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) (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] paracyclophe 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.[1–3] 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-xyylene.[4,5] PPX (trade name Parylene) gained technical relevance when Gorham observed that the p-xylene dimer [2.2]paracyclophe 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.[6] Besides by CVD, PPX can also be synthesized via wet chemistry. The Wurtz-type coupling reaction[7,8] and the Gilch polymerization[9] 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,[10] medical devices,[11] and paper artifacts[12] or as sealing to prevent the leaching of additives out of elastomers.[13] PPX is also used in microelectronic mechanical systems.[14–16] Organic light-emitting diodes,[17] or in biological and medical applications.[18–20] 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.[21–23]

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.[7,24–27] 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]paracyclophe 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−1) that explains the high reactivity of this moiety.[28] 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.[29] Although the principal process is similar for PPX with lateral substituents, the vaporization and deposition temperatures are mostly higher for the precursors (substituted paracyclopheines). Precursors with large or temperature-sensitive substituents could be critical as they...
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.[30] 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.[31]

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.[32] Theoretically, it is not necessary to break both ethylene bonds to generate a radical 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.[6] Another proof was obtained by pyrolysis of 4-ethynyl[2.2]paracyclophane when a copolymer consisting of roughly 80% poly(ethynyl-p-xylene) and 20% poly(p-xylene) was formed.[33] As shown by Jensen and co-workers, some substrates such as some metals, their salts, and organometal complexes inhibited the growth of PPX.[34,35] 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,[36] nanotrenches,[37] fiber mats,[38,39] or open cell sponges[40] 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.[41] 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
with increasing distance (Figure 3).\cite{42} Investigations on microchannels proved this result and additionally showed that the degree of deposited PPX also was dependent on the used derivative.\cite{36}

Complex PPX structures were also created using the oblique angle deposition approach.\cite{43,44} 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.\cite{43}

2.1. Derivatives of PPX

In general, PPX can be functionalized at the phenylene moiety and at the ethanediylene moiety. Due to the insolvibility of PPX, its functionalization is challenging but several functional groups could be attached to PPX by wet chemistry.\cite{45,46} 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.\cite{47,48} 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.\cite{49}

\begin{table}[h]
\centering
\small
\begin{tabular}{|l|c|c|c|}
\hline
Property & PPX-N & PPX-C & PPX-D \\
\hline
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 \\
\hline
\end{tabular}
\caption{Properties of commercial PPX collected from the study by Fortin and Lu.\cite{32}}
\end{table}

2.1.1. Difunctionalized [2.2]Paracyclophanes as Precursors

Difunctionalized paracyclophane result in PPX with homogeneous chemical composition.

Through the introduction of bulky groups at the benzyl ring, soluble PPX could be obtained.\cite{50,51} 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 \(-10 \ ^\circ\text{C}\) and a 5% decomposition temperature of 442 \ ^\circ\text{C}.\cite{50} 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.\cite{42} Copyright 1981, Wiley Periodicals, Inc.](image1)

![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.\cite{43} Copyright 2007, American Chemical Society.](image2)
Introduction of \( n \)-alkyl chains at the benzylic ring also yielded soluble PPX (Scheme 1).\[^{[51]}\] 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-xylene) 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.\[^{[52]}\] 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.\[^{[53]}\] The resulting copolymers contained less than 15\% of alkylated \( p \)-xylene and were still transparent for thicknesses between 5 and 15 \( \mu \)m. All copolymers were insoluble as a result of the high PPX-C content. The maximum decomposition temperatures for all samples were 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.\[^{[54]}\] 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.\[^{[55]}\] The anhydride 2 was used for patterning cells and proteins on different materials.\[^{[56]}\]

### Table 2. Summary of properties of \( n \)-alkyl-substituted PPXs. Adapted with permission.\[^{[51]}\]

| \( n \)-Alkyl chain | \( T_{50}, T_{	ext{max}} \) [°C] | \( T_g \) [°C] | \( T_m \) [°C] | Young’s modulus [GPa] |
|---------------------|-----------------|--------|----------|------------------|
| Methyl              | 469, 491        | 53     | 245      | 2.51\[^{[50]}\] |
| Ethyl               | 463, 489        | 17     | –        | 1.08\[^{[50]}\] |
| Propyl              | 459, 488        | 2      | –        | 0.42/0.31\[^{[50]}\] |
| Butyl               | 444, 485        | –4     | 118      | 0.16\[^{[50]}\] |
| Pentyl              | 439, 485        | –11    | 110      | 0.12\[^{[50]}\] |
| Hexyl               | 440, 487        | –21    | 121      | 0.06\[^{[50]}\] |
| Heptyl              | 430, 486        | –26    | 120      | 0.06\[^{[50]}\] |
| Octyl               | 428, 484        | –29    | 117      | 0.04\[^{[50]}\] |

\[^{a}\]As-deposited film was tested; \[^{b}\]Between 25 and 400 °C, no melting peak was observable; \[^{c}\]Solvent-cast films were tested.

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 these 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.\[^{[57]}\]

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.\[^{[19,21,22,58,59]}\] 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.\[^{[60]}\] 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.
to the reactive PPX coating. Functionalized PPX was also used to immobilize proteins by site-specific and nonspecific coupling approaches. Therefore, maleimide- and N-hydroxysuccinimide-substituted PPX copolymer was synthesized. 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. 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 benzyllic 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. 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 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. 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.

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–1 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. 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. 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]. 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.
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, \([2.2]\text{paracyclophane}\) 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.\(^{[69]}\) 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). \(\varepsilon\)-Caprolactone could be grafted to a PPX surface by using poly(hydroxymethyl-\(p\)-xylylene-co-\(p\)-xylylene) as macroinitiator.\(^{[70]}\)

An interesting approach, the so-called solventless adhesive bonding, to glue materials together was developed by Lahann and co-workers.\(^{[71]}\) 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 \([2.2]\text{paracyclophane}\) 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.\(^{[72]}\) Later \(\alpha\)-bromo-\(p\)-xylene derivative was used successfully as a starting material to receive a phenyl-functionalized PPX (Table 3, entry 1).\(^{[73]}\) 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.\(^{[74-76]}\) A controlled molecular structure, where the head/tail linkage dominates, was obtained with a phenyl as...
substituent.[74] 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).[75] The phenyl-functionalized PPX (entry 2) was chloromethylated and afterwards PCL was grafted on the PPX,[77] 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.[74] 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 \( \alpha,\alpha' \)-dichloroxylenone and a subsequent annealing step also gave PPV-PPX copolymers.[79] 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 \( p \)-xylene were also successfully used for the PPX synthesis.[10] 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 a trifluoroacetyl group at the phenyl group inhibited the crystallization and made the PPE synthesis possible.[80]

Not only halogenated \( p \)-xylene moieties are suitable for the PPX synthesis, readily available \( p \)-xylene diesters were also used successfully.[81,84] 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.[85] Senkevich showed that poly(\( \alpha,\alpha' \)-dimethyl-\( p \)-xylene) could be made out of dimethoxy precursors.[82,83] 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.[82] 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

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

Figure 8. Microstructured surface after the CVD of poly(4-methyl-2-bromoobutyrate-\( p \)-xylene-co-\( p \)-xylene), subsequent ATRP of OEGMA, and the exposure to fluorescence-labeled fibrinogen to show the nonspecific adsorption of proteins. The inlet shows the histogram of the intensity of fluorescence. Reproduced with permission.[69] Copyright 2008, Wiley-VCH.
Table 3. Summary of the successfully polymerized PPX derivatives from “activated” p-xylene by CVD.

| Entry | Structure | p-Xylene precursor | T<sub>g</sub> [°C] | T<sub>5%</sub> [°C] | References |
|-------|-----------|---------------------|-------------------|-----------------|------------|
| 1     | Br<br>α-Bromo | 107 354 [73]         |                   |                 |            |
| 2     | Cl<br>α-Chloro | 120 420 [74,75]     |                   |                 |            |
| 3     | Cl<br>α-Chloro | 126 404 [75]         |                   |                 |            |
| 4     | Cl<br>α-Chloro | 117 393 [75]         |                   |                 |            |
| 5     | Cl<br>α-Chloro | 97 368 [75]          |                   |                 |            |
| 6     | Cl<br>α-Chloro | 125 419 [75]         |                   |                 |            |
| 7     | Cl<br>α-Chloro | 129 460 [75]         |                   |                 |            |
| 8     | Cl<br>α-Chloro | 109 390 [75]         |                   |                 |            |
outgassing of impurities.\textsuperscript{[82,83]} 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.\textsuperscript{[86]} However, derivatives of \textit{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 \textit{p}-xylene species in cold solvent and the addition of this solution to the comonomer.\textsuperscript{[87]} 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 \textit{p}-xylene moiety after this was formed by pyrolysis (Figure 9). When styrene (ST) was passed together with the \textit{p}-xylene moiety through the pyrolysis zone, no copolymerization was observed.\textsuperscript{[88]} 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 \textit{p}-xylylene monomer\textsuperscript{[90]} than for the dimer.\textsuperscript{[91]} A decrease for the activation barrier can be achieved by electronegative substituents. For example, the activation barrier for the reaction of the monomer \textit{CH}$_2$=C(CN)$_2$ with \textit{p}-xylene is comparable with the \textit{p}-xylylene

| Entry | Structure | \textit{p}-Xylene precursor | \texti{tg} [°C] | \texti{T} \textsubscript{5%} [°C] | References |
|-------|-----------|-----------------------------|----------------|-----------------|------------|
| 9     | ![Structure](image) | \textit{α}-Chloro | 89 | 444 | [76] |
| 10    | ![Structure](image) | \textit{α,α'}-Diester | – | – | [81] |
| 11    | ![Structure](image) | \textit{α,α'}-Diester | – | – | [81] |
| 12    | ![Structure](image) | \textit{α,α'}-Diester | – | – | [81] |
| 13    | ![Structure](image) | \textit{α,α'}-Dimethoxy | – | – | [82,83] |
| 14    | ![Structure](image) | \textit{α,α,α'}-Tribromo | – | – | [80] |
diradical dimer formation. But most copolymerizations of \( p \)-xylene 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 \( p \)-xylene monomers to initiate the copolymerization of \( p \)-xylene with vinyl monomers.\(^{[29]}\) Furthermore, it was shown that independently of the last attached unit in the growing polymer chain, the connection of \( p \)-xylene 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. Schaefgen and co-workers copolymerized PPX successfully with maleic anhydride and chloroprene (Table 4, entries 1 and 2),\(^{[72,93]}\) whereas other comonomers such as ST did not give copolymers. They used the Szwarc route with \( p \)-xylene 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

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**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]       |
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. The solubility allowed 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 increased 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. 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-xylene-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 64000–100000 Da were lower than the values for the PPX-butyl homopolymer. 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-xylene-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-xylenes with unsaturated fluorenes.
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.\textsuperscript{[99]} 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 \textsuperscript{[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 comonomers 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(\textit{para-}xylylene)

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