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# Soluble and Amorphous, Phenyl-Substituted Poly(1,4-xylylene) by Chemical Vapor Deposition

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**Introduction.** Poly(1,4-xylylene) (PPX) and its derivatives have gained significant interest for fundamental research as well as for technical applications.[1−3] Vapor phase pyrolysis at reduced pressure of paracyclophanes[4] or diesters of α,α′-dihydroxy-1,4-xylenes[5] or α,α′-dibromo-1,4-xylenes in the presence of Zn/Cu[6] yields monomers, predominantly 1,4-quinodimethanes, which can form PPXs upon chemical vapor deposition (CVD) on cold substrates. This process is generally called the vapor coating process. The products of this process are solvent- and pinhole-free PPX films. Many of these PPXs exhibit very good solvent resistance, high melting points, and high degrees of crystallinity. Although soluble derivatives of poly(1,4-xylylene) were prepared by the vapor coating process, molecular weight data are based upon counting of radical chain ends by ESR spectroscopy or on viscosimetry. To the best of our knowledge, no molecular weight data are published for PPXs prepared via CVD based on gel permeation chromatography (GPC) or light scattering. The knowledge of the molecular weights and their distributions obtained by CVD is of interest for understanding the mechanism of the chain propagation as well as for applications which rely on high molecular weight material. We basically want to understand how regioselectivity and molecular weight distribution can be controlled in the polyreactions proceeding via 1,4-quinodimethanes.

The concept of improving the solubility of aromatic polymers as well lowering their crystallinity by lateral phenyl substituents has been shown for aromatic polyesters,[7] polyaramides,[8] and poly(phenylenevinylenes).[9] Phenyl-substituted PPX (PPPX) seems to be an ideal candidate for obtaining a readily soluble amorphous PPX combined with very good thermal resistance predominantly limited by the sensitivity of the methylene moieties. The PPPX obtained by the vapor coating process with 2-phenyl-1,4-xylylene was insoluble and intractable,[10] which is most likely due to a nonlinear structure. Therefore we tried to synthesize PPPX applying phenyl-substitued diesters of α,α′-dihydroxy-1,4-xylenes but were not successfull.[11] Based on our previous experiments with α,α′-dihalogeno-1,4-xylenes, where we obtained films of α-halogeno-substituted PPXs as precursors for PPV by the vapor coating process,[12] we report here on a new synthetic approach to PPX and PPPX by CVD using α-bromo-1,4-xylene as starting material.

**Experimental Section. Synthesis of α-Bromo-2-phenyl-1,4-xylene (2).** A 500 mL flask was charged with 50 g (275 mmol) of 2-phenyl-1,4-xylene (**1**)[13] and 300 mL $CCl_4$. The mixture was heated to reflux and 12.8 mL (250 mmol) of bromine was added dropwise while the reaction mixture was illuminated with a 500 W lamp. Heating was continued for 30 min after addition of bromine and then cooled to room temperature. The mixture was subsequently washed with aqueous $NaSO_3$, aqueous $NaCO_3$, aqueous NaCl, and $H_2O$ and then dried over $MgSO_4$. After removal of $CCl_4$, the crude product was fractionated twice by vacuum distillation, bp 105 °C, $10^{-3}$ Torr. Yield of **2**: 51 g (197 mmol), 72% (based on **1**).

IR (KBr, $cm^{-1}$): 3059, 3026, 2962, 2973, 2921, 2859, 1952, 1903, 1812, 1766, 1610, 1569, 1488, 1443, 1379, 1270, 1220, 1147, 1113, 1074, 1024, 885, 822, 779, 745, 730, 701.

$^1$H-NMR ($CDCl_3$, $\delta$/ppm): 2.28 (s, 0.6 H), 2.40 (s, 2.4 H), 4.46 (s, 1.6 H), 4.52 (s, 0.4 H), 7.10−7.50 (m, 8 H). Anal. Calcd for $C_{14}H_{13}Br$ ($M$ = 261.16 g/mol): C, 64.39; H, 5.02. Found: C, 64.26; H, 5.13.

**Synthesis of Poly(phenyl-1,4-xylylene) (3) by CVD.** The quartz boat in the vaporization zone of the preheated (900 °C) pyrolysis apparatus (see ref 12) was charged under an argon atmosphere with 1.89 g of **2** (7.2 mmol). 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 product was dissolved in THF, reprecipitated in methanol, and dried under vacuum at 80 °C. Yield: 0.91 g of **3** (5.04 mmol), 70% (after subtraction of nonconverted **2**). $T_g = 107$ °C, $M_n = 8700$, $M_w = 55\,000$ (both from GPC with chloroform versus polystyrene standards).

IR (KBr, $cm^{-1}$): 3044, 3012, 2921, 2857, 1613, 1487, 1451, 824, 757, 702. $^1$H-NMR ($CDCl_3$, $\delta$/ppm): 2.23−2.40 (m, 0.23 H), 2.70 (m, 2 H), 2.91−2.98 (m, 2 H), 6.77−7.35 (m, 8 H). $^{13}$C-NMR: 20.92, 34.58, 35.01, 37.37, 37.53, 126.63, 126.75, 127.20, 127.33, 127.46, 127.96, 129.13, 129.28, 129.40, 129.95, 130.10, 130.25, 130.65, 130.80, 136.21, 136.65, 136.79, 139.18, 139.27, 139.39, 139.49, 141.62, 141.79, 141.84. Anal. Calcd for $(C_{14}H_{12})_n$ ($M$ = 180.25 g/mol): C, 93.29; H, 6.71. Found: C, 93.17; H, 6.35.

**Results and Discussion.** The bromination of **1** results in two isomeric products (Scheme 1) which can be identified by $^1$H- and $^{13}$C-NMR spectroscopy. The overall yield of **2** was 72% based on the amount of **1**. The 2-isomer is obtained according to $^1$H-NMR spectroscopy in 57.6% yield and the 3-isomer in 14.4% yield. The proportion of the isomers should be insignificant for the polyreaction to **3**. The vapor phase pyrolysis of **2** resulted in the formation of HBr and **3** as transparent coatings in 70% yield of **3** based on converted **2**. **3** obtained via vapor phase pyrolysis of **2** exhibits very good solubility in solvents like THF or chloroform, which is in contrast to the product obtained via vapor phase pyrolysis of 1,4-xylene.[10] The improved solubility allowed structural analysis by $^1$H- and $^{13}$C-NMR spectroscopy in solution and molecular weight analysis by GPC.

The $^1$H-NMR spectrum of **3** exhibits large signal groups in the aliphatic region at 2.70−2.98 ppm (Figure 1). Each of the signals can be resolved to at least three individual signals or at least shoulders. The small signals from 2.26 to 2.40 ppm represent presumably methyl end groups. A $P_n$ of 26, corresponding to $M_n$ = 4700 g/mol, can be calculated from the integrals if each homologue of **3** is terminated by two methyl groups. The signals of the aromatic protons are represented by a multiplet from 6.77 to 7.35 ppm. Focused on one carbon atom of the methylene group four different diad structures are possible (Figure 2), which should result in four signals in the $^{13}$C-NMR spectrum. The $^{13}$C-NMR spec-

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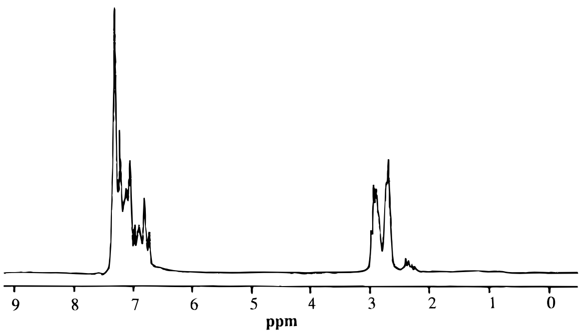
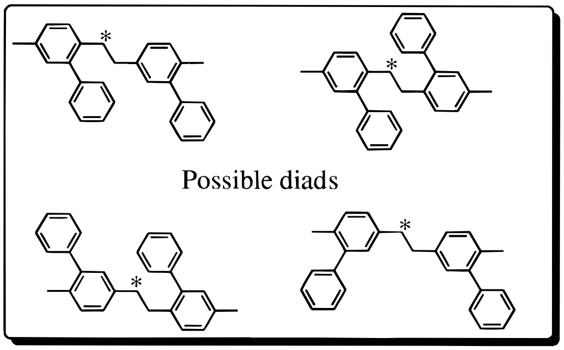


**Figure 1.** $^1$H-NMR spectrum of **3** in $CDCl_3$.



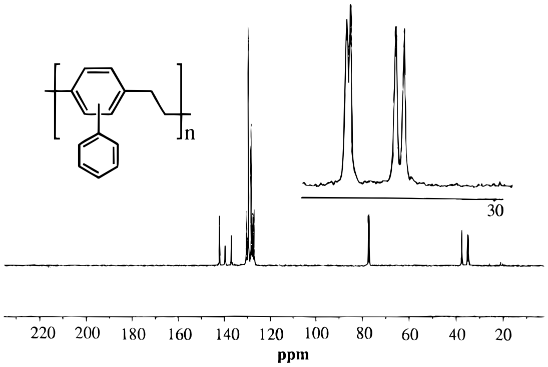
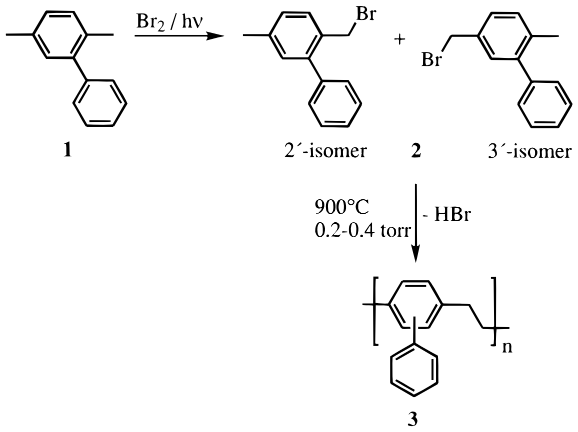


**Figure 2.** $^{13}$C-NMR spectrum of **3** in $CDCl_3$.

**Scheme 1**



trum of **3** indeed shows four signals in the aliphatic region between 34.58 and 37.53, which is consistent with a statistical arrangement of the phenyl substitutent along the polymer backbone of **3** (Figure 2). This means that the bulky phenyl substituent does not induce any regioselectivity in the polyreaction of the phenyl-substituted 1,4-quinodimethane. The small signal at 20.92 ppm was attributed to alkyl end groups.

A $M_w = 55\,000$ and a $M_n = 8700$ was measured for **3** by GPC versus polystyrene standards, which is higher than found by end group analysis via $^1$H-NMR spectroscopy. $M_w/M_n$ is monomodal but rather high (6.32), which is obviously due to the reaction conditions. The polyreaction of quinodimethanes in the course of CVD can be regarded as substance polyreaction with high conversions, which is of course limited by the mobility of the reactive chain ends. The corresponding base-induced polyreaction of **2** resulted in a monomodal $M_w/M_n = 2.37$, which underlines the assumption that the mobility of the reactive chain ends has a significant impact on the width of the molecular weight distribution.

The 5% weight loss of **3** measured by thermogravimetric analysis was detected at 354 °C, which is somewhat lower than for PPX. In contrast to PPX, **3** is amorphous with a $T_g$ at 107 °C. PPX exhibits a glass transition at 13 °C[14] and a melting point at 420 °C (with decomposition).[15] The amorphous character of **3** certainly contributed to the improved solubility of **3**.

**Conclusions.** Phenyl-substituted PPX, which is soluble and amorphous, can be obtained from phenyl-substituted α-bromo-1,4-xylene by vapor phase pyrolysis and subsequent CVD. The enhanced solubility of product **3** allows structural and molecular weight analysis. The phenyl substituents are arranged statistically along the polymer backbone with regard to diad structures. The molecular weight obtained by this new synthetic approach is high enough to produce free-standing films. The liberation of HBr during the vapor phase pyrolysis is certainly a major drawback for coating of sensitive substrates, but the good access to α-halogenated 1,4-xylenes will allow the preparation of a wide variety of PPXs and the investigation of their structure−property relationships, which is presently underway. However, the search for new, less corrosive leaving groups instead of HBr is still a challenge worthy of intensive efforts.

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