Poly(pentafluorobenzyl 2-ylidene-acetate): Polymerization and Postpolymerization Modification

Zengwen Li, Hongxin Zhang, Patrick Theato, and Stefan Bräse*

The polymerization of 2,3,4,5,6-pentafluorobenzyl 2-diazoacetate is conducted at ambient temperature and catalyzed by [(l-prolinate)RhI(1,5-dimethyl-1,5-cyclooctadiene)] or [(l-prolinate)RhI(1,5-cyclooctadiene)] yielding C1 polymers with molecular weights of 3000–4000 g mol$^{-1}$ and dispersity between 1.1 and 1.3. Incorporation of the pentafluorobenzyl group into the C1 polymer results in a different solubility when compared to its C2 analog poly(2,3,4,5,6-pentafluorobenzyl methacrylate). Efficient postmodifications via para-fluoro-thiol reaction with different thiols are conducted with this C1 polymethylene.

1. Introduction

Carbon–carbon main chain polymers are one of the most important classes of polymers that are indispensable in our daily life. Unlike ordinary vinyl polymerization, the newly developed polymerization of alkyl and aryl diazoacetates has received increasing attention in the past two decades. Transition-metal-catalyzed polymerization of diazoacetates results in polymers with only one carbon atom per repeating unit and a tethered ester branch on each of these main chain carbon atoms, so-called C1 polymers or polymethylenes. Consequently, C1 polymers feature unique properties compared to the corresponding vinyl C2 polymers. For example, hydroxyl-containing C1 polymers are more hydrophilic than their corresponding vinyl type C2 polymers. Noteworthy, classical vinyl homopolymerization of maleic acid or its derivatives cannot be conducted to yield such densely accumulated side groups on the polymer backbone.

Fluorine-containing polymers show unique properties such as considerably low surface energies, good transparency, low moisture absorption, low refractive index, and unique solubility. Denser packing of partial F-substituted phenyl groups, such as in a substituted C1 polymethylene, provides the chances not only to vary the solubility distinctively but also to address new applications. To the best of our knowledge, other functional groups that have been introduced into C1 polymers so far are epoxide, alkene, benzyl, ethylene glycol, phosphonic acid, long alkyl chains, mesogens, polycyclic aromatic hydrocarbons, and substituted cyclophosphazenes.

Postpolymerization modification is a versatile synthetic tool that introduces chemical functionalities to macromolecules, which cannot be prepared by direct polymerization from its corresponding monomers. For a functional group to be utilized for the postpolymerization modification, the following conditions must be met: i) be stable during the polymerization process; ii) allow for selective and highly efficient chemical modification under mild reaction conditions. The most commonly utilized functional groups for postpolymerization modifications are the active epoxide, dienes, and alkynes. Further, it is well-known that the pentafluorophenyl ester as a representative activated ester allows for a postmodification of vinyl polymers via amidation or transesterification. Unfortunately, it is impossible to synthesize the corresponding C1 polymer tethered with a pentafluorophenyl ester, mostly because the corresponding monomer pentafluorophenyl 2-diazoacetate (N$_2$CHCO$_2$C$_6$F$_5$) is not stable. At least all our attempts have failed. Ihara et al. have recently described the synthesis of difluorophenyl 2-diazoacetate, its C1 polymerization, and modification resulting in a five-membered cyclic imide structure which is similar to the product of the postpolymerization modification of poly(benzyl-2-ylidene-acetate).

Another important fluorinated group suitable for a postpolymerization modification is the pentafluorobenzyl (PFB) unit, which can undergo selective thiol substitution reactions of the para-fluoride (PFTR reaction). Recently, the group of Roth has reported the synthesis of poly(2,3,4,5,6-pentafluorobenzyl methacrylate) (pPFBMA) and its successful para-fluoro...
postpolymerization modifications.\[15\] To the best of our knowledge, PFB-functional motifs have only been employed in synthesizing linear polymers, hyperbranched polymers, precision networks, and vinyl types polymers, i.e., C2 polymers.\[16\] Even though PFB is an important linker of the PFTR reaction, it has not yet been explored in C1 polymer chemistry. Hence, introducing the PFB motif to C1 polymer chemistry is considerably important as it will expand the toolbox of the postmodification of C1 polymers.

Herein, for the first time, the investigation of the polymerization of pentafluorobenzyl 2-diazoacetate yielding a PFB containing C1 polymer poly(pentafluorobenzyl 2-ylidene-acetate) (pPFBDA) and its postmodification via the para-fluoro-thiol reaction (PFTR) are presented (for other (oligo)fluorobenzyl 2-diazoacetate).\[a\]

2. Results and Discussion

First, pentafluorobenzyl 2-diazoacetate (Scheme 1) and was prepared according to the literature.\[20\] For this, pentafluorobenzyl alcohol and 2,2,6-trimethyl-4H-1,3-dioxin-4-one were reacted overnight to yield (pentafluorophenyl)methyl acetoacetate, which was subsequently used for the next reaction with tosyl azide without any purification. After adding lithium hydroxide solution, pentafluorobenzyl 2-diazoacetate was obtained in a 78% yield. The monomer was characterized by \(^1\)H NMR and \(^19\)F NMR spectroscopy confirming its structure and purity, and the data are shown in Figures S1 and S2 (Supporting Information). Polymerization of pentafluorobenzyl 2-diazoacetate was investigated by utilizing two different rhodium catalysts (Table 1). The polymerization of pentafluorobenzyl 2-diazoacetate was conducted with [(L-prolinate)Rh\(_1\)(1,5-dimethyl-1,5-cyclooctadiene)] or [(L-prolinate)Rh\(_1\)(1,5-cyclooctadiene)] with a feed ratio of [monomer]/[Rh] = 50 in chloroform at ambient temperature for 72 h and yielded the respective polymers after three times precipitation in \(n\)-hexane with molar masses \(M_n = 3000–4000\) g mol\(^{-1}\) (determined by size exclusion chromatography calibrated with pMMA standards using DMAC as eluent, Figure S3, Supporting Information), however only in modest yields of 7–16%. Yellowish products were obtained when the reaction time was decreased to 24 h, which indicates the generation of oligomers and an

<table>
<thead>
<tr>
<th>Run</th>
<th>Polymer</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Yield[^{a}]</th>
<th>(M_n) [^{a}]</th>
<th>(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PFBDA</td>
<td>Rh(_1)</td>
<td>CDCl(_3)</td>
<td>10–16%</td>
<td>3410</td>
<td>1.26</td>
</tr>
<tr>
<td>2</td>
<td>PFBDA</td>
<td>Rh(_2)</td>
<td>CDCl(_3)</td>
<td>7%</td>
<td>3580</td>
<td>1.19</td>
</tr>
</tbody>
</table>

\[^{a}\]Yields range obtained after repeating two times; \[^{b}\] One SEC data of the two repeating times.

(Scheme 1) and was prepared according to the literature.\[20\]

Table 1. Screen the polymerization of pentafluorobenzyl 2-diazoacetate.

2.1. Synthesis and Polymerization of Pentafluorobenzyl 2-diazoacetate

The monomer pentafluorobenzyl 2-diazoacetate can be synthesized following the general diazo compound synthesis.
incomplete polymerization. The slow polymerization process is most probably due to the steric hindrance of the pentafluorobenzyl group. Propagation of monomer PFBDA is slower than the reported propagation of ethyl diazoacetate, and it is assumed that the generation of oligomers leads to a low yield of the polymer. PFBDA is obtained as a solid white powder, and its structure was confirmed by $^1$H NMR, $^{19}$F NMR, and IR spectroscopy (see Figures 1A,B and 2A. Catalyst [(L-prolinate)RhI (1,5-dimethyl-1,5-cyclooctadiene)] resulted in slightly better yields with similar molecular weights $M_n$. As known from the literature, diene ligands act as a stabilizing ligand to Rh during the propagation steps,[21] which indicates that 1,5-dimethyl-1,5-cyclooctadiene coordinated Rh intermediates are much more stable during the propagation of monomer. Based on the literature, N,O-ligands are involved in the initiation steps and hence influence the polymer yields as well, which indicates the dissociation of prolinate from [(L-prolinate)RhI(1,5-dimethyl-1,5-cyclooctadiene)] is easier due to the larger steric hindrance of (1,5-dimethyl-1,5-cyclooctadiene). The specific reason is not clear so far. The resulting polymers are best soluble in toluene; hence toluene was utilized to run the polymerizations. Unexpectedly, this did not increase the polymer yields, and only about 10–16% polymer was obtained.

After screening various deuterated solvents, the best NMR spectra of pPFBDA were obtained in toluene-$d_8$, as shown in Figure 1. Figure 1A shows the $^1$H NMR spectrum of pPFBDA, with the signals for the main chain methine protons a) and side-chain benzyl protons b) appearing at 3.2–3.8 and 4.5–6 ppm.

Figure 1. $^1$H NMR A) and $^{19}$F NMR B) spectra of pPFBDA in toluene-$d_8$.

Figure 2. A), ATR-IR spectrum of pPFBDA. B), TGA curve of pPFBDA upon heating at 10 °C min$^{-1}$ under nitrogen.
Table 2. Solubility of polymer poly (pentafluorobenzyl 2-yildene-acetate) (pPFBDA) and poly(2,3,4,5,6-pentafluorobenzyl methacrylate) (pPFBMA).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility of pPFBDA</th>
<th>Solubility of pPFBMA[a]</th>
<th>Solvent</th>
<th>Solubility of pPFBDA</th>
<th>Solubility of pPFBMA[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>–</td>
<td>–</td>
<td>CH$_3$CN</td>
<td>±</td>
<td>+</td>
</tr>
<tr>
<td>THF</td>
<td>+</td>
<td>+</td>
<td>CH$_3$Cl</td>
<td>±</td>
<td>n.d.</td>
</tr>
<tr>
<td>DMSO</td>
<td>±</td>
<td>+</td>
<td>Toluene</td>
<td>+</td>
<td>n.d.</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>–</td>
<td>–</td>
<td>n-hexane</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>±</td>
<td>+</td>
<td>DMF</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Dioxane</td>
<td>±</td>
<td>n.d.</td>
<td>DMAC</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Benzene</td>
<td>–</td>
<td>n.d.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] Symbols: “+”: soluble; “−”: insoluble; “±”: partly soluble; “n.d.”: no comparative literature data; [a] Data about the solubility of pPFBMA was referred to the literature. Picture of the solubility data can be found in supporting information. 1.5 mg samples were dispersed in 1 mL corresponding solvent for the check of solubility.

2.2. Solubility of pPFBDA

First tests for NMR spectroscopy measurements already revealed that pPFBDA does not have good solubility in many solvents. Thus, the solubility of pPFBDA in different organic solvents was investigated at ambient temperature, which is summarized in Table 2, along with the reported solubility of pPFBMA. When comparing the solubility of pPFBDA with its C$_2$-analogue pPFBMA, differences in the solubility can be noted. Of all screened solvents, pPFBDA was soluble in toluene, N,N-dimethylacetamide, N,N-dimethylformamide, and tetrahydrofuran but was insoluble in n-hexane, methanol, benzene, and water. Interestingly, pPFBDA was partially soluble in chloroform, acetonitrile, dichloromethane, and 1,4-dioxane, while its C$_2$ analog pPFBMA was soluble in various solvents, such as chloroform, N,N-dimethylacetamide (DMAC), Dimethyl sulfoxide (DMSO), acetonitrile, anisole, diethyl ether, pyridine, and 2,2,2-trifluoroethanol.
of the two peaks; however, their origin is unknown. Additionally, tolerated in the PFTR reaction (Figure 3E).

Noteworthy, the hydroxyl group of 11-mercaptoundecan-1-ol is aliphatic chains, the quantitative conversion was still achieved.

\[ R - SH \quad DBU \quad 45^\circ C \]

![Scheme 3](image)

Scheme 3. Para-fluoro-thiol postmodification of pPFBDA with various thiols. In all cases, anhydrous THF was used as a solvent, and conversions were confirmed by \(^{19}\)F NMR or FT-IR spectroscopy. With regards to 1 equiv. of pPFBDA repeat unit, 1.1 equiv. thiols, and 1.1 equiv. of the base was loaded and heated at 45 °C for 2 h.

splitting of the two peaks, which most possibly comes from the tactivity of the postmodified pPFBDA, mentioned in the literature; however, their specific origin on how the postmodifications changed the tactivity is not yet known. \(^{15,16}\) \(^{19}\)F NMR spectra in Figure 3D–G show clearly the expected two peaks for nonsymmetric substituted para-tetrafluorobenzene at δ ≈ −135 ppm and δ ≈ −142 ppm. In Figure 3B,E, even though the substrates have long aliphatic chains, the quantitative conversion was still achieved. Noteworthy, the hydroxyl group of 11-mercaptoundecan-1-ol is tolerated in the PFTR reaction (Figure 3E).

Interestingly, \(^{19}\)F NMR spectra 3B and 3G showed the splitting of the two peaks; however, their origin is unknown. Additionally, \(^{19}\)F NMR spectra 3E, 3F, and 3G are overlaid by sharp peaks at δ ≈ −135 ppm and δ ≈ −142 ppm, which likely originate from a partial ester cleavage during the postmodification yielding (2,3,5,6-tetrafluoro-4-(alkylthio)phenyl)methanol. As to 3F, the precursor polymer is soluble in solvent THF; however, after the postmodification reaction, the postmodified polymer is not soluble in THF because of the postmodified polymer owing so many polar functional groups. Only postmodified oligomers can be purified by precipitation, and hence, the sharp peaks were shown, and it shows the disappearance of the peak of Para-fluoro and the downfield shift of Meta-Fluoro. Based on the changes of solubility and the conversion of oligomers, the substrate of 3F also works in this postmodification. For cysteamine, even though quantitative conversion can be achieved (Figure 3G), slightly swollen products were generated during the reaction, which indicates that the amine may also have participated in the reaction and resulted in the crosslinked reaction.

Efforts to employ (3-mercaptopropyl)trimethoxysilane in the postmodification of pPFBDA under the established reaction conditions resulted in an insoluble product, likely due to the condensation reaction of the trimethoxysilane under the basic conditions. IR spectroscopy, however, revealed that the carbonyl C=O band remained intact, while the substitution on the pentfluorobenzyl ring took place (see Figure S5, Supporting Information).

3. Conclusions

A novel reactive polymethylene pPFBDA was prepared by Rh-catalyzed C1 polymerization of 2,3,4,5,6-pentafluorobenzyl 2-diazooacetate. Subsequent postmodifications via PFTR reaction were investigated. Noteworthy, pPFBDA shows differences in solubility compared to its C2 polymer analog pPFBMA. Postmodifications with aliphatic and aromatic thiols proceeded quantitatively as documented by \(^{19}\)F NMR or IR spectroscopy, and hence it resembles an efficient postpolymerization modification tool for the synthesis of functional polymethylenes. Compared to its C2 analog pPFBMA, no obvious influence on the modification efficiency of pPFBDA due to the density of active groups on the polymer backbone was discovered, underlining its potential for the synthesis of functional polymethylenes. Noteworthy, postmodifications of pPFBDA with various thiols were successful.

4. Experimental Section

Materials and Instrumentation: Unless otherwise stated, all chemicals were commercially available and used as received without further purification. Yields refer to isolated and purified products. [(L-prolinate)Rh\(^+\)(1, 5-dimethyl-1,5-cyclooctadiene)], \([18]\) [(L-prolinate)Rh\(^+\)(1,5-cyclooctadiene)], and N,N’ditosylhydrazine were synthesized as described in the literature. \(^{19}\)F NMR (377 MHz) spectra were recorded in deuterated solvents on a Bruker Advance I 400 spectrometer (AV400 I). Residual solvent signals of CHCl\(_3\) (δH = 7.26 ppm, δC ≈ 77.2 ppm) were used as reference. FT-IR spectra were recorded on a Bruker VERTEX 80 in an attenuated total reflectance (ATR) setup.

Characterization: Size exclusion chromatography (SEC) measurements were performed with DMAC as eluant containing 0.03 wt % LiBr on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 µm Mixed C columns (300 × 7.5 mm) followed by three PLgel 5 µm Mixed C columns (300 × 7.5 mm), and a differential refractive index detector at 50 °C with a flow rate of 1.0 mL min\(^{-1}\). The SEC system was calibrated against linear polystyrene or poly(methyl methacrylate) standards with molecular weights ranging from 160 to 6 × 10\(^3\) g mol\(^{-1}\). Calculations for the molecular weight of poly(N,N-dimethyl acrylamide) and poly(N-isopropyl acrylamide)/polyethylene were carried out according to a poly(methyl methacrylate) calibration, i.e., K = 14.1 × 10\(^{-3}\) dl g\(^{-1}\), a = 0.70 (PS). The molecular weight dispersity is abbreviated as D.

Monomer Synthesis: Step A: The synthesis of pentafluorobenzyl acetoacetate was done by charging a round bottom flask with pentafluorobenzyl alcohol (25 g, 126 mmol, 1.0 eq.) and 2,2,6-trimethyl-4H-1,3-dioxin-4-one (17.69 g, 125 mmol, 1.0 eq.) in 50 mL toluene. The reaction was heated overnight under reflux. Subsequently, the solvent was evaporated, and the crude product was used to synthesize propargyl 2-diazooacetate without further purification and analysis.

Step B: The synthesis of propargyl 2-diazooacetate was done by dropwise addition of tosyl azide (9.09 g, 46 mmol, 1.3 eq.) in 30 mL acetonitrile to a solution of 80 mL acetonitrile containing pentafluorobenzyl acetoacetate (10 g, 35.44 mmol, 1.0 eq.) and triethylamine (3.94 g, 39 mmol, 1.1 eq.). The reaction mixture was stirred overnight at room temperature. Subsequently, lithium hydride (2.54 g, 106 mmol, 3.0 eq.) in 100 mL water was added, and the mixture was stirred for an additional 4 h at room temperature. Afterward, the crude product was extracted three times with diethyl ether, and the combined organic phases were washed with water and dried over magnesium sulfate. For further purification, the residue
after solvent evaporation was purified by column chromatography with dichloromethane as eluent. The product was obtained as a yellow liquid. Yield: 7.4 g (78%). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$/ppm) $\delta$5.20 (2H, OCH$_2$), 4.73 (1H, CHCOO). $^{19}$F NMR (377 MHz, CDCl$_3$, $\delta$/ppm) $\delta$−140.68–143.52 (m, 2F, ortho-F), $\delta$−151.23–155.13 (m, 1F, para-F), $\delta$−160.37–166.80 (m, 2F, meta-F).

pPFBDA: Analogous to other polymerizations, $^{[23]}$ pentafluorobenzyl 2-diazoacetate (1.2 g, 4.5 mmol, 50 equivalents) and [(L-prolinate)RhI1,5-dimethyl-1,5-cyclooctadiene)] (34 mg, 0.09 mmol) were separately dissolved in 7.5 mL chloroform. Then, the monomer solution was rapidly added to the catalyst solution and the resulting solution was stirred for 72 h at room temperature, after filtering through Celite, the polymer was precipitated in hexane for 3 times and yielded a pale light solid. Yield: 160 mg (16%). $^1$H NMR (400 MHz, d$_8$-Toluene, $\delta$/ppm) $\delta$5.04 (br, 2H, OCH$_2$), 3.53 (br, 1H, CHCOO). $^{19}$F NMR (377 MHz, d$_8$-Toluene, $\delta$/ppm) $\delta$−143.80 (m, 2F, ortho-F), $\delta$−153.51 (m, 1F, para-F), $\delta$−162.54 (m, 2F, meta-F).

FT-IR (ATR) $\tilde{\nu}$ (cm$^{-1}$): 2950, 1739 (C═O), 1652, 1512 (C$_6$F$_5$), 1134, 1058, 952, 931.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

diazoacetate, para-fluoro-thiol reaction, rhodium, thiols


