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

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The polymerization of 2,3,4,5,6-pentafluorobenzyl 2-diazoacetate is conducted at ambient temperature and catalyzed by [(L-prolinate)Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] or [(L-prolinate)Rh^{I}(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 compare 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.[1] 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.[2] 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.[2b, 3] 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.[2b] To the best of our knowledge, other functional groups that have been introduced into C1 polymers so far are epoxide,[4] alkene,[5] benzyl,[6] ethylene glycol,[7] phosphonic acid,[8] long alkyl chains,[9] mesogens,[10] polycyclic aromatic hydrocarbons,[11] and substituted cyclophosphazenes.[12]

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.[4,13] 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.[14] Unfortunately, it is impossible to synthesize the corresponding C1 polymer tethered with a pentafluorophenyl ester, mostly because the corresponding monomer pentafluorophenyl 2-diazoacetate ($N_2CHCO_2C_6F_5$) 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 [2b] which are similar to the product of the postpolymerization modification of poly(benzyl-2-ylidene-acetate).[6]

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(2,3,4,56-pentafluorobenzyl methacrylate) (pPFBMA) and its successful para-fluoro

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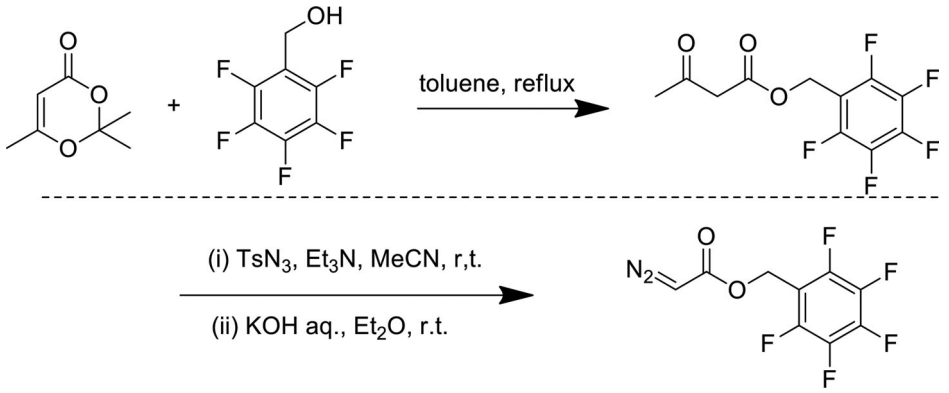
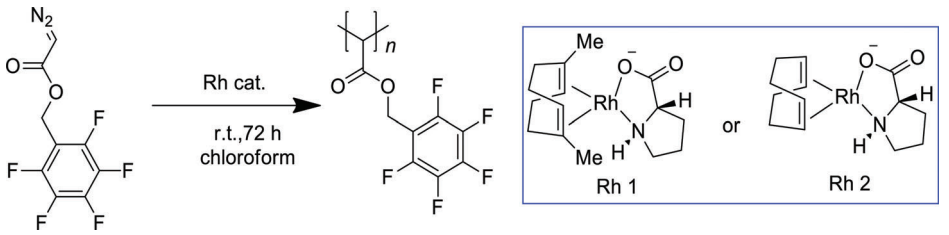


Scheme 1. Synthesis of pentafluorobenzyl 2-diazoacetate (PFBDA).



Scheme 2. Rhodium-catalyzed C1 polymerization of pentafluorobenzyl 2-diazoacetate yielding poly(pentafluorobenzyl 2-ylidene-acetate) (PPFBDA).

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**) can be easily synthesized by the general diazo-compound synthesis in good yields.[18,19] Next, polymerization of pentafluorobenzyl 2-diazoacetate was conducted under the catalysis of rhodium at ambient temperature.[20] And finally, postpolymerization modification of pPFBDA with various thiols via the PFTR reaction is explored. Meanwhile, the solubility of pPFBDA was also studied. pPFBDA was found to be completely soluble in toluene and partially soluble in the common solvents, such as dichloromethane, chloroform, acetonitrile, 1,4-dioxane (**Scheme 2**).

2.1. Synthesis and Polymerization of Pentafluorobenzyl 2-diazoacetate

The monomer pentafluorobenzyl 2-diazoacetate can be synthesized following the general diazo compound synthesis (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^{I}(1, 5-dimethyl-1,5-cyclooctadiene)] or [(*L*-prolinate)Rh^{I}(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 1. Screen the polymerization of pentafluorobenzyl 2-diazoacetate.

Run	Polymer	Catalyst	Solvent	Yield[a)]	M_n[b)]	$Đ$
1	PFBDA	Rh 1	$CDCl_3$	10–16%	3410	1.26
2	PFBDA	Rh 2	$CDCl_3$	7%	3580	1.19

[a)] Yields range obtained after repeating two times; [b)] One SEC data of the two repeating times.

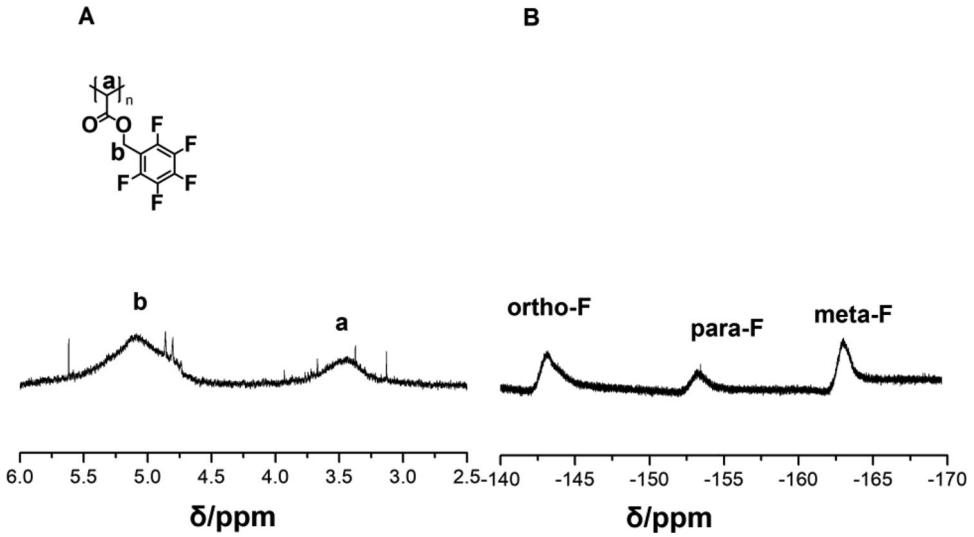


Figure 1. ^{1}H NMR A) and ^{19}F NMR B) spectra of pPFBDA in toluene-*d*8.

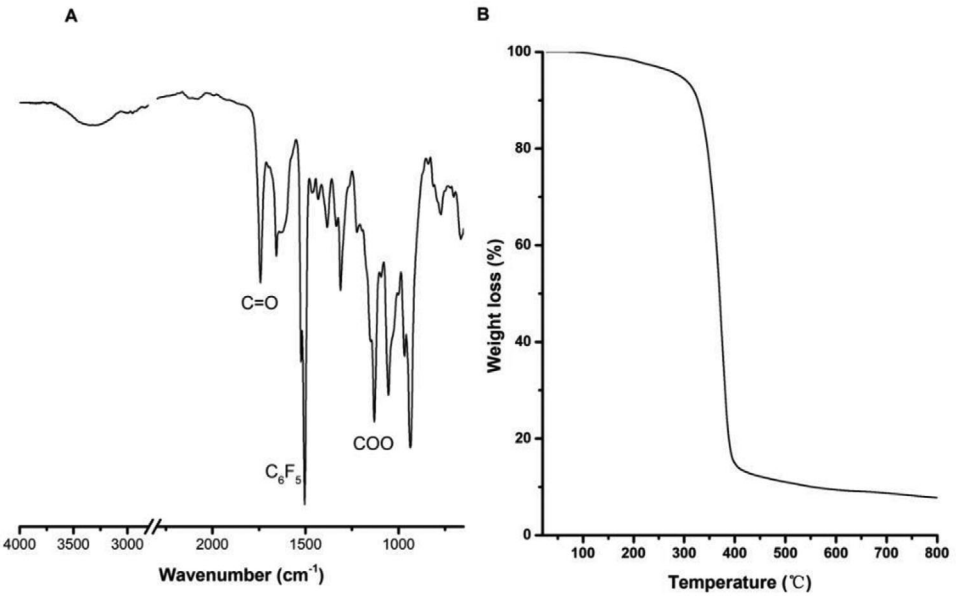


Figure 2. A), ATR-IR spectrum of pPFBDA. B), TGA curve of pPFBDA upon heating at 10 °C min^{-1} under nitrogen.

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. pPFBDA is obtained as a solid white powder, and its structure was confirmed by ^{1}H NMR, ^{19}F NMR, and IR spectroscopy (see **Figures 1**A,B and **2**A. Catalyst [(*L*-prolinate)Rh^{I} (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)Rh^{I}(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

Table 2. Solubility of polymer poly (pentafluorobenzyl 2-yildene-acetate) (pPFBDA) and poly(2,3,4,56-pentafluorobenzyl methacrylate) (pPFBMA).

Solvent	Solubility of pPFBDA	Solubility of pPFBMA[a)]	Solvent	Solubility of pPFBDA	Solubility of pPFBMA[b)]
Water	–	–	CH_3CN	±	+
THF	+	+	CH_2Cl_2	±	n.d.
DMSO	±	+	Toluene	+	n.d.
CH_3OH	–	–	*n*-hexane	–	–
$CHCl_3$	±	+	DMF	+	+
Dioxane	±	n.d.	DMAC	+	+
Benzene	–	n.d.			

[a)] Symbols: "+": soluble; "–": insoluble; "±": partly soluble; "n.d.": no comparative literature data; [b)] Data about the solubility of pPFBMA was referred to the literature;[15a] 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.

(Figure 1A), respectively. The main chain methine signals (a) are quite broad and indicate that the products are probably atactic polymers, according to the literature of other C1 polymers.[18] The obtained ^{19}F NMR spectrum (Figure 1B) clearly shows the existence of the pentafluorobenzyl unit with signals at −143, −153, and −162 ppm, respectively, similar to the reported methacrylic analog poly(pentafluorobenzyl methacrylate) (pPFBMA) by Roth et al.[15a] However, in contrast to pPFBDA, the reported ^{1}H NMR spectrum for pPFBMA features two peaks at 5.03 and 5.07 ppm as the benzyl CH_2 signals the ^{1}H NMR spectrum of pPFBDA showed differences for the benzyl CH_2 signals, as they appeared broader. Furthermore, the IR spectrum (Figure 2A) shows a strong band at 1502 cm^{-1}, typical for the aromatic $-C_6F_5$ vibration, and a strong band at 1732 cm^{-1} originating from the ester C═O carbonyl stretch. Additionally, the ester C–O group leads to a sharp signal at 1130 cm^{-1}.

Next, pPFBDA was characterized by thermogravimetric analysis (TGA), revealing that the onset temperature for the thermal decomposition of pPFBDA (Figure 2B) is 270 °C. differential scanning calorimetry (DSC) analysis (see Figure S4, Supporting Information) revealed that pPFBDA exhibits a glass transition temperature at $T_g = -18$ °C, which is significantly lower than the glass transition temperature of the pPFBMA ($T_g = 65$ °C)[15a] and poly(2,3,4,5,6-pentafluorostyrene) ($T_g = 95$ °C).[22]

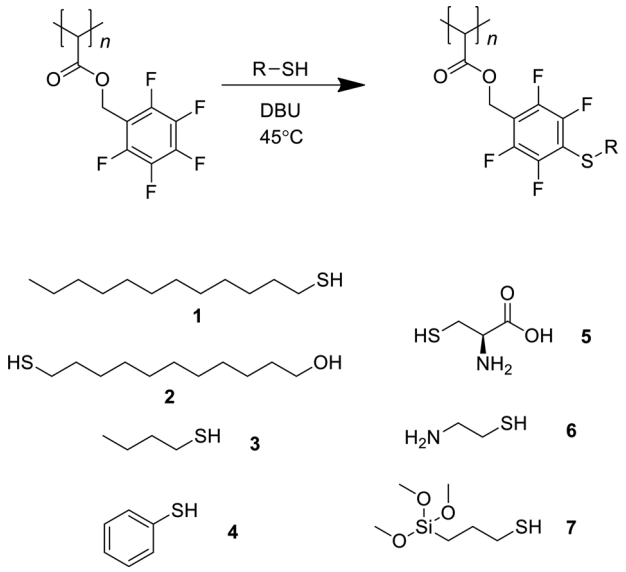
2.2. Solubility of pPFBDA

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.[15a] When comparing the solubility of pPFBDA with its C2-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 C2 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.

2.3. Postmodification of pPFBDA via PFTR

With pPFBDA in hand, its postmodification via the PFTR with different nucleophilic thiols was conducted. Dodecanethiol was utilized as a standard substrate to screen the PFTR conditions using K_2CO_3 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base.[16d, 16e] It was found that the use of DBU as a base at 45 °C resulted in full conversion within 2 h. The solubility of postmodified products was improved, which allowed for monitoring the conversions of all thiols except (3-mercaptopropyl)trimethoxysilane by ^{19}F NMR spectroscopy in $CDCl_3$. Subsequently, various aliphatic nucleophilic thiols, including those featuring a hydrophilic or hydrophobic moiety and thiophenol as an aromatic thiol, were tested for the postmodification process (**Scheme 3**). After precipitating the polymers for three times into *n*-hexane, the isolated products were characterized by ^{19}F NMR or FT-IR spectroscopy. (Fourier-transform infrared spectroscopy), and the results of postpolymerization modification are summarized in Scheme 3 and **Figure 3**B–G. Notably, because of the low yield of PPFBDA, the utilized PPFBDA for postmodification was not from the same batch (Batch 1: Figure 3C,D; Batch 2: Figure 3B; Batch 3: Figure 3E–G), and few samples containing some oligomers showed sharp peaks in ^{19}F NMR spectral (Figure 3B–G).

Quantitative conversion and selective substitution of the para-fluoride was achieved for the PFTR with dodecanethiol, 11-mercaptoundecan-1-ol, *n*-butanethiol, thiophenol, *L*-cysteine, cysteamine, (3-mercaptopropyl)trimethoxysilane, as shown by the absence of signals for the *para*-fluoride –at 153 ppm in the ^{19}F NMR spectrum of postmodified pPFBDA and a downfield shift of ≈29 ppm to roughly –135 ppm for the adjacent *meta*-fluorides (see Figures S6–S11, Supporting Information). ^{19}F NMR spectra of pPFBDA and postmodified products with thiophenol and various thiols are presented in Figure 3B–G. The signal at around δ/ppm = −123 was related to the DBU hydrofluoride salt due to the excess DBU in the reaction, labeled in Figure 3. Compared to the reported conversions of pPFBMA with thiols, no influence of the dense packing of side groups of pPFBDA on the conversion was found. Interestingly, ^{19}F NMR spectra 3B and 3C showed



Scheme 3. Para-fluoro-thiol postmodification of pPFBDA with various thiols[a]. [a]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 tacticity of the postmodified pPFBDA, mentioned in the literature; however, their specific origin on how the postmodifications changed the tacticity is not yet known. [15a]^{19}F NMR spectra in Figure 3D–G show clearly the expected two peaks for a nonsymmetric substituted para-tetrafluorobenzene at $\delta \approx -135$ ppm and $\delta \approx -142$ 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 2 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 $\delta \approx -135$ ppm and $\delta \approx -142$ 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 pentafluorobenzyl 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-diazoacetate. 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^{I}(1, 5-dimethyl-1,5-cyclooctadiene)],[18][(L-prolinate) Rh^{I}(1,5-cyclooctadiene)], and *N,N'*-ditosylhydrazine were synthesized as described in the literature.[19] ^{19}F NMR (377 MHz) spectra were recorded in deuterated solvents on a Bruker Advance I 400 spectrometer (AV400 I). Residual solvent signals of $CHCl_3$ ($\delta_H = 7.26$ ppm, $\delta_C = 77.2$ 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 eluent containing 0.03 wt % LiBr on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 µm bead-size guard column (50 × 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 × 10^6 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^{-5} dL g^{-1}, $\alpha = 0.70$ (PS). The molecular weight dispersity is abbreviated as *Đ*.

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-diazoacetate without further purification and analysis.

Step B: The synthesis of propargyl 2-diazoacetate 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 hydroxide (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

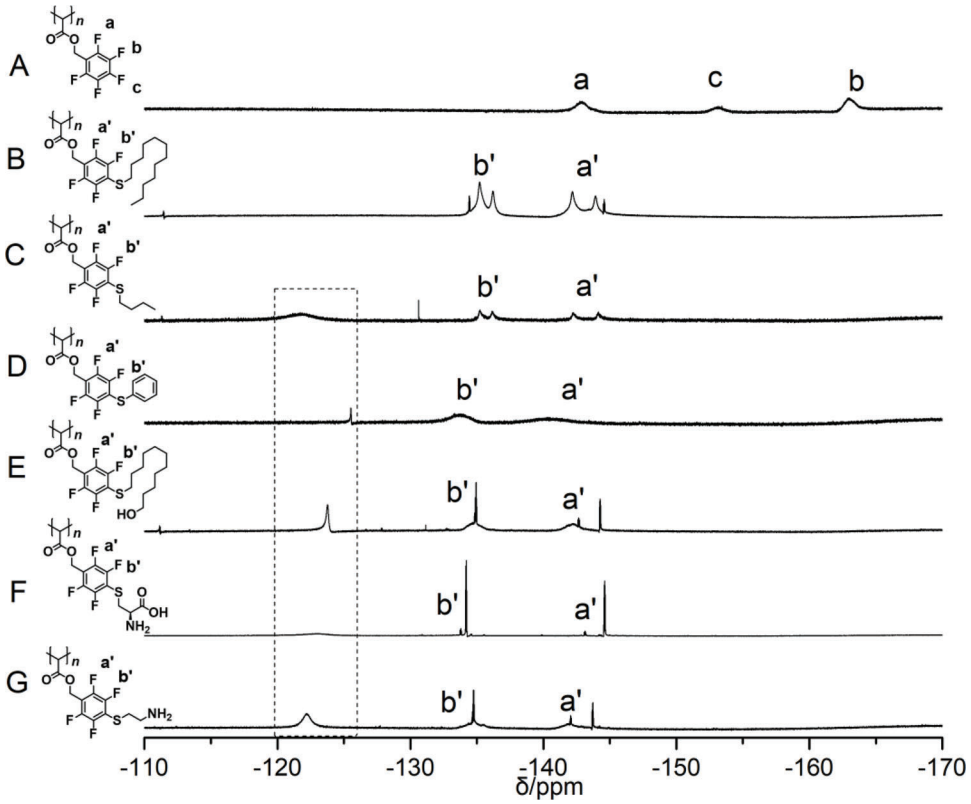


Figure 3. Conversions of PFTR reactions investigated for postpolymerization modification of pPFBDA, as determined by ^{19}F NMR in $CDCl_3$ except A), measured in d8-toluene. Peaks highlighted around $\delta = -123$ ppm were related to the DBU hydrofluoride, which could not be thoroughly removed in all cases.

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%). ^1H NMR (400 MHz, $CDCl_3$, δ/ppm) δ 5.20 (2H, OCH_2), 4.73(1H, CHCOO). ^{19}F NMR (377 MHz, $CDCl_3$, δ/ppm) −140.68–143.52 (m, 2F, *ortho-F*), −151.23–155.13 (m, 1F, *para-F*), −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)Rh^I1,5-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%). ^1H NMR (400 MHz, *d*8-Toluene, δ/ppm) 5.04 (br, 2H, OCH_2), 3.53 (br, 1H, CHCOO). ^{19}F NMR (377 MHz, *d*8-Toluene, δ/ppm) −143.80 (m, 2F, *ortho-F*), −153.51 (m, 1F, *para-F*), −162.54 (m, 2F, *meta-F*). FT-IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2950, 1739 (C═O), 1652, 1512(C_6F_5), 1134,1058, 952, 931.

General Procedure of Postmodification of pPFBDA: Polymer pPFBDA (20 mg, 0.083 mmol) and 0.5 mL THF were loaded in a vial. Afterward 1.1 equivalent thiol and 1.1 equivalent DBU were added. Then the solution was stirred at 45 °C for 2 h. After precipitating into methanol or *n*-hexane, the product was obtained, as confirmed by ^{19}F NMR spectroscopy. Dodecanethiol[a]: ^{19}F NMR (377 MHz, $CDCl_3$, δ/ppm): −134, −135, −136 (m, 2F, meta-F), −142, −143, −144 (m, 2F, ortho-F). 11-Mercaptoundecan-1-ol[a]: ^{19}F NMR (377 MHz, $CDCl_3$, δ/ppm): −135, −136 (m, 2F, meta-F), −142, −145 (m, 2F, ortho-F). *n*-Butanethiol[a]: −135, −137 (m, 2F, meta-F), −143, −145 (m, 2F, ortho-F). Thiophenol[a]: −134 (m, 2F, meta-F), −141 (m, 2F, ortho-F). L-Cysteine[a]: −133, −134 (m, 2F, meta-F), −143, −144 (m, 2F, ortho-F). Cysteamine[a]: −135, −136 (m, 2F, meta-F), −142, −143 (m, 2F, ortho-F), (3-mercaptopropyl)trimethoxysilane[a]: FT-IR $\tilde{\nu}$ (cm^{-1}): 3426 (O–H), 2927 (C–H), 1741(C═O), 1644 (S═C), 1502, 1478, 1115 (C–F, C–S, and C–Si), 752. [a]The product was purified by precipitation into *n*-hexane.

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

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