

# Functionalization of Poly(*para*-xylylene)s—Opportunities and Challenges as Coating Material

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The chemical vapor deposition (CVD) of poly(*para*-xylylene)s (PPX) is an enabling technology for materials design as well as for numerous high-performance applications. Additionally, PPX possesses of a unique set of structure–property relationships that can be tuned over a wide range. Different strategies vary from functionalization of the most used precursor [2.2]paracyclophane to the testing of new precursors and the copolymerization with various monomers. In this review, some recent developments on synthesis and properties of this unique class of polymers, the PPX, are reported.

## 1. Introduction

The synthesis of polymers by chemical vapor deposition (CVD) gained a lot of attention over the last several years due to the unique approach and the concomitant properties.<sup>[1–3]</sup> One of the best established polymers obtained by CVD is poly(*para*-xylylene) (PPX) that exhibits outstanding thermal and chemical properties and is in use for numerous technical applications. PPX by CVD was first reported by Szwarc through pyrolysis of *p*-xylene.<sup>[4,5]</sup> PPX (trade name Parylene) gained technical relevance when Gorham observed that the *p*-xylene dimer [2.2]paracyclophane can be used as precursor for PPX in the CVD process (also coined as Gorham process), which provides quantitative conversion of the dimer without any by-products.<sup>[6]</sup> Besides by CVD, PPX can also be synthesized via wet chemistry. The Wurtz-type coupling reaction<sup>[7,8]</sup> and the Gilch polymerization<sup>[9]</sup> should be mentioned without going into detail because the obtained products are either insoluble or cannot be processed.

Due to a high solvent resistance even at high temperatures, high melting point, low dielectric constant, and very good barrier properties, PPX was mainly used as protective coating, for example, for electronics,<sup>[10]</sup> medical devices,<sup>[11]</sup> and paper artifacts<sup>[12]</sup> or as sealing to prevent the leaching of additives out of elastomers.<sup>[13]</sup> PPX is also used in microelectronic mechanical

systems,<sup>[14–16]</sup> organic light-emitting diodes,<sup>[17]</sup> or in biological and medical applications.<sup>[18–20]</sup> A relatively new area in the PPX research is the formation of reactive coatings. This can be achieved by the introduction of functional groups that are able to react in polymer analogous reactions.<sup>[21–23]</sup>

This review should also provide an overview of the opportunities that especially functionalized PPXs made by CVD provide. First, some general remarks and examples of PPX made by CVD will be given before functionalized PPX will be

discussed. A short chapter regarding the copolymerization with vinyl comonomers will complete this article.

## 2. Background of PPX

The synthesis, properties, and applications of the commercially available PPXs have already been reviewed several times;<sup>[7,24–27]</sup> therefore, only some important aspects and limitations of the CVD of PPX will be highlighted to get an understanding of the process and chemistry.

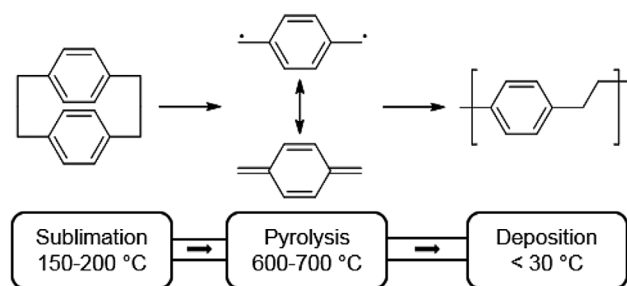
CVD polymerizations generate homogeneous films that are pinhole-free, depending on the film thickness (for PPX, the threshold is about 700 nm). **Figure 1** shows the PPX synthesis following the Gorham process that nowadays is mostly used. The dimer [2.2]paracyclophane first gets vaporized at reduced pressure and at elevated temperatures. In a second heating chamber, the pyrolysis zone, the gaseous dimers were cracked and form *p*-quinodimethane that is the actual monomer for the CVD of PPX. The *p*-quinodimethane can exist in singlet or triplet state and the energy difference between these two states was determined to be very low (8–9 kcal mol<sup>−1</sup>) that explains the high reactivity of this moiety.<sup>[28]</sup> The now-formed species condensates at ambient temperature (below 30 °C) on almost any surface with spontaneous polymerization. The prevailing view is that a diradical trimer has to be formed to initiate the polymerization. The described mechanism is the same for all commercially available PPXs (**Figure 2**). Calculations only indicate that the number of monomer molecules that have to form the diradical is different. For the unsubstituted PPX (PPX-N) and poly(*p*-chloro-xylylene) (PPX-C), a trimer is sufficient while poly(*p*-dichloroxylylene) (PPX-D) needs a tetramer to start the polymerization.<sup>[29]</sup> Although the principal process is similar for PPX with lateral substituents, the vaporization and deposition temperatures are mostly higher for the precursors (substituted paracyclophanes). Precursors with large or temperature-sensitive substituents could be critical as they

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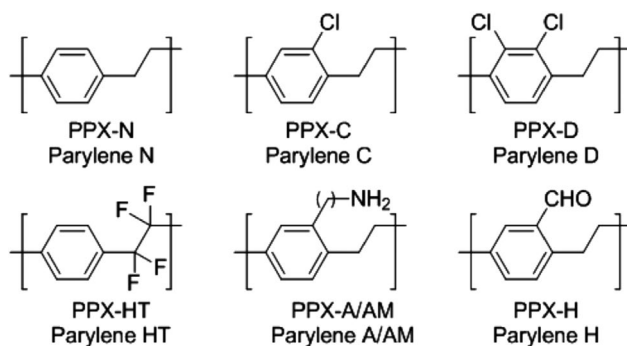
**Figure 1.** Schematic image of the polymerization process of [2.2]paracyclophane to PPX via CVD.

might decompose during vaporization or during the formation of quinomethane. Potential chain-transfer reaction with substituents has not yet been investigated.

PPX is partially crystalline. The degree of crystallinity depends on the deposition temperature and deposition rate. Additionally, existing different crystal modifications and the  $\alpha$ -modification can be converted irreversible into the  $\beta_1$ -modification at 220 °C while the  $\beta_1$  can be converted reversible into the  $\beta_2$ -modification at 270 °C before the PPX melts under decomposition at 420 °C.<sup>[30]</sup> The control of crystallinity is essential because properties such as the barrier behavior depend strongly on the degree of crystallinity. Therefore, the deposition temperature has a large impact on the resulting properties of the polymer. Decreasing deposition temperatures led to an increasing growth rate and molecular weight that cause improved thermal stability.<sup>[31]</sup>

**Table 1** summarizes some properties of commercial PPX (trade name Parylene). The choice of the right PPX type depends on the application area. Parylene C is often used as barrier material, whereas the fluorinated Parylene HT or Parylene AF-4 exhibits a better thermal and UV stability. Amine- and aldehyde-functionalized PPX are suitable for bioactive coatings. Some suppliers offer more PPX derivatives, for example, with a higher thermal stability without using halogens, but no details on their structure are given.

The exact mechanism is still unknown in detail. It is still unclear whether the polymerization proceeds by polyrecombination or by radical polymerization or by a combination of both. Several experimental and theoretical investigations investigated the mechanism. The kinetics of the PPX polymerization via [2.2]paracyclophane was nicely summarized by Fortin and Lu and will, therefore, not be discussed further.<sup>[32]</sup> Theoretically, it is not necessary to break both ethylene bonds to generate a radical



**Figure 2.** Chemical structure of the most common commercial PPX or Parylenes (trade name).



**Tobias Moss** joined Prof. Greiner's group after finishing his studies in polymer science at the University of Bayreuth in 2013. Within his Ph.D. thesis, he worked on chemical functionalization of PPX precursors to be used in chemical vapor deposition. Furthermore, the investigation of wetting behavior of PPX-coated surfaces using

an industrial process was part of his thesis. He graduated successfully in 2019. Since 2018, he is working as Manager Innovation and Application Development at Chemische Fabrik Budenheim KG where he leads a team for the development of new polymer additives.



**Andreas Greiner** received his Ph.D. degree in chemistry from the University of Marburg in 1988 and did his postdoc in 1989 at the University of California, Santa Barbara, USA. He was appointed associate professor for organic chemistry and macromolecular chemistry at the University of Mainz in 1999. In 2000, he became

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that can polymerize. With the monofunctionalized precursor 4-acetyl[2.2]paracyclophane and two substrates with different temperatures, two homopolymers were obtained and this verified the cleavage of both ethylene bridges.<sup>[6]</sup> Another proof was obtained by pyrolysis of 4-ethynyl[2.2]paracyclophane when a copolymer consisting of roughly 80% poly(ethynyl-*p*-xylylene) and 20% poly(*p*-xylylene) was formed.<sup>[33]</sup> As shown by Jensen and co-workers, some substrates such as some metals, their salts, and organometal complexes inhibited the growth of PPX.<sup>[34,35]</sup> This could be used for the fabrication of patterned PPX films.

The most important advantage of the gas phase polymerization is the ability to coat even complex structures homogeneously. Microdevices,<sup>[36]</sup> nanotrenches,<sup>[37]</sup> fiber mats,<sup>[38,39]</sup> or open cell sponges<sup>[40]</sup> were coated successfully with PPX. Recently, we observed that porous materials such as sugar cubes can act as templates for the generation of ultralight PPX foams.<sup>[41]</sup> These foams exhibit interesting properties such as good thermal insulation or the ability to separate oil/water mixtures. Although complex structures can be coated, it is known that the thickness of coatings through small holes decreases

**Table 1.** Properties of commercial PPX collected from the study by Fortin and Lu.<sup>[32]</sup>

Property	PPX-N	PPX-C	PPX-D
Glass transition temperature [°C]	13–80	35–80	110
Melting point [°C]	420	290	380
Young's modulus [GPa]	2.4	3.2	2.8
Elongation at break [%]	30	200	10
Contact angle [°]	79	87	97

with increasing distance (Figure 3).<sup>[42]</sup> Investigations on microchannels proved this result and additionally showed that the degree of deposited PPX also was dependent on the used derivative.<sup>[36]</sup>

Complex PPX structures were also created using the oblique angle deposition approach.<sup>[43,44]</sup> In this process, the substrate was tilted slightly and the deposited PPX formed columns (Figure 4). The structuring causes a change of the surface properties, for example, the contact angle increases significantly and the water drop adheres well to the generated rough surface.<sup>[43]</sup>

## 2.1. Derivatives of PPX

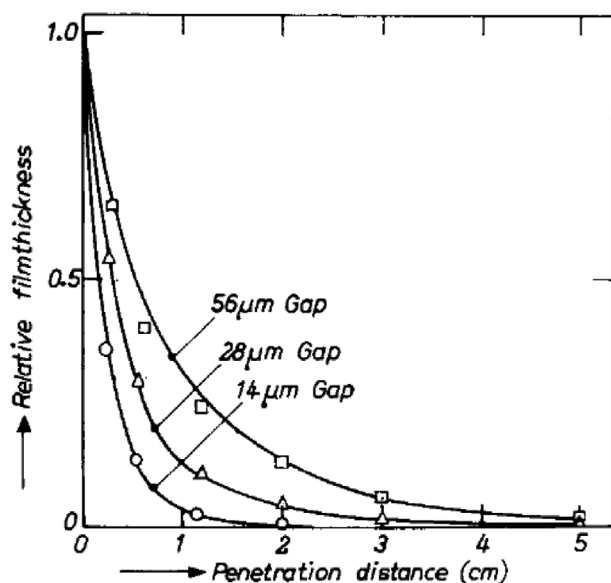
In general, PPX can be functionalized at the phenylene moiety and at the ethanediylene moiety. Due to the insolubility of PPX, its functionalization is challenging but several functional groups could be attached to PPX by wet chemistry.<sup>[45,46]</sup> The reaction conditions were often harsh and the advantage of a solvent-free coating process gets lost. Another approach was the treatment with UV or plasma so that polar groups such as aldehydes and carboxylic acids formed at the surface.<sup>[47,48]</sup> However, these groups are not very stable. The best way to modify PPX is the functionalization of the precursor before

the polymerization. The challenge is to synthesize precursors that are volatile, thermally stable at the pyrolysis temperature, and that can form a *p*-quinodimethane that polymerizes. As the Gorham process already is established, a lot of work was successfully done with functionalized [2.2]paracyclophanes. Here, the syntheses of several derivatives are known in literature due to their application possibilities in other areas of chemistry.<sup>[49]</sup>

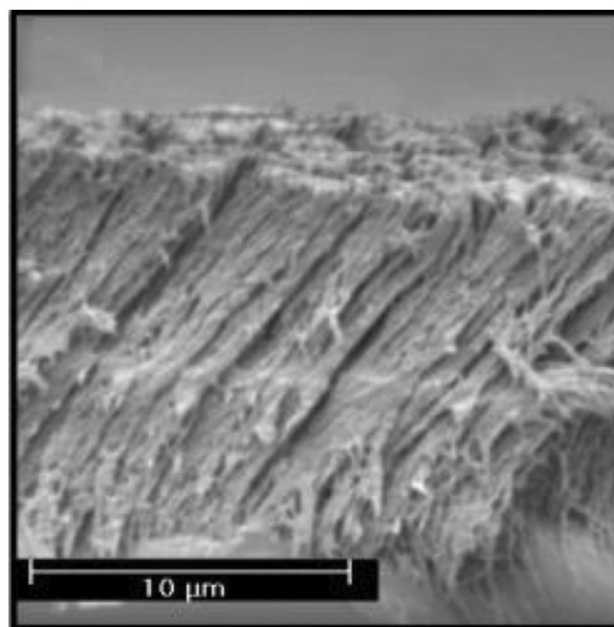
### 2.1.1. Difunctionalized [2.2]Paracyclophanes as Precursors

Difunctionalized paracyclophane result in PPX with homogenous chemical composition.

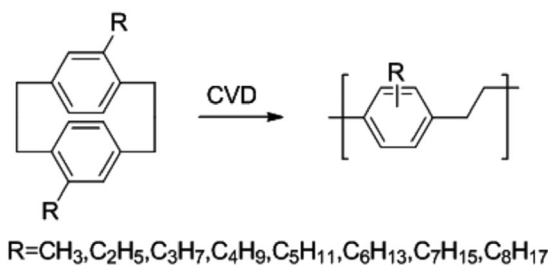
Through the introduction of bulky groups at the benzyl ring, soluble PPX could be obtained.<sup>[50,51]</sup> The solubility allowed the characterization of these polymers with standard methods such as gel permeation chromatography (GPC) or NMR spectroscopy. Molecular weights of up to 1 000 000 were received with GPC measurements and NMR analysis showed a “splitting” of the signals that indicated head-to-tail as well as tail-to-tail and head-to-head linkage. Siloxane substituents gave an amorphous, colorless polymer with a glass transition temperature of −10 °C and a 5% decomposition temperature of 442 °C.<sup>[50]</sup> Elongation tests showed good mechanical properties for this polymer with a Young's modulus of 0.02 GPa and an average elongation at break of 470% that was significantly better than the commercial PPX. The wetting behavior was also changed due to the siloxane groups. A solvent-cast film had a contact angle of 103°, whereas the as-deposited film and an electrospun sample reached values of 135°. This can be explained by the higher roughness the previous two samples had in comparison to the solvent-cast one.



**Figure 3.** PPX film thickness measured (points) and calculated (lines) in dependency of the distance to the inlet. Reproduced with permission.<sup>[42]</sup> Copyright 1981, Wiley Periodicals, Inc.



**Figure 4.** SEM image of the cross section of PPX deposited via the oblique angle deposition approach that led to column formation. Adapted with permission.<sup>[43]</sup> Copyright 2007, American Chemical Society.



**Scheme 1.** Schematics of the CVD of 4,12-dialkyl[2.2]paracyclophanes to poly(*n*-alkyl-*p*-xylylene)s.

Introduction of *n*-alkyl chains at the benzylic ring also yielded soluble PPX (**Scheme 1**).<sup>[51]</sup> At least a propyl group is necessary to get a soluble PPX at ambient conditions. Water contact angles of these samples were only slightly higher than for PPX-N or PPX-C, but with increasing length of the alkyl chain, the glass transition temperature, decomposition temperature, and Young's modulus were decreased (**Table 2**). The elongation at break (best value 380%) was also improved in comparison to the commercial PPX as already shown for the siloxane-modified PPX. Based on this promising results, stents were coated with poly(*n*-propyl-*p*-xylylene) and after the expansion of the stent, no damage or delamination of the coating was observable. These polymers were also suitable for electrospinning. The electrospun nonwovens showed superhydrophobic properties when they were fabricated at higher humidity.<sup>[52]</sup> Superhydrophobicity only occurred when the fibers had pores, and therefore a double-scale roughness was existing. The nonwoven retained the superhydrophobicity also after thermal and mechanical treatments (**Figure 5**) and a long-term storage at ambient conditions neither influenced this behavior.

Galeotti et al. copolymerized the alkyl-functionalized PPX with the commercial PPX-C, and thus improved the thermal and mechanical properties.<sup>[53]</sup> The resulting copolymers contained less than 15% of alkylated *p*-xylene and were still transparent for thicknesses between 5 and 15 μm. All copolymers were insoluble as a result of the high PPX-C content. The maximum decomposition temperatures for all samples were

**Table 2.** Summary of properties of *n*-alkyl-substituted PPXs. Adapted with permission.<sup>[51]</sup>

<i>n</i> -Alkyl chain	$T_{5\%}$ , $T_{max}$ [°C]	$T_g$ [°C]	$T_m$ [°C]	Young's modulus [GPa]
Methyl	469, 491	53	245	2.51 <sup>a)</sup>
Ethyl	463, 489	17	– <sup>b)</sup>	1.08 <sup>a)</sup>
Propyl	459, 488	2	– <sup>b)</sup>	0.42 <sup>a)</sup> /0.31 <sup>c)</sup>
Butyl	444, 485	–4	118	0.16 <sup>c)</sup>
Pentyl	439, 485	–11	110	0.12 <sup>c)</sup>
Hexyl	440, 487	–21	121	0.06 <sup>c)</sup>
Heptyl	430, 486	–26	120	0.06 <sup>c)</sup>
Octyl	428, 484	–29	117	0.04 <sup>c)</sup>

<sup>a)</sup>As-deposited film was tested; <sup>b)</sup>Between 25 and 400 °C, no melting peak was observable; <sup>c)</sup>Solvent-cast films were tested.

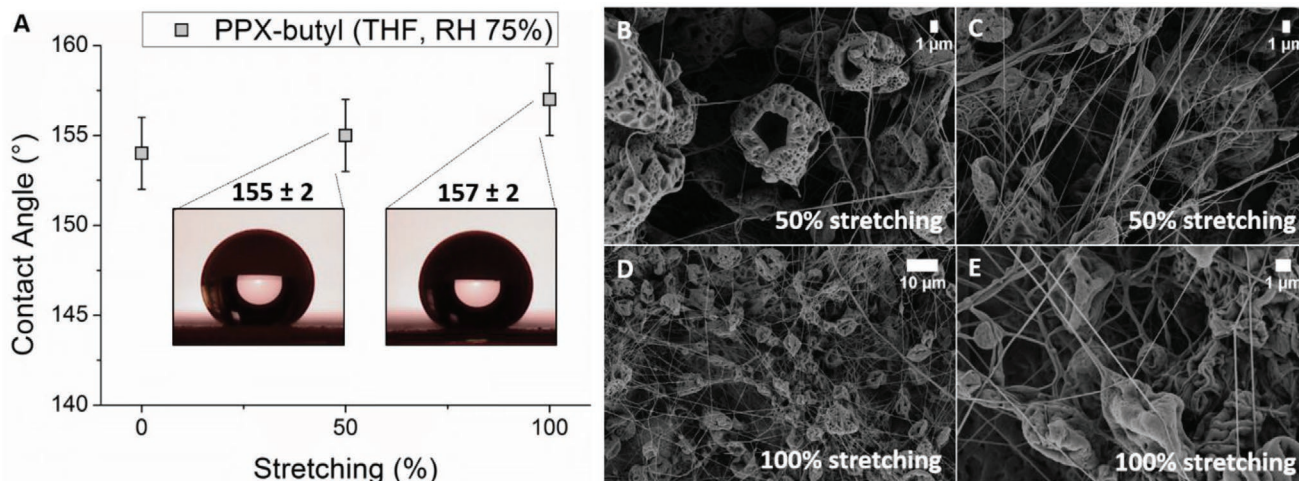
very high with >500 °C and differ only slightly from PPX-C homopolymer. The barrier properties and biocompatibility were not affected significantly by the introduction of alkylated repeating units. It was also shown that with increasing alkyl content and increasing length of the alkyl chain, the Young's modulus decreased so that the lowest value (0.3 GPa) was obtained for an octyl-copolymer. This value corresponds to a 13 times reduction in comparison to the PPX-C homopolymer. It was concluded that this correlated with an enhanced elasticity of the PPX. To make a statement concerning the elasticity of the Young's modulus is not sufficient and further investigations such as cyclic mechanical measurements should have been done.

Functionalized [2.2]paracyclophanes are also accessible by a Diels–Alder reaction and subsequent dimerization of the obtained *p*-quinodimethane moiety.<sup>[54]</sup> Through this route, tetra(methoxy carbonyl) [2.2]paracyclophane was obtained that could be polymerized. Further conversion of the precursor led to anhydride- and lactone-functionalized paracyclophanes that were also polymerized successfully and the resulting polymers are shown in **Figure 6**.<sup>[55]</sup> The anhydride **2** was used for patterning cells and proteins on different materials.<sup>[56]</sup>

### 2.1.2. Monofunctionalized [2.2]Paracyclophanes as Precursors

Several functionalized PPX surfaces were fabricated by using a monosubstituted [2.2]paracyclophane. The CVD of those precursors yielded a copolymer consisting of *p*-xylene and the substituted *p*-xylene building block. As mentioned above exists the copolymer not necessarily of the similar content of both moieties. Due to different vapor pressures of the formed quinodimethanes, it is challenging to create copolymers with equal contents of each monomer moiety. In general, these copolymers are insoluble and have a good adhesion to various substrates. Some of the obtained copolymers were amorphous.<sup>[57]</sup>

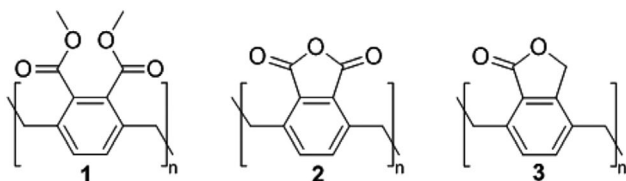
Lahann and co-workers have developed several functionalized coatings by using monosubstituted [2.2]paracyclophane as a starting material. They used the generated coatings mainly for the immobilization of biomolecules such as proteins or cells. Some reviews and book chapters concerning the use of (reactive) PPX coatings are available and therefore only some examples are highlighted here.<sup>[19,21,22,58,59]</sup> **Scheme 2** shows copolymers that were made by CVD of monosubstituted [2.2]paracyclophanes that were mostly used successfully to immobilize biomolecules. Therefore, it is important that the biomolecule offers a suitable functional group. Some of the PPX functionalities need an extra activation step before the immobilization can take place. This can lead to a contamination of the coated device with solvent. To avoid these problems, a one-step coating approach that provided linkable groups at the surface was developed. The introduction of an active ester group allowed the direct linkage of molecules containing amino groups.<sup>[60]</sup> A biotin-based diamine was used as test ligand. Biotin is known for its good interactions with streptavidin that is an often-used immobilization protein. An approach comparable to that shown in **Figure 7** was used and proved the success of the immobilization of biomolecules



**Figure 5.** A) Poly(*n*-butyl-*p*-xylylene) nonwovens showed superhydrophobic properties when electrospun at 75% humidity. SEM images proved that mechanical treatment with stretching of B,C) 50% and D,E) 100% had no influence on the bead-on-string architecture and porous surface morphology. Reproduced with permission.<sup>[52]</sup> Copyright 2016, Wiley-VCH.

to the reactive PPX coating. Functionalized PPX was also used to immobilize proteins by site-specific and nonspecific coupling approaches. Therefore, maleimide- and *N*-hydroxy-succinimide-substituted PPX copolymer was synthesized.<sup>[61]</sup> The simultaneous pyrolysis of two different precursors in separated sublimation and pyrolysis zones allowed the formation of copolymers consisting of three building blocks. If the inlets to the deposition chamber were opposite to each other, gradient copolymers were obtained.<sup>[62]</sup> The usage of different functional groups allowed the orthogonal immobilization of different biomolecules.

The introduction of unsaturated groups unlocked further reactions due to the higher reactivity of these groups. Both vinyl and ethynyl groups were attached to the benzylic ring of the backbone. Lahann and co-workers tried to polymerize the mono- and disubstituted ethynyl[2.2]paracyclophane in which only the monosubstituted precursor gave side product-free and stable polymer films.<sup>[63]</sup> Like other PPX, the poly(ethynyl-*p*-xylylene-*co-p*-xylylene) copolymer exhibits insolubility and good adhesion to various substrates. It was observed that cross-linking probably occurs at elevated temperatures but no further investigation concerning this observation was done in this study. Conversion with an azide-containing biotin ligand and subsequent incubation with streptavidin solution was performed to test the ability of the ethynyl groups to “click” (Figure 7). By using the microcontact printing

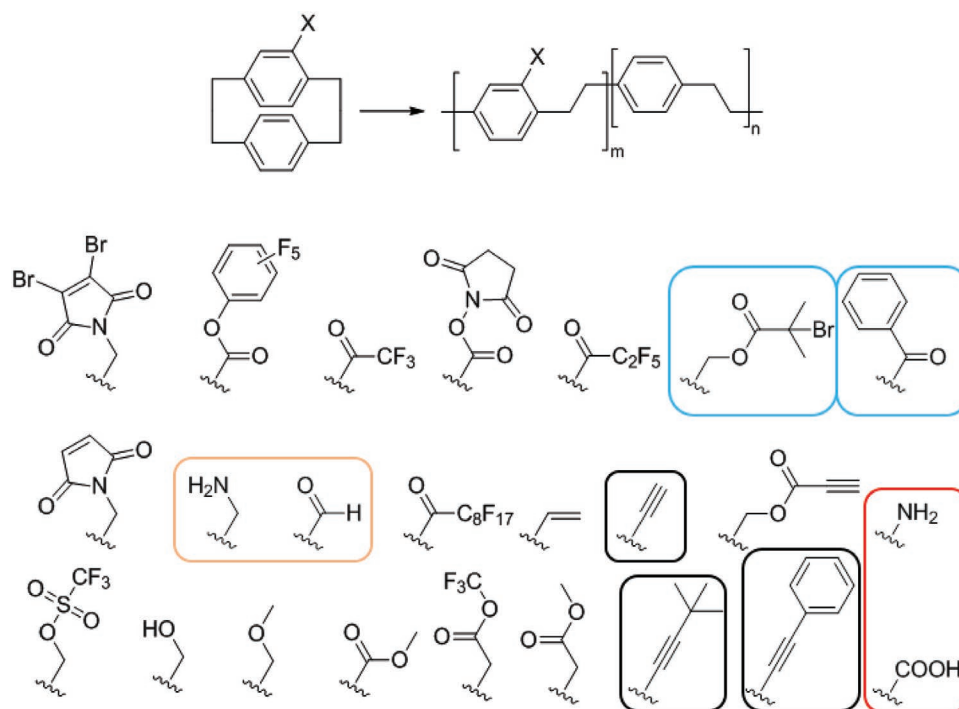


**Figure 6.** Structure of poly(dimethoxy carbonyl-*p*-xylylene) (1), poly(dicarboxylic anhydride-*p*-xylylene) (2), and poly( $\gamma$ -butyryl lactone-*p*-xylylene) (3).

approach, the spatial control of this process was confirmed. Later, the ethynyl as well as the vinyl-functionalized PPX was used for thiol–ene and thiol–yne “click” reactions of thiol-functionalized polyethylene glycol.<sup>[64]</sup> Also investigations on the cross-linking were later done and examinations via DSC of the ethynyl precursor proved that cross-linking starts at 160 °C.<sup>[33]</sup> The copolymer poly(ethynyl-*p*-xylylene-*co-p*-xylylene) was not analyzed with DSC due to a less amount of polymer. But IR spectroscopy indicated the cross-linking for the copolymer due to the loss of the C–H stretch vibration. Measurements of the coefficient of thermal expansion before and after the annealing showed a significant decrease from 121 to 53 ppm °C<sup>-1</sup> after the cross-linking. Recently, phenylethynyl and *tert*-butylethynyl PPX copolymers were synthesized and it was shown that these polymers exhibit good thermal stabilities due to cross-linking.<sup>[65]</sup> The poly(*tert*-butylethynyl-*p*-xylylene-*co-p*-xylylene) possessed a low index of refraction and had no optical birefringence, whereas the phenylethynyl polymer had properties comparable to PPX-N.

Another way to cross-link PPX was accidentally discovered by Pu and co-workers when they tried to copolymerize a carboxyl-functionalized and an amino-functionalized [2.2]paracyclophane.<sup>[66]</sup> The analysis indicated the formation of amides or imides or both. The resulting material was transparent and less crystalline than PPX. The thermal degradation started slowly at 260 °C and after 400 °C, a second degradation took place. Surprisingly, the copolymer did not decompose completely and 30 wt% still remained at 800 °C.

Versatile opportunities for reactions on a PPX layer were gained through the development of poly(benzoyl-*p*-xylylene-*co-p*-xylylene).<sup>[67]</sup> Due to its structural similarity to benzophenone, this polymer can UV cross-link through hydrogen abstraction with innumerable compounds. The coating of poly(4-benzoyl-*p*-xylylene-*co-p*-xylylene) and a subsequent photopatterning with poly(ethylene oxide) was shown to be a strategy to prevent the undesired protein adsorption.<sup>[68]</sup>



**Scheme 2.** Summary of PPX copolymers made by CVD of monosubstituted [2.2]paracyclophane. Many of the shown copolymers were used for the immobilization of biomolecules such as proteins or cells. The framed functional groups were additionally used for other applications such as cross-linking (black and red frame), solventless adhesive bonding (orange), or macroinitiators (blue). The frames around two groups notify the combined use for the corresponding application.

As shown, the grafting of other polymers to PPX surfaces could enable new applications. One attempt was the use of a controlled polymerization. In a three-step synthesis, [2.2]paracyclophane could be functionalized with a 2-bromoisobutyrate group and after the CVD, the polymer poly(4-methyl-2-bromoisobutyrate-*p*-xylylene-*co-p*-xylylene) acted as ATRP initiator.<sup>[69]</sup> The grafting of oligo(ethylene glycol) methyl ether methacrylate (OEGMA) was done successfully and resulted in hydrogel films that exhibit non-fouling properties. Through masking of the substrate during the CVD, the spatially controlled grafting of OEGMA was possible (**Figure 8**).  $\epsilon$ -Caprolactone could be grafted to a PPX surface by using poly(hydroxymethyl-*p*-xylylene-*co-p*-xylylene) as macroinitiator.<sup>[70]</sup>

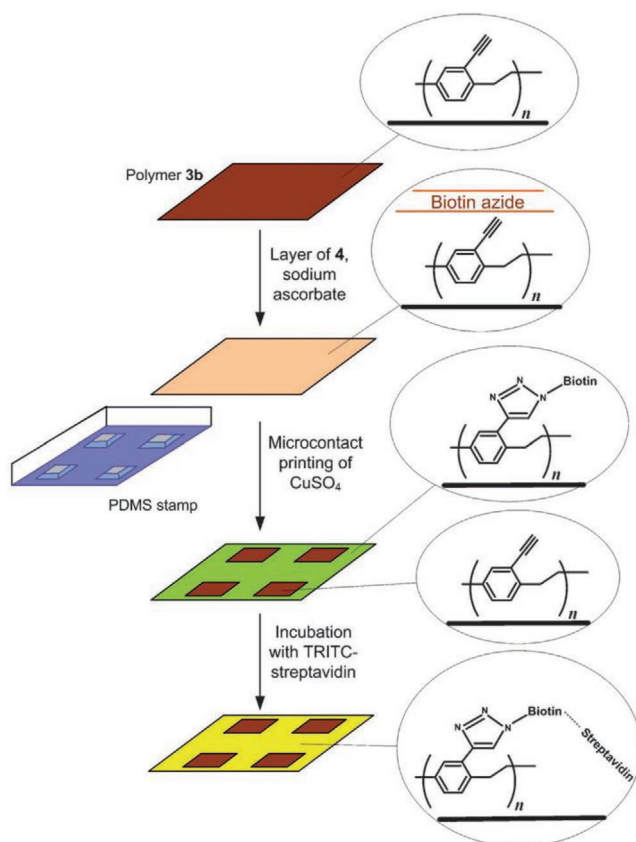
An interesting approach, the so-called solventless adhesive bonding, to glue materials together was developed by Lahann and co-workers.<sup>[71]</sup> They coated one sample with a poly(aminomethyl-*p*-xylylene-*co-p*-xylylene) and the other with poly(formyl-*p*-xylylene-*co-p*-xylylene). Afterwards, the samples were brought in contact with each other and were treated thermally (140 °C). The treatment induced the reaction of the amine with the aldehyde and an imine bond was formed. No reaction was observed when the reactive surfaces were brought in contact without the subsequent thermal treatment. Even when the samples were treated alone, no reaction was observed. Additionally, it was shown that the aldehyde groups, which were not in contact with amine groups, were suitable for the immobilization of hydrazide-functionalized biotin even after the thermal treatment.

### 2.1.3. Other Precursors

PPX formation via [2.2]paracyclophanes is the most commonly used approach because of the relatively easy handling and cleanliness, without by-product formation. Nevertheless, there are some drawbacks such as the difficulty in synthesis of novel precursors, their high costs, and the sublimation of the cyclophanes that did not allow a high throughput. Thus, investigations for using other molecules as a starting material were made. These compounds have to be volatile, thermally stable, and the ability to form the appropriate quinodimethane moiety. To get quantitative PPX yields, the quinodimethane moieties have to be formed quantitatively from the starting material.

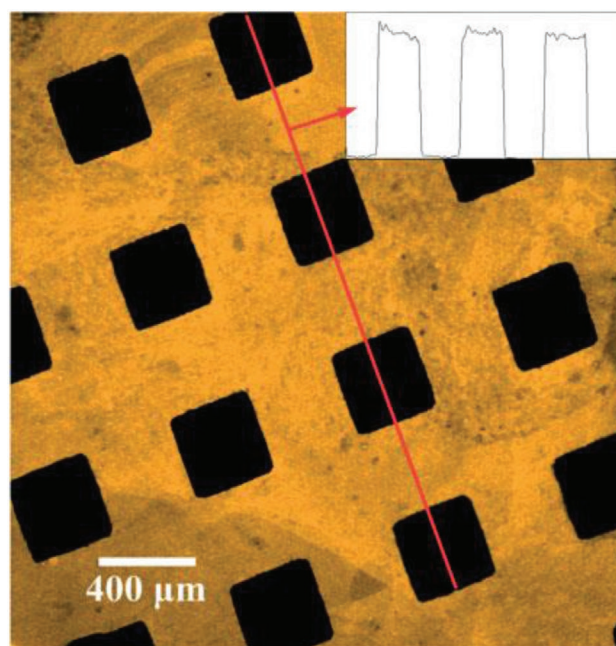
Early investigations used 1-halomethyl-4-methylbenzenes, but only for the chlorinated educt, PPX was obtained, whereas the brominated educt gave a yellow polymer that still contained bromine.<sup>[72]</sup> Later  $\alpha$ -bromo-*p*-xylylene derivative was used successfully as a starting material to receive a phenyl-functionalized PPX (**Table 3**, entry 1).<sup>[73]</sup> The product was transparent, amorphous, and soluble. Due to the solubility, it could be shown that the bulky phenyl substituent did not have any influence on the regioselectivity. The drawback of this synthesis route is the formation of hydrogen bromide that causes problems for sensitive substrates.

Other soluble, amorphous, and mostly fusible PPX derivatives could be obtained by introducing functional groups in  $\alpha$ -position.<sup>[74–76]</sup> A controlled molecular structure, where the head/tail linkage dominates, was obtained with a phenyl as



**Figure 7.** Scheme of the patterned immobilization of a biotin azide ligand onto a poly(ethynyl-*p*-xylylene-*co-p*-xylylene)-coated surface. Subsequent conversion with streptavidin proved the ability to act as bioactive coating. Reproduced with permission.<sup>[63]</sup> Copyright 2006, Wiley-VCH.

substituent.<sup>[74]</sup> Glass transition temperatures were only marginally changed by the different phenyl substituents (Table 3, entries 2–8), whereas the thermal stability can be tuned depending on the inductive effect of the substituent on the phenyl moiety. The surface energy was lowered significantly by using fluorinated substituents (entries 4, 7, and 8).<sup>[75]</sup> The phenyl-functionalized PPX (entry 2) was chloromethylated and afterwards PCL was grafted on the PPX,<sup>[77]</sup> and it was also used as precursors for the poly(phenylenevinylene) (PPV) formation. The dehydrogenation with varying amounts of 1,2-dichloro-3,4-dicyanoquinone lead to *p*-phenylenevinylene-*p*-xylylene copolymers of diverse composition.<sup>[74]</sup> Several other routes for the synthesis of PPV via PPX as precursor were developed. The PPV synthesis through a dehydrohalogenation step of a halogenated PPX precursor is favored. The pyrolysis of  $\alpha,\alpha$ -dichloroxylylene and a subsequent annealing step also gave PPV-PPX copolymers.<sup>[78,79]</sup> Here the composition of PPX to PPV units was controlled through reaction temperatures and by using a copper substrate that causes an increase in PPX fragments. Trihalogenated *p*-xylenes were also successfully used for the PPX synthesis.<sup>[37]</sup> The resulting dihalogenated PPX should be converted to poly(phenylene ethynylene) (PPE) by a double dehydrohalogenation via the PPV intermediate. But this was only partially successful due to the high thermal stability and crystallization of the halogenated PPV. The usage of



**Figure 8.** Microstructured surface after the CVD of poly(4-methyl-2-bromoisobutyrate-*p*-xylylene-*co-p*-xylylene), subsequent ATRP of OEGMA, and the exposure to fluorescence-labeled fibrinogen to show the nonspecific adsorption of proteins. The inset shows the histogram of the intensity of fluorescence. Reproduced with permission.<sup>[69]</sup> Copyright 2008, Wiley-VCH.

a trifluoroacetyl group at the phenyl group inhibited the crystallization and made the PPE synthesis possible.<sup>[80]</sup>

Not only halogenated *p*-xylylene moieties are suitable for the PPX synthesis, readily available *p*-xylylene diesters were also used successfully.<sup>[81,84]</sup> It was shown that here also the quinodimethane formed and carbon dioxide was one of the pyrolysis products. The formed pyrolysis oil contained a bunch of side products such as 4-ethylstyrene, 4-ethyltoluene, unreacted starting material, and so on. No configurational structural defects were detectable and the resulting material compares well with PPX made via Gorham's process.

Besides esters, alkoxy- and aryloxy-functionalized *p*-xylenes are suitable for the CVD. When diethers were used, several side products formed, but they have an advantage opposite the diesters, in particular a higher vapor pressure and a higher hydrolytically stability.<sup>[85]</sup> Senkevich showed that poly( $\alpha,\alpha$ -dimethyl-*p*-xylylene) could be made out of dimethoxy precursors.<sup>[82,83]</sup> The formed methoxy by-product did not really disturb the polymerization, because of its low molecular weight, it just "fly-by" the deposition chamber. The synthesis of the tetramethylated homopolymer was not successful and was explained with the steric hindrance but a copolymer with PPX could be achieved. Here, the right ratio of starting materials was important to get an alternating copolymer and no PPX block formation.<sup>[82]</sup> Aims of the studies were to improve the oxidative stability of PPX. The dimethyl homopolymer exhibits a good thermal stability up to 420 °C, but this was only deduced from thickness measurements and it was also emphasized that PPX should be annealed close to their degradation temperature after the deposition to provide higher densities and induce the

**Table 3.** Summary of the successfully polymerized PPX derivatives from “activated” *p*-xylenes by CVD.

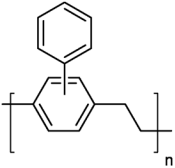
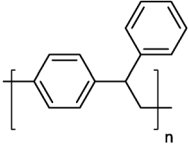
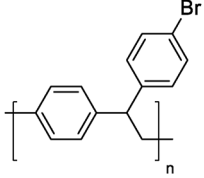
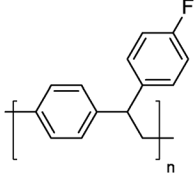
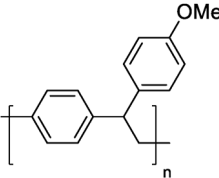
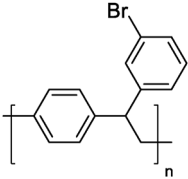
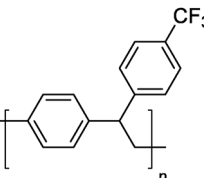
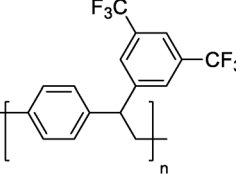
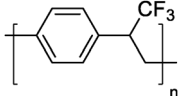
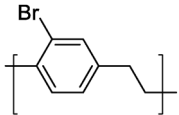
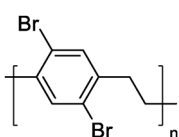
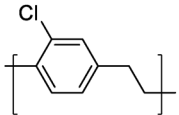
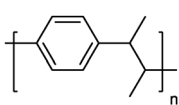
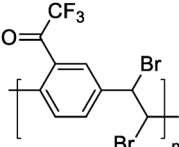
Entry	Structure	<i>p</i> -Xylene precursor	$T_g$ [°C]	$T_{5\%}$ [°C]	References
1		$\alpha$ -Bromo	107	354	[73]
2		$\alpha$ -Chloro	120	420	[74,75]
3		$\alpha$ -Chloro	126	404	[75]
4		$\alpha$ -Chloro	117	393	[75]
5		$\alpha$ -Chloro	97	368	[75]
6		$\alpha$ -Chloro	125	419	[75]
7		$\alpha$ -Chloro	129	460	[75]
8		$\alpha$ -Chloro	109	390	[75]



Table 3. Continued.

Entry	Structure	<i>p</i> -Xylene precursor	$T_g$ [°C]	$T_{5\%}$ [°C]	References
9		$\alpha$ -Chloro	89	444	[76]
10		$\alpha, \alpha'$ -Diester	–	–	[81]
11		$\alpha, \alpha'$ -Diester	–	–	[81]
12		$\alpha, \alpha'$ -Diester	–	–	[81]
13		$\alpha, \alpha'$ -Dimethoxy	–	–	[82,83]
14		$\alpha, \alpha, \alpha'$ -Tribromo	–	–	[80]

outgassing of impurities.<sup>[82,83]</sup> Nevertheless, the results indicated a higher oxidative stability for the homopolymer as well as for the copolymer.

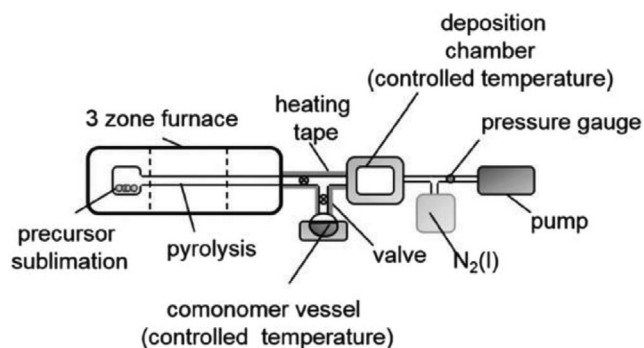
The big disadvantage of all these polymerizations with different types of precursors is the necessity to purify the product because of the formation of by-products. Suitable methods are the annealing under vacuum or the extraction. However, both purification methods have drawbacks. For example, it was shown that the extraction with solvents has an influence on the crystallinity of the polymer.<sup>[86]</sup> However, derivatives of *p*-xylene can serve as precursors for the PPX formation and represent as an alternative to the Gorham process that also has some drawbacks. But there are still some problems to solve until these compounds become a real alternative starting material.

## 2.2. PPX Copolymers

It was shown how versatile PPX can be used. But some applications require different properties so that copolymerization could lead to the needed properties. Already in the early days of the PPX chemistry, the copolymerization was investigated but only partially successful. Thus, the requirements for a successful copolymerization will be discussed.

One method for the copolymerization was the trapping of reactive *p*-xylene species in cold solvent and the addition of this solution to the comonomer.<sup>[87]</sup> By this copolymerization technique, the advantages of the CVD will get lost and will not be discussed further. But there are also PPX copolymers that were made out of the gaseous phase. Crucial for this copolymerization are the different volatilities of the used moieties. The comonomer has to be fed into the deposition chamber so that it can react with the reactive *p*-xylene moiety after this was formed by pyrolysis (Figure 9). When styrene (ST) was passed together with the *p*-xylene moiety through the pyrolysis zone, no copolymerization was observed.<sup>[88]</sup> A different approach is the solid on liquid deposition (SOLID) process in which the copolymerization is achieved by deposition onto a reactive liquid. On the surface of the liquid, the film formation takes place and the comonomer can be inserted.

Some theoretical investigations on monomer reactivity and copolymerization mechanism were published recently. Calculations indicated that the activation barrier for the copolymerization with vinyl molecules is higher for the *p*-xylylene monomer<sup>[90]</sup> than for the dimer.<sup>[91]</sup> A decrease for the activation barrier can be achieved by electronegative substituents. For example, the activation barrier for the reaction of the monomer  $\text{CH}_2=\text{C}(\text{CN})_2$  with *p*-xylylene is comparable with the *p*-xylylene

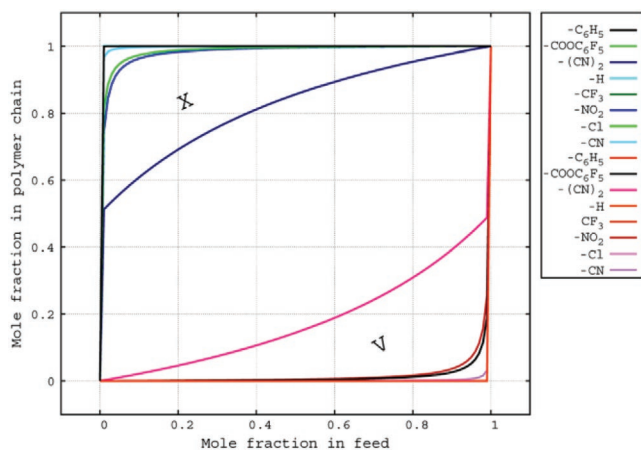


**Figure 9.** Schematic illustration of the setup that has to be used for copolymerization of PPX moieties with other gaseous comonomers. Reproduced with permission.<sup>[89]</sup> Copyright 2016, Royal Society of Chemistry.

diradical dimer formation. But most copolymerizations of *p*-xylylene with vinyl monomers will be initiated by the diradical dimer formation. These results are in good accordance with the result of Desu and co-workers who reported the necessity of at least three *p*-xylylene monomers to initiate the copolymerization of *p*-xylylene with vinyl monomers.<sup>[29]</sup> Furthermore, it was shown that independently of the last attached unit in the growing polymer chain, the connection of *p*-xylylene is energetically preferred in contrast to a vinyl monomer. Only strong electronegative substituents at the vinyl can lead to a comparable reactivity (**Figure 10**). These calculations cannot explain the real composition of so far synthesized copolymers because they are based on ideal conditions for monomer availability.

### 2.2.1. Gaseous Comonomers

Although the copolymerization is a known and often-used tool in polymer chemistry to tune materials properties, only a few examples of PPX copolymers made by CVD are described in literature. Schaeffgen and co-workers copolymerized PPX



**Figure 10.** Diagram of the copolymerization for the *p*-xylylene (X)-vinyl (V) system. The upper part represents the reactivity of the *p*-xylylene monomer, whereas the lower part shows the vinyl moiety. The diagram exhibits that the copolymer composition is almost independent of the mole fraction of the two monomers. Reproduced with permission.<sup>[92]</sup> Copyright 2012, American Chemical Society.

**Table 4.** Summary of the successfully copolymerized comonomers with PPX by CVD.

Entry	Comonomer	References
1		[72,93]
2		[72,93,94]
3		[94]
4		[94]
5		[94]
6		[95,96]
7		[95]
8		[95]
9		[97]
10		[89]

successfully with maleic anhydride and chloroprene (**Table 4**, entries 1 and 2),<sup>[72,93]</sup> whereas other comonomers such as ST did not give copolymers. They used the Szwarc route with *p*-xylylene as precursor and only obtained low yields. The success was verified by IR spectroscopy or elementary analysis, respectively, because the copolymers were insoluble. For the

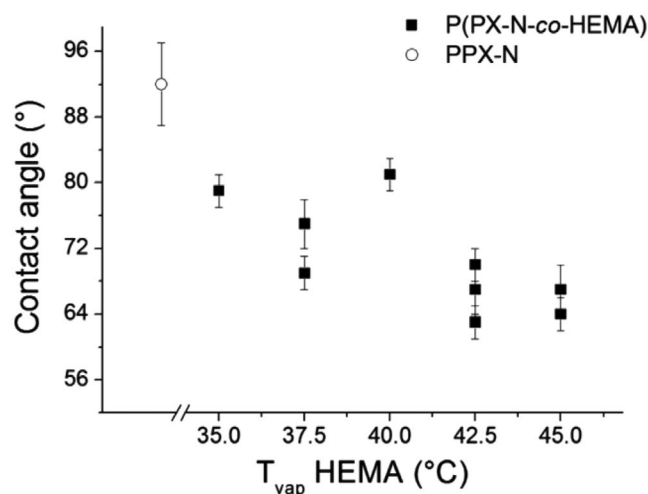
anhydride copolymer, a swelling in chloroform and acetone was observed.

Several years later, Sochilin et al. were able to copolymerize [2.2]paracyclophane with ST, maleic anhydride (MA), *N*-vinylpyrrolidone (*N*-VP), and 4-vinylpyridine (4-VP) by controlling the substrate temperature.<sup>[94]</sup> Only MA could be copolymerized when the substrate was left at room temperature. For the other comonomers, the substrate temperature had to be decreased up to  $-80$  °C. The copolymers of PPX and ST or *N*-vinylpyrrolidone (Table 4, entries 3 and 4) were brittle and not transparent, whereas the 4-VP (entry 5) copolymer exhibited good optical and mechanical properties. This study showed the importance of the deposition temperature to get homogeneous films. It was further observed that the substrate temperature decreased with the boiling and melting points of the used comonomers, and therefore concluded that the ability of comonomers to copolymerize is basically a function of their ability to condense on the substrate.

Further investigations in the 1990s showed the copolymerization with the vinyl comonomers 9-vinylanthracene (9-VA),<sup>[95]</sup> 4-vinylbiphenyl (4-VB),<sup>[95]</sup> and perfluorooctyl methacrylate (PFOMA)<sup>[95,96]</sup> (entries 6–8) at room temperature. It has to be noted that also chloro-substituted PPX was used. The properties of the homopolymers could be tuned significantly through the copolymerization. For example, led the insertion of 4-VB in PPX to a higher thermal stability in air. A steric shielding of the  $\text{CH}_2$  group or an electronegatively stabilization could be responsible for this effect. The crystallinity could be reduced by copolymerization with different amounts of PFOMA. As a result of crystallinity reduction, the refractive index and dielectric constant were decreased.

The presented copolymers consist mainly of PPX and lower contents of the corresponding comonomer. By copolymerization of poly(chloro-*p*-xylylene) and *N*-phenyl maleimide (NPM) at elevated deposition temperatures, the content of the PPX in the copolymer could be decreased significantly.<sup>[97]</sup> Different rate-limiting steps are responsible for the different deposition rates. By increasing the deposition temperature, the limiting step of the *p*-xylene moiety changes from mass flow control to surface reaction control while the comonomer still obeys mass flow control.<sup>[97]</sup> The reactivity and volatility of the comonomer is crucial for this copolymerization technique because nearly all common monomers are too volatile. One problem that occurred in this study was the inhomogeneous copolymer composition. For a deposition temperature of 70 °C, it was observed that by increasing distance into the reactor, the NPM content also increased, which means that the reactive *p*-xylene moiety was consumed faster. Whereas the deposition at 40 °C shows the contrary behavior and the NPM content decreases drastically. The properties of the obtained copolymer are comparable to the NPM homopolymer that can be explained with the low *p*-xylene content.

A drawback of the previously presented copolymers is their compositional inhomogeneity. Additionally, all presented copolymers were insoluble, and therefore there is a lack of detailed analyses. For the first time, a soluble copolymer made by CVD was synthesized by our group by copolymerization of 2-hydroxyethyl methacrylate (HEMA) (entry 10) and alkyl-substituted [2.2]paracyclophane.<sup>[89]</sup> The solubility allowed



**Figure 11.** Plot of water contact angles against HEMA evaporation temperatures indicates an increasing HEMA content in the copolymers with increasing evaporation temperature. Reproduced with permission.<sup>[89]</sup> Copyright 2016, Royal Society of Chemistry.

the characterization of the copolymer with standard methods such as NMR or GPC. The importance of the reactor design and the direction of the deposition compared to the gas flow were also discussed. Here, it was observed that the content of HEMA increases with increasing distance into the deposition chamber for alkyl copolymers when the deposition occurs parallel to the monomer flow. This result is in good accordance with the previous results and can be explained with the higher consumption of the reactive *p*-xylene moiety.<sup>[97]</sup> The influence of the evaporation and deposition temperatures was also investigated. The HEMA content increased with increasing evaporation temperature and this observation was independent of the deposition temperature.

The NMR analysis of the soluble poly(butyl-*p*-xylylene-co-HEMA) copolymer showed a splitting of several carbon signals. The head-to-tail isomerism is responsible for this splitting. Also the random distribution of the HEMA without block construction could be proven by NMR analysis. Molecular weight was determined with GPC against polystyrene standards. The obtained values of 64 000–100 000 Da were lower than the values for the PPX-butyl homopolymer.<sup>[51]</sup>

The copolymerization of HEMA and *p*-xylene was also done in a commercially available deposition unit and enables for the first time the synthesis in a bigger scale. An increasing HEMA content was again obtained with an increasing evaporation temperature. Besides IR spectroscopy, a decreasing contact angle proved the integration of higher HEMA amounts (Figure 11). The biocompatibility of poly(butyl-*p*-xylylene-co-HEMA) was tested with human umbilical vein endothelial cells and no cytotoxicity was detected.

### 2.2.2. The SOLID Process

A different method for creating PPX copolymers is the SOLID process that was successfully used by Bolognesi et al. for the copolymerization of *p*-xylylenes with unsaturated fluorenes.<sup>[98]</sup>

Incorporation of the fluorene moieties leads to a change in the photoluminescence properties of the PPX and almost reached the values of polyfluorenes. Acrylates and methacrylates were also copolymerized successfully with PPX-C by this method.<sup>[9]</sup> In this study, it was also shown that via the SOLID process, reactive groups can be incorporated into the PPX. The incorporated ester groups reacted with amines and allowed a further functionalization of the PPX film.

One major issue of all the presented copolymers is the residues of the comonomer in the final material whereby an additional cleaning step is required. Ideally, further investigations find comonomers that make the purification of the copolymer needless so that all positive aspects of the CVD can be maintained also for copolymers.

### 3. Conclusion

The CVD of PPX is a unique coating technique with a lot of advantages and leads to a polymer coating with extraordinary properties. Although this approach is already known for some decades, there is still a lack of understanding of the polymerization mechanism. Hence, especially in the last several years, research on the functionalization of PPX was done. A wide range of functional groups could be incorporated in the coatings and allowed the usage of PPX in new application areas. Bulky substituents on the benzyl ring gave soluble polymers that were processable by, for example, electrospinning or spin-casting and that could be analyzed with NMR and GPC. On the other hand, allowed amino or ester groups the immobilization of biomolecules. This functionalization enables the usage of PPX in different fields, but there are still some challenges that have to be solved. The coating efficiency of the approach is very poor and only relatively thin polymer coating is feasible. Also the synthesis of the precursor [2.2]paracyclophane molecules is very time and cost consuming; therefore, the upscaling to industrial scale is impossible. A solution for this problem could be the usage of other precursors such as  $\alpha$ -halo or  $\alpha,\alpha'$ -diester *p*-xylenes that are often easily accessible. Here, the challenge is the receiving of a pure product due to the appearance of side-reactions.

The copolymerization with monomers that are not part of the xylene family was also done successfully to obtain novel properties. Here, the identification of suitable comonomers is crucial because it has to be volatile, thermally stable, and reactive enough to copolymerize with the xylene moiety. A problem that occurred was the presence of unreacted monomers in the resulting polymer film so that a subsequent purification step is necessary.

In summary, the CVD of PPX offers a huge potential for diverse applications, but a lot of research has to be done to solve the still existing problems. Present limitations of the CVD polymerization process are the need for extensive precursor (paracyclophanes) synthesis; the high temperatures required for vaporization and pyrolysis that limit the choice of substituents; the homogeneity of the deposited film thickness and film composition; relatively long reaction times, the potential of unreacted radical chain ends of the PPX macromolecules, which could lead to unwanted hydroperoxide formation upon

contact to air; the limited control on the solid-state morphology throughout the polymerization; and for the technical application, the batch-type character of the process. All of these limitations are surely challenges for future developments of this extremely promising and useful coating technique by CVD of PPX and its derivatives, their solution, will further consolidate the role of this CVD process as a true cross-sectional technology.

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### Conflict of Interest

The authors declare no conflict of interest.

### Keywords

chemical vapor deposition, functionalization, poly(*para*-xylylene)

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