymer synthesis, the reaction mechanism, and the molecular structure of the polymers. Perspectives as well as limitations of this synthetic route will be critically evaluated.

Experimental Part

Materials. Compounds **1** and acid chlorides were purchased from Aldrich if not otherwise stated and were purified by distillation or recrystallization. Compound **1j** was prepared as described previously.[8] The dibrominated [2.2]paracyclophane was prepared as described previously.[9]

Measurements. ^{1}H NMR spectra were recorded with a Bruker AC 300 (300 MHz) as well as ^{13}C NMR spectra (75 MHz). FT-IR spectra were recorded by a Perkin-Elmer type 1600 FT-IR spectrometer.

^{13}C cross magic angle spinning (CP-MAS) NMR spectra were obtained with a Bruker MSL 300 spectrometer at a ^{13}C resonance frequency of 75.47 MHz and a rotor frequency of about 3 kHz. Total suppression of sidebands (TOSS) was achieved by a pulse sequence introduced following ref 10.

*Synthesis of **2j***. A flame-dried flask was charged under argon atmosphere with 2.14 g (0.010 mol) of **1j**. A 10 mL (11.04 g, 0.141 mol) aliquot of acetyl chloride was added dropwise at 0 °C. The mixture was stirred for 1 h at room temperature. Excess acetyl chloride was removed by vacuum distillation. The solid residue was recrystallized from ethanol/water. For yield and characterization data see Table 1.

*General Procedure for the Synthesis of **3** by Vapor-Phase Pyrolysis of **2** and Subsequent Chemical Vapor Deposition*. A quartz boat in the vaporization zone of the preheated (600−900 °C) pyrolysis apparatus was charged under argon atmosphere with 0.4 g of **2**. The apparatus was evacuated, and the pressure was kept between 0.2 and 0.4 mbar. Films of **3** were formed at the glass walls of the tube behind the pyrolysis zone above the cooling trap. The films were rinsed with THF and methanol, removed from the glass surface, and dried in a vacuum at 80 °C. Reaction parameters and yields are given in Tables 2−4.

*Poly(p-xylylene), **3a***. IR (cm^{-1}): 3016, 2921, 2855, 1894, 1690, 1607, 1514, 1453, 1416, 1278, 1139, 1019, 822, 543. ^{13}C CP-MAS (δ, ppm): 40, 129, 140, 142.

*Poly(chlor-p-xylylene), **3b***. IR (ν, cm^{-1}): 3020, 2925 2861 1891, 1606, 1558, 1490, 1447, 1262, 1204, 1151, 1045, 876, 823, 686. ^{13}C CP-MAS (δ, ppm): 37, 131, 138, 143.

*Poly(brom-p-xylylene), **3c***. IR (cm^{-1}): 3014, 2925, 2860, 1896, 1741, 1605, 1556, 1490, 1454, 1399, 1340, 1265, 1202, 1157, 1102, 1040, 950, 874, 826, 790, 758, 673, 598. ^{13}C CP MAS (δ, ppm): 37, 39, 132, 139, 143.

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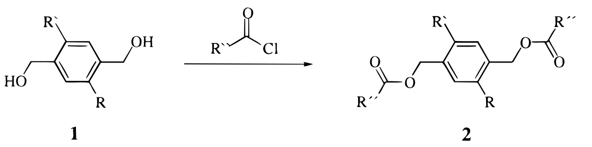
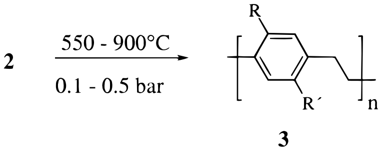
Scheme 1



	1a, 2a	b	c	d	e	f	g	h	i
R	H	H	H	Cl	Cl	Cl	Br	Br	Br
R´	H	H	H	H	H	H	H	H	H
R´´	CH_3	C_2H_5	$C(CH_3)_3$	CH_3	C_2H_5	$C(CH_3)_3$	CH_3	C_2H_5	$C(CH_3)_3$

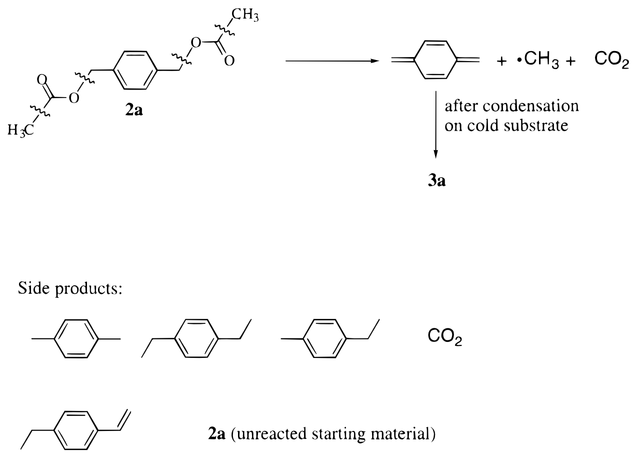
	j	k	l	m
R	C_6H_5	C_6H_5	C_6H_5	Br
R´	H	H	H	Br
R´´	CH_3	C_2H_5	$C(CH_3)_3$	$C(CH_3)_3$

Scheme 2



	3a	b	c	d	e
R	H	Cl	Br	C_6H_5	Br
R´	H	H	H	H	Br

Scheme 3



*Poly(2,5-dibromo-p-xylylene), **3e***. IR (cm^{-1}): 2935, 2864, 1470, 1453, 1367, 1264, 1190, 1115, 1055, 887, 760.

Results and Discussion

Starting Materials. The starting materials for the preparation of PPXs by chemical vapor deposition were synthesized by esterification of α,α′-dihydroxy-*p*-xylenes (Scheme 1). Details for the synthetic procedure are presented in the experimental part exemplarily for compound **2j**. The data for molecular characterization (elemental analysis, mp, IR, ^1H NMR, and ^{13}C NMR spectra) are summarized in Table 1.

Polyreactions. The PPXs **3** were prepared by vaporization and pyrolysis of compounds **2** at temperatures between 550 and 900 °C in a two-zone oven connected to a CVD apparatus which was described in a previous publication[11] (Scheme 2). The 1,4-quinodimethanes that were obtained from the pyrolysis of **2** were vapor deposited on glass substrates at temperatures below 150 °C forming **3** by polyreaction.[12] It is important to note that the polyreaction takes place outside of the pyrolysis, oven which means that the reaction temperatures for the polyreaction are below 150 °C depending on the condensation temperature of the different quinodimethanes at a pressure <1 bar. Condensation temperatures of quinodimethanes are typically between 30 and 150 °C at <1 bar depending on the substituent.[1]

PPXs were isolated as thin films which were washed with THF and methanol in order to remove pyrolysis oils. The composition of the pyrolysis oils will be discussed later. The yields of **3** presented here are average values of two polyreactions under identical conditions, allowing a deviation from the average value of ±5%. In general, the yields of **3** were ruled by the substituent of the phenylene moieties and by the nature of R″ in the starting material **2**. The temperature in the pyrolysis zone (T_p) was varied between 550 and 900 °C, which was of significant influence on product yields (Table 2). PPX **3a** was prepared by pyrolysis of **2a**−**c** (runs 1−18, Table 2). The optimum T_p for the preparation of **3a** starting from **2a**−**c** was found at 900 °C (yield 23−29%), with the exception of **2b** which was pyrolyzed at 850 °C (yield 23%). The choice of R″ in the starting material **2** had no significant impact on the yield of **3a** but ruled T_p necessary for pyrolysis of **2**.

Chloro-substituted PPX **3b** was obtained by pyrolysis of **2d**−**f** (runs 19−30, Table 3). Yields were comparable to the yields of **3a**, but the optimum for T_p was at 800 °C with respect to the yields. The bromo-substituted PPX **3c** was prepared by pyrolysis of **2g**−**i** (runs 31−45, Table 4). The yields of **3c** were significantly higher with **2h** (yield 46%) as starting material. In contrast to this, no polyreaction was observed upon pyrolysis of **2j**−**l** (runs 46−48, Table 4) which should yield the phenyl-substituted PPX **3d**. The dibromo-substituted PPX **3e** was obtained with a yield of 13% by pyrolysis of **2m** at $T_p = 900$ °C (run 50, Table 4).

Reaction Mechanism. It is well-known that the formation of **3a** by pyrolysis of paracyclophane proceeds by cleavage of the ethylene bridge of paracyclophane and with the formation of quinodimethane.[2] These species are highly reactive and undergo spontaneous polyreaction during the course of physical condensation on cool substrates. The products of this polyreaction are PPX films.

The reaction mechanism for the formation of **3a** starting from **2** was investigated with **2a** as starting material. The formation of quinodimethane upon pyrolysis of **2a** was proofed by the formation of α,α′-diiodo-*p*-xylyenes with iodine following a procedure of Landrum and Errede[13] and identification of the product by GC analysis. The formation of quinodimethane proceeds obviously by elimination of CO_2 since the presence of CO_2 has been proved by IR spectroscopy of the volatile pyrolysis products (Scheme 3). Additionally, traces of ethene were detected by IR spectroscopy. In the pyrolysis oil numerous side products were found and identified by the GC/mass technique. The components of the pyrolysis oil of the pyrolysis of **2a** at $T_p = 900$ °C

Table 1. Yields, Elemental Analysis, Melting Points Refractive Point, and Spectroscopic Data of Compounds 2

code, formula, yield (%)	analysis, calcd (found)		$T_m{}^a$ (°C)	$n_D{}^{20}$	^{1}H NMR chemical shifts^b (ppm)	^{13}C NMR chemical shifts^b (ppm)	IR spectra wavenumber (cm^{-1})
	C	H					
2a, $C_{12}H_{14}O_4$ (222.24), 80	64.85 64.73	6.35 6.41	46		2.39 (s, 6H), 6.79−6.82 (d, 4H), 7.02-7.08 (d, 2H), 7.13−7.19 (d,2H), 7.46−7.47 (d, 4H), 7.48 (s, 2H), 9.60 (s, 2H)	20.19, 65.84, 128.16, 136.02, 173.97	3014, 2963, 1738, 1460, 1229, 838, 773
2b, $C_{14}H_{18}O_4$ (250.29), 81	67.18 67.28	7.25 7.26	8	1.4720	1.13 (t, 6H), 2.35 (q, 4H), 5.08 (s, 4H), 7.32 (s, 4H)	8.83, 27.39, 65.54, 128.16, 136.02, 173.97	3006, 2963, 2944, 2983, 2884, 1790, 1739, 1620, 1519, 1462, 1423, 1380, 1274, 1175, 1082, 1017, 953, 808, 766, 691
2c, $C_{18}H_{26}O_4$ (306.40), 78	70.56 69.89	8.55 8.58	36		1.22 (s, 18H), 5.09 (s, 4H), 7.32 (s, 4H)	27.15, 38.77, 65.66, 127.76, 136.22, 178.26	3053, 2971, 2934, 2872, 1732, 1518, 1480, 1397, 1206, 1152, 1034, 939, 844, 805, 772
2d, $C_{12}H_{13}ClO_4$ (256.67), 94	56.16 56.14	5.10 5.07	49		2.13 (s, 3H), 2.14 (s, 3H), 5.08 (s, 2H), 5.21 (s, 2H), 7.25−7.43 (m,3H)	20.40, 63.29, 64.97, 126.46, 129.04, 129.92, 133.80, 137.79, 170.56	3026, 2937, 2876, 1976, 1748, 1449, 1380, 1232, 1042, 823, 700
2e, $C_{14}H_{17}ClO_4$ (284.74), 97	59.05 58.95	6.02 6.03	7	1.5065	1.10 (t, 3H), 1.12 (t, 3H), 2.34 (q, 2H), 2.35 (q, 2H), 5.02 (s, 2H), 5.15 (s, 2H), 7.14−7.35 (m, 3H)	8.77, 8.83, 27.28, 62.96, 64.62, 126.22, 128.75, 129.66, 133.46, 133.53, 137.80, 173.69, 173.73	3031, 2983, 2944, 2884, 1740, 1614, 1499, 1463, 1378, 1346, 1178, 1084, 1058, 1017, 951, 878, 825, 806, 693
2f, $C_{18}H_{25}ClO_4$ (340.85), 97	63.43 64.31	7.39 6.90		1.4693	1.18 (s, 9H), 1.19 (s, 9H), 5.02 (s, 2H), 5.13 (s, 2H), 7.16-7.34 (m, 3H)	27.13, 27.26, 63.31, 64.82, 125.94, 128.52, 129.44, 133.48, 139.04, 178.03	3029, 2983, 2944, 2884, 1740, 1614, 1463, 1378, 1346, 1178, 1083, 1017, 951, 878, 825, 806, 693
2g, $C_{12}H_{13}BrO_4$ (301.14), 97	47.86 47.97	4.35 4.35	68		2.10 (s, 3H), 2.12 (s, 3H), 5.05 (s, 2H), 5.16 (s, 2H), 7.34 (AA′BB′, ^3J 7.87 Hz, 2H), 7.56 (s, 1H)	20.78, 20.83, 64.85, 65.47, 123.41, 127.11, 129.86, 132.30, 137.91, 170.48, 170.54	3026, 2934, 1926, 1746, 1448, 1377, 1232, 1036, 823, 684
2h, $C_{14}H_{17}BrO_4$ (329.20), 95	51.09 51.18	5.20 5.13	24	1.5035	1.03 (t, 3H), 1.05 (t, 3H), 2.26 (q, 2H), 2.32 (q, 2H), 4.94 (s, 2H), 5.05 (s, 2H), 7.21 (AA′BB′, ^3J 7.86 Hz, ^{5}J 1.56 Hz, 2H), 7.45 (d, 1H)	8.85, 8.91, 27.28, 64.51, 65.14, 123.16, 126.87, 129.61, 132.02, 135.11, 137.90, 173.65, 173.73	3006, 2983, 2963, 2944, 2884, 1790, 1739, 1620, 1519, 1462, 1423, 1380, 1274, 1175, 1082, 1017, 953, 808, 766, 691
2i, $C_{18}H_{25}BrO_4$ (385.30), 99	56.11 57.33	6.54 4.31		1.4781	1.18 (s, 9H), 1.20 (s, 9H), 2.02 (s, 2H), 5.10 (s, 2H), 5.11 (s, 2H), 7.28 (AA′BB′, ^{3}J 7.95 Hz, ^5J 1.47 Hz, 2H), 7.50 (d, 1H)	27.00, 27.05, 38.61, 38.73, 64.53, 65.33, 123.02, 126.46, 129.34, 130.79, 131.65, 135.23, 138.13, 177.70, 177.80	3026, 2976, 2936, 2880, 1825, 1812, 1778, 1734, 1703, 1610, 1566, 1480, 1460, 1397, 1368, 1281, 1144, 1035, 1005, 907, 817, 795, 770, 676
2j, $C_{18}H_{18}O_4$ (298.34), 99	72.47 72.43	6.08 6.14	44		1.22 (s, 18H), 5.09 (s, 4H), 7.32 (s, 4H)	20.77, 20.81, 63.94, 127.05, 127.15, 127.41, 128.06, 128.18, 128.95, 129.65, 129.80, 133.22, 135.99, 139.89, 142.30, 170.50, 170.66	3029, 2958, 1805, 1741, 1490, 1445, 1379, 1362, 1228, 1027, 996, 824, 772, 704
2**k**, $C_{20}H_{22}O_4$ (326.39), 94	73.60 73.50	6.79 6.68	−60	1.5369	1.12 (t, 3H), 1.16 (t, 3H), 2.33 (q, 2H), 2.38 (q, 2H), 5.04 (s, 2H), 5.15 (s, 2H), 6.89-7.41 (m, 8H)	9.00, 27.49, 63.87, 65.56, 127.10, 127.41, 128.19, 128.98, 129.65, 129.75, 133.31, 136.14, 139.96, 142.48, 173.94, 174.14	3051, 2984, 2885, 1835, 1792, 1519, 1463, 1380, 1347, 1274, 1177, 1082, 1016, 953, 915, 809, 766, 691
2l, $C_{24}H_{30}O_4$ (382.50), 80	75.36 75.13	7.91 8.02	58	1.5065	1.18 (s, 9H), 1.24 (s, 9H), 5.02 (s, 2H), 5.15 (s, 2H), 7.25-7.45 (m, 8H)	27.14, 27.19, 38.72, 38.81, 64.15, 65.56, 126.58, 127.44, 128.26, 129.00, 129.26, 129.38, 133.33, 136.43, 140.12, 142.36, 178.13, 178.28	3056, 2967, 2878, 1722, 1572, 1543, 1480, 1460, 1421, 1397, 1368, 1280, 1161, 1031, 952, 919, 824, 769, 730, 702
2m, $C_{18}H_{24}Br_2O_4$ (464.19), 97	46.58 46.12	5.21 5.13	91		1.25 (s, 18H), 5.10 (s, 4H), 7.55 (s, 2H)	27.21, 38.95, 64.76, 121.77, 133.14, 137.19, 177.84	3089, 2976, 2875, 1744, 1529, 1484, 1456, 1399, 1378, 1368, 1352, 1282, 1144, 1057, 1038, 1002, 939, 910, 876, 826, 762

[a] T_m = melting point; measured by DSC (heating rate 10 °C/min). [b] ^{1}H NMR and ^{13}C NMR spectra were measured in THF.

Table 2. Starting Materials, T_p, and Yields for the Synthesis of 3a

run no.	start. material	T_p (°C)[a]	yield **3a** (%)[b]
1	**2a**	900	26
2	**2b**	900	15
3	**2c**	900	23
4	**2a**	850	24
5	**2b**	850	23
6	**2c**	850	21
7	**2a**	800	15
8	**2b**	800	6
9	**2c**	800	16
10	**2a**	750	9
11	**2b**	750	6
12	**2c**	750	11
13	**2a**	700	2
14	**2b**	700	11
15	**2c**	700	9
16	**2a**	650	0.6
17	**2b**	650	0
18	**2c**	650	6

[a] T_p is the pyrolysis temperature in the pyrolysis zone. [b] The yield was calculated based on the amount of starting material.

Table 3. Starting Materials, T_p, and Yields for the Synthesis of 3b

run no.	start. material	T_p (°C)[a]	yield **3** (%)[b]
19	**2d**	900	26
20	**2e**	900	26
21	**2f**	900	26
22	**2d**	850	22
23	**2e**	850	18
24	**2f**	850	24
25	**2d**	800	3
26	**2e**	800	30
27	**2f**	800	32
28	**2d**	750	1
29	**2e**	750	13
30	**2f**	750	15

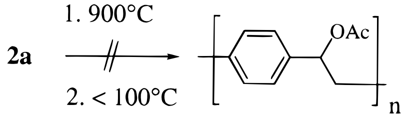
[a] T_p is the pyrolysis temperature in the pyrolysis zone. [b] The yield was calculated based on the amount of starting material.

Table 4. Starting Materials, T_p, and Yields for the Synthesis of 3c−e

run no.	start. material	T_p (°C)[a]	yield **3** (%)[b]
31	**2g**	900	0
32	**2g**	850	0
33	**2g**	800	8
34	**2g**	750	9
35	**2g**	700	0
36	**2h**	900	46
37	**2h**	850	27
38	**2h**	800	30
39	**2h**	750	18
40	**2h**	700	0
41	**2i**	900	18
42	**2i**	850	8
43	**2i**	800	9
44	**2i**	750	16
45	**2i**	700	5
46	**2j**	700−900	0
47	**2k**	700−900	0
48	**2l**	700−900	0
50	**2m**	900	13
49	**2m**	800	11

[a] T_p is the pyrolysis temperature in the pyrolysis zone. [b] The yield was calculated based on the amount of starting material.

Scheme 4



are *p*-xylene, 4-ethyltoluene, 1,4-diethylbenzene, 4-ethylstyrene, 4-propylstyrene, and unreacted **2a**. The presence of these products can be explained by recombination, disproportionation, or transfer reactions of initial radicals formed upon pyrolysis of **2a**. The presence of considerable amounts of 1,4-diethenylbenzene supports the speculation of the formation of methyl radicals since the formation of 1,4-diethynylbenzene could be explained by recombination of methyl radicals and quinodimethane. No traces of linear or cyclic oligo(*p*-xylyenes) or high molecular weight compound were found by high-resolution gel permeation chromatography in the pyrolysis oils or in the extracts of the PPX films prepared from **2a**. Here the absence of soluble high molecular weight material is important for the discussion of the reaction pathway since it is well-known that the CVD process of other difunctionalized *p*-xylenes such as the α,α′-dibromo-*p*-xylenes yields poly(α-bromo-*p*-xylylene) and PPX as side product.[11] The corresponding poly(α-acetoxy-*p*-xylylene) (Scheme 4) is not known in the literature to the best of our knowledge, but it can be speculated that it is readily soluble in polar aprotic solvents since very good solubility was found for the poly(α,α′-diacetoxy-*p*-xylylene).[14] Consequently, poly(α-acetoxy-*p*-xylylene) should be detected in the extracts of the PPX films prepared from **2a** if it is formed as side product. In the case of insolubility it should be detectable by IR spectroscopy, which has not been the case as mentioned below.

The formation of paracyclophane has not been observed. The unexpected ^{13}C CP-MAS NMR spectrum of **3a** can be explained in terms of different crystalline modifications and is not due to the presence of paracyclophane as described previously (see also below).[15]

Molecular Structure of the PPXs Obtained by Pyrolysis of 2. The examination of the molecular structure with respect to defects is crucial for the evaluation of a new synthetic approach. It is well-known that linear **3a** is obtained by pyrolysis of paracylophane. The yields are generally very good. Compound **3a** prepared by pyrolysis of **2a**−**c** was compared to **3a** prepared by the paracyclophane route in order to verify its molecular structure and the versatility of the synthetic procedure.

The solubility of **3** prepared from **2** is ruled by the substituent on the phenylene moieties. Compounds **3a**−**c** and **3e** are soluble only in high boiling solvents above 200 °C in solvents such as α-chloronaphthalene, which clearly proved that these polymers are not cross-linked as was reported for PPX prepared by pyrolysis of *p*-xylene.

The IR spectrum of **3a** prepared by pyrolysis of **2a** is in close agreement with the IR spectrum of **3a** prepared from paracyclophane and does not show any evidence for the presence of carbonyl moieties (Figure 1A,B). No evidence for carbonyl moieties was found also in the IR spectra of compounds **3b**−**e** prepared by pyrolysis of **2**. The absence of carbonyl moieties is important for the discussion of the mechanism of this reaction (Scheme 3) and in order to prove that the product is free of unreacted starting material which can be of significance for applications. However, as shown previously elsewhere, long-term annealing at higher temperatures results in oxidation indicated by carbonyl moieties.[16] The IR spectra of annealed PPX prepared from **2a** or paracyclophane are shown exemplarily in Figure 1C,D. Whereas no indication for carbonyl moieties were found

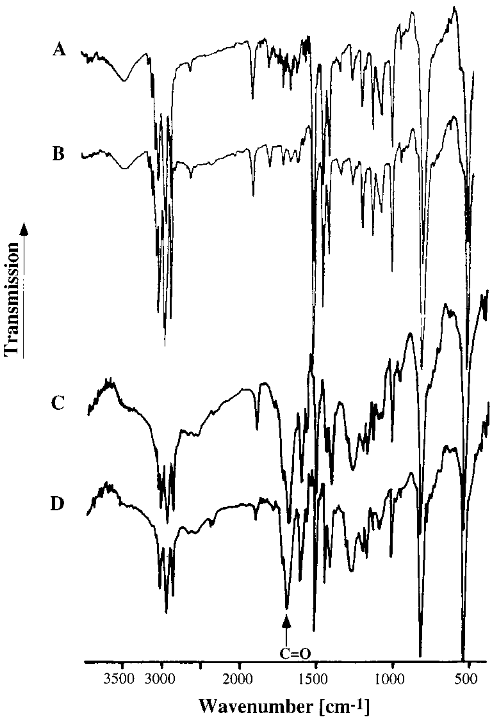


Figure 1. IR spectra of pristine PPX prepared from **2a** (A) and from [2.2]paracyclophane (B) and IR spectra of PPX prepared from **2a** (C) and from [2.2]paracyclophane (D) annealed for 200 h at 140 °C in air.

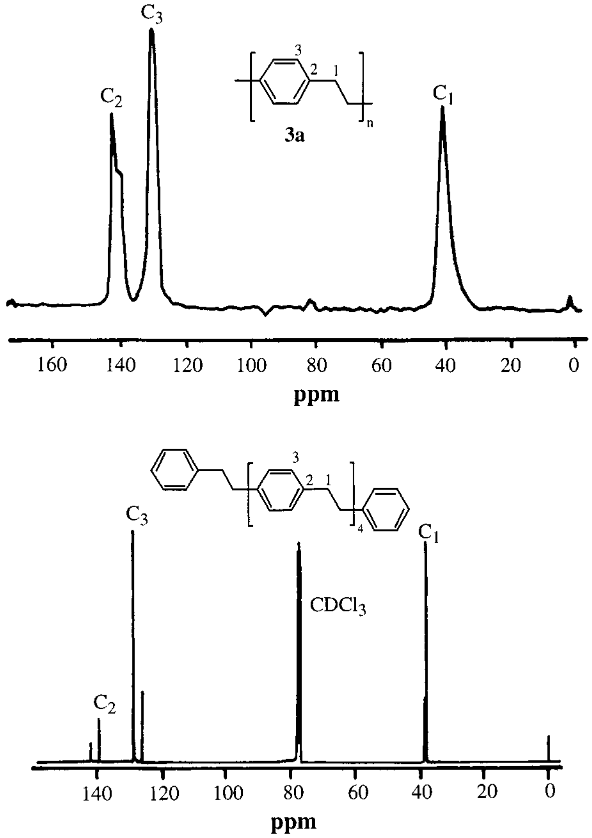


Figure 2. ^{13}C CP-MAS spectrum of **3a** (a, top) and 4,4′-bis(4-(4-phenethyl)phenethyl)bibenzyl (b, bottom).

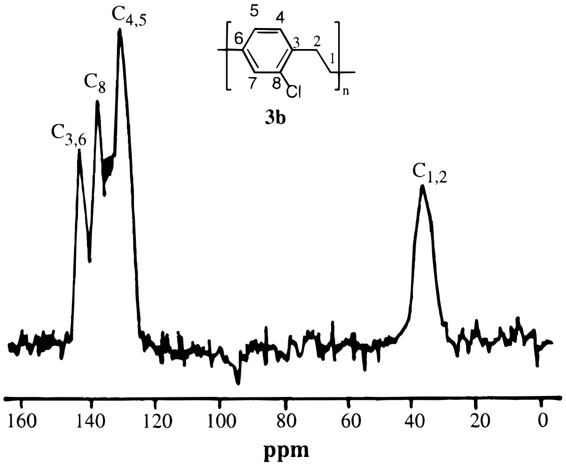


Figure 3. ^{13}C CP-MAS NMR spectrum of **3b.**

in pristine PPX regardless of the starting material (**2a** or paracyclophane), large signals for carbonyl moieties were observed in the annealed products. The vibration for carbonyl moieties centered around 1700 cm^{-1} was observed for PPX already after annealing for 30 h in air. Compounds **3b** and **3c** showed similar behavior on annealing. Quantitative analysis by IR spectroscopy at 140 °C in air for **3a**−**c** over a period of 300 h showed a linear increase of the amount of carbonyl moieties. The rate of oxidation does not differ significantly for **3a**−**c**.

The ^{13}C CP-MAS NMR spectrum of **3a** prepared from **2a** shows signals at 39.8 , 129.2, 139.6, and 141.3 ppm. The signal at 39.8 ppm is assigned to the aliphatic C_1 atom of **3a**. The signal at 129.2 ppm is attributed to the aromatic C_3 atom, and signals at 139.6 and 141.3 ppm were assigned to the aromatic C_2 atom. The assignments for **3a** were verified by identification in the ^{13}C NMR spectrum of a monodispers oligo-PPX measured in $CDCl_3$ (Figure 2b). Additional signals in the spectrum of the oligomer are due to the detectability of end groups. The signal splitting of the C_2 atom of **3a** is due to different crystalline modifications as already pointed out.[15]

The ^{13}C CP-MAS NMR spectrum of **3b** prepared from **2d** shows signals at 36.5, 130.4, 137.5, and 142.6 ppm (Figure 3), which is in good agreement of previous reports for **3b** prepared from chlorinated paracyclophanes.[17] The signal of the aliphatic C atoms is inhomogeneously broadened which is due to the different chemical surrounding of the C_1 and C_2 atoms. The signal at 130.4 ppm is assgined to the C_2 atom, the signal at 137.5 ppm to the C_3 atom, and the signal at 142.6 ppm to the C_4 atom.

The ^{13}C CP-MAS NMR spectrum of **3c** prepared from **2h** shows signals at 36.6, 38.9, 132.2, 139.0, and 142.6 ppm (Figure 4). The signal at 36.6 ppm was assigned to the aliphatic C_1 atom and the signal at 38.9 ppm to the C_2 atom. The fact that the signals of the aliphatic C atoms can be resolved indicates a rather regular diade structure with respect to statistics of the position of the bromo substituent at the phenylene moieties in the diades which is of interest for the discussion of the mechanism of the chain growth. A more or less statistic chain growth should yield three different diades (A, B, C, Scheme 5). This is supported by the ^{13}C NMR spectra of corresponding bromo-substituted bibenzyls (Figure 5). The deviation from the statistical arrangement of the diades in **3c** can be explained by a selective chain growth as indicated in Scheme 5. The steric demand of the bromo substituents favors diades of types A and C rather than B. The difference in the chemical shift of the C_1 atom in **3b** in comparison to the C_2 atom should be similar to the difference of the shift of the

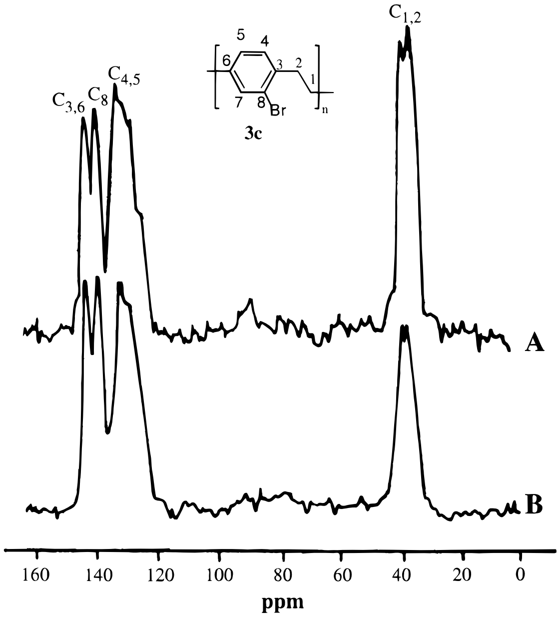
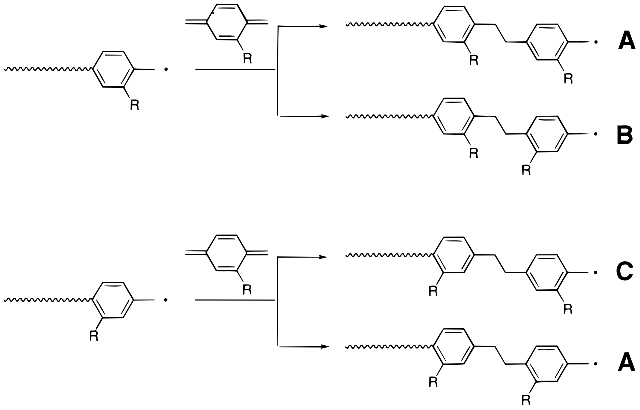


Figure 4. ^{13}C CP-MAS spectrum of **3c** prepared from **2g** (A) and from dibrominated [2.2]paracyclophane (B) according to ref 1.

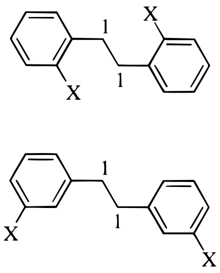
Scheme 5



aliphatic C atoms in **3c** according to corresponding chloro-substituted bibenzyls (Figure 5), but the signals of the aliphatic C atoms were not resolved in the ^{13}C CP-MAS NMR spectrum of **3b** which indicates statistical diades structure and consequently a less selective chain growth in comparison to **3c**. This can be explained by the smaller size of the chloro substituent.

Conclusions

Free-standing films of poly(*p*-xylylene)s can be prepared from readily available esters of α,α′-dihydroxy-*p*-xylylene by vapor-phase pyrolysis. Both ester groups are eliminated, resulting in the formation of corresponding 1,4-quinodimethanes which polymerize upon physical condensation on solid substrates. The formation of several low molecular weight side products has been observed. Analysis of the polymers by IR and NMR spectroscopy does not indicate any configurational structural defects in the polymer and compares well to PPXs prepared from corresponding paracyclophanes. According to NMR spectra, the size of lateral substituents has a significant influence on the positional distribution along the polymer main chain.



δ / ppm

X	Cl	Br
C_1	33.7	36.6

X	Cl	Br
C_1	37.2	37.3

Figure 5. ^{13}C NMR spectra (in $CDCl_3$) of different dihalogenated bibenzyls.

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References and Notes

(1) Gorham, W. F *J. Polym. Sci., Part A-1* **1966**, *4*, 3027.
(2) Beach, W. F.; Lee, C.; Bassett, D. R.; Austin, T. M. In *Encylopedia of Polymer Science and Engineering*; Wiley: New York, 1989.
(3) Iwatsuki, S. *Adv. Polym. Sci.* **1984**, *58*, 93.
(4) Greiner, A.; Mang, S.; Schäfer, O.; Simon, P. *Acta Polym.* **1997**, *48*, 1.
(5) Moore, J. A.; Lang, C.-I.; Yang, T.-M. *ACS Symp. Ser.* **1995**, *614*, 449.
(6) Simon, P.; Greiner, A. *Polym. J.* **1992**, *24*, 1317.
(7) Greiner, A.; Simon, P. US Patent 5,310,858, 1994.
(8) Simon, P. Dissertation Marburg, 1993.
(9) Gorham, W. F. Brit. Pat. 883937-883941, 1966.
(10) Dixon, W. T.; Schäfer, J.; Sefic, M.; Stejskal, M. D.; McKay, R. A. *J. Magn. Reson.* **1982**, *49*, 341.
(11) Schäfer, O.; Greiner, A.; Pommerehne, J.; Guss, W.; Vestweber, H.; Tak, H. Y.; Bässler, H.; Schmidt, C.; Lüssem, G.; Schartel, B.; Stümpflen, V.; Wendorff, J. H.; Spiegel, S.; Möller, C.; Spiess, H. W. *Synth. Met.* **1996**, *82*, 1.
(12) As long as it is not proved whether chain growth proceeds by vinylic polymerization or polyrecombination, the term polyreaction should be selected.
(13) Errede, L. A.; Landrum, B. F. *J. Am. Chem. Soc.* **1957**, *79*, 4952.
(14) Wege, V.; Greiner, A. *Acta Polym.* **1995**, *46*, 391.
(15) Schmidt, C.; Stümpflen, V.; Wendorff, J. H.; Hasenhindl, A.; Gronski, W.; Ishaque, M.; Greiner, A. *Acta Polym.* **1998**, *49*, 232.
(16) Baker, T. E.; Fix, G. L.; Judge, J. S. *J. Electrochem. Soc.* **1980**, *127*, 1851.
(17) Loy, D. A.; Assink, R. A.; Jamison, G. M.; McNamara, W. F.; Schneider, D. A. *Macromolecules* **1995**, *28*, 5799.

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