Synthesis and Post-polymerization Modification of Polymethylene and Polyethylene Derivatives

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M.Sc. Zengwen Li

geboren in Shandong, China

KIT-Dekan:	Prof. Dr. Manfred Wilhelm
Referent:	Prof. Dr. Stefan Bräse
Korreferent:	Prof. Dr. Manuel Tsotsalas
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The experimental achievement described in this thesis has been carried out between October 2016 and December 2017 at the Institute for Technical and Macromolecular Chemistry, University of Hamburg, between April 2018 and November 2020 in Karlsruhe Institute of Technology (KIT) under the supervision of Professor Dr. Patrick Théato, and from December 2020 to July 2021 in Karlsruhe Institute of Technology (KIT) under the supervision of Professor Dr. Stefan Bräse.

Die in dieser Arbeit beschriebenen Forschungsergebnisse wurden von Oktober 2016 bis Dezember 2017 am Institut für Technische und Makromolekulare Chemie, Universität Hamburg, von April 2018 bis November 2020 im Karlsruher Institut für Technologie (KIT) unter der Betreuung von Professor Dr. Patrick Théato, von Dezember 2020 bis Juli 2021 im Karlsruher Institut für Technologie (KIT) unter der Leitung von Professor Dr. Stefan Bräse durchgeführt.

Erklärung

Hiermit versichere ich, die vorliegende Arbeit selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet sowie Zitate kenntlich gemacht zu haben. Die Dissertation wurde bisher an keiner anderen Hochschule oder Universität eingereicht. Die elektronische Version der Arbeit stimmt mit der schriftlichen überein und die Abgabe und Archivierung der Primärdaten gemäß Abs. A (6) der Regeln zur Sicherung guter wissenschaftlicher Praxis des KIT ist gesichert.

Abstract

The radical polymerization of carbon-carbon double bonds is currently the most mature approach for preparing polymeric materials from vinyl monomers such as ethylene or methyl methacrylate. Compared to non-functionalized analogs, polymers tethered with polar grafted groups show a continuously extending range of unique material properties. However, the radical polymerization of monomers tethered with highly polar functional groups remains challenging. Fortunately, rhodium-mediated C1 polymerization with diazocarbonyl compounds is available to prepare polymethylenes and provides the possibility to synthesize polymers grafted with highly polar side groups. Diazocarbonyl compounds utilized as monomers for the C1 polymerization are quite sensitive to temperature and light, which results in a considerably limited scope of the monomers available for C1 polymerization. Therefore, post-polymerization modification with its extensively available and highly efficient reactions provides an alternative approach to further decorate polymers with potentially novel functions.

My thesis mainly focuses on the rhodium mediated C1 polymerization to prepare polymethylenes tethered with polar side chains and demonstrates various methods to modify the obtained polymethylenes. First, various functional polymethylenes tethered with propargyl, pentafluorobenzyl, 4-fluorophenolate, 3,5-difluorophenolate, and (2,2-dimethyl-1,3-dioxolan-4-yl)methanolate as side groups were successfully prepared and characterized. Subsequently, post-polymerization modification via copper-catalyzed azide-alkyne reaction (CuAAC), para-fluoro-thiol reaction (PFTR), and deprotection of 2,2-dimethyl-1,3-dioxolane via hydrolysis were demonstrated. Similarities and differences in terms of post-modification efficiency of the functional polymethylenes compared with their structural analogs (polyethylenes) are disclosed and discussed as well.

Although post-modification is a robust and highly efficient method to prepare novel polymers, the organic reactions utilized for post-modification are still relatively limited. Hence, the discovery of highly efficient and mild methodologies for the post-modification of polymers via currently developed organic reactions, such as cross-coupling reactions or carbon-hydrogen bond activation (C–H bond activation), are also meaningful. They can enrich the toolbox of post-polymerization modification and be promising to prepare a large amount of novel polymeric materials. Specifically, copper-catalyzed reactions between poly(propargyl acrylate) (PPA) and various diazo compounds are presented and discussed in this dissertation. The quantitative conversion was obtained when the same reaction was used in the post-modification of PPA. Unexpectedly, a part allenic motif in the obtained polymer was discovered, utterly different from the only 3-alkynoate obtained in its corresponding small molecule. The ratio of the two isomers allenic motif and 3-alkynoate is about 1: 1. This is the first time that the highly active allenic functional motif was attached to the polymer side chains via a post-modification method.

Zusammenfassung

Die radikalische Polymerisation von Kohlenstoff-Kohlenstoff-Doppelbindungen ist derzeit der ausgereifteste Ansatz zur Herstellung von polymeren Materialien aus Vinylmonomeren wie Ethylen oder Methylmethacrylat. Im Vergleich zu nicht funktionalisierten Analoga zeigen Polymere, an welche gepfropfte polare Gruppen gebunden sind, einen sich kontinuierlich erweiternden Bereich einzigartiger Materialeigenschaften. Die radikalische Polymerisation von Monomeren mit hochpolaren, funktionellen Gruppen bleibt jedoch eine Herausforderung. Glücklicherweise steht die Rhodium-vermittelte C1-Polymerisation mit Diazocarbonylverbindungen zur Herstellung von Polymethylenen zur Verfügung und bietet die Möglichkeit, mit hochpolaren Seitengruppen gepfropfte Polymere zu synthetisieren. Diazocarbonylverbindungen, die als Monomere für die C1-Polymerisation verwendet werden, sind sehr temperatur- und lichtempfindlich, was zu einem erheblich begrenzten Umfang der für die C1-Polymerisation verfügbaren Monomere führt. Daher bietet die Post-Modifikation nach der Polymerisation mit ihren umfassend verfügbaren und hocheffizienten Reaktionen einen alternativen Ansatz, um Polymere mit möglicherweise neuartigen Funktionen weiter zu dekorieren.

Diese Arbeit konzentriert sich hauptsächlich auf die Rhodium-vermittelte C1-Polymerisation zur Herstellung von Polymethylenen mit polaren Seitenketten, und zeigt verschiedene Methoden zur Modifizierung der erhaltenen Polymethylene auf. Zunächst wurden verschiedene funktionelle Polymethylene mit Propargyl-, Pentafluorbenzyl-, 4-Fluorphenolat-, 3,5-Difluorphenolat-, und (2,2-Dimethyl-1,3-dioxolan-4-yl)methanolat-Seitengruppen erfolgreich hergestellt und charakterisiert. Anschließend wurde nach der Polymerisation eine Post-Modifikation über eine kupferkatalysierte Azid-Alkin-Reaktion (CuAAC), eine Para-Fluor-Thiol-Reaktion (PFTR) und eine Entschützung von 2,2-Dimethyl-1,3-dioxolan durch Hydrolyse

gezeigt. Gemeinsamkeiten und Unterschiede der funktionellen Polymethylene mit ihren Strukturanaloga (Polyethylene) werden ebenfalls gezeigt und diskutiert.

Obwohl die Post-Modifikation eine robuste und hocheffiziente Methode zur Herstellung neuer Polymere ist, sind die Anzahl der für die Post-Modifikation verwendeten organischen Reaktionen immer noch eher begrenzt. Daher ist auch die Entdeckung hocheffizienter und milder Methoden zur Postmodifikation von Polymeren über derzeit entwickelte organische Reaktionen wie Kreuzkupplungsreaktionen oder Aktivierung von Kohlenstoff-Wasserstoff-Bindungen (CH-Bindungsaktivierung) von Bedeutung. Sie können nicht nur das Portfolio der Post-Polymerisationsmodifikation bereichern, sondern auch vielversprechend sein, um eine große Menge neuartiger Polymermaterialien herzustellen. Insbesondere werden in dieser Dissertation kupferkatalysierte Reaktionen zwischen Poly(propargylacrylat) (PPAc) und verschiedenen Diazoverbindungen vorgestellt und diskutiert. Eine quantitative Umsetzung wurde erhalten, wenn die gleiche Reaktion bei der Postmodifikation von PPAc verwendet wurde. Unerwarteterweise wurde ein Teil des Allenmotivs in dem erhaltenen Polymer entdeckt, welches sich vollständig von dem einzigen 3-Alkinoat unterscheidet, das im entsprechenden kleinen Molekül erhalten wurde. Das Verhältnis der beiden Isomere Allen-Motiv und 3-Alkinoat beträgt etwa 1:1. Bemerkenswerterweise wurde das hochaktive Allen-Funktionsmotiv zum ersten Mal über ein Postmodifikationsverfahren an Polymerseitenketten ligiert.

Contents

1. Theory and Introduction

Since Staudinger demonstrated and characterized "macromolecules"[1] and was awarded the Noble Prize in Chemistry (1953) for his discoveries in the field of polymer chemistry, in the last century, polymer chemistry has witnessed monumental developments of constantly improving polymerization that can result in novel materials.[2] Polymer products have been widely utilized in many areas of our daily life and secure the high quality of life, e.g., food packing, light-weight construction and engineering materials, functional textiles, corrosion-resistant coatings, durable adhesives, agricultural films used to enhance food production, and biomedical applications ranging from artificial teeth and dental fillings to advanced drug-release systems and biocompatible materials for bone, cartilage, and tissue replacement, which are irreplaceable by conventional materials made by wood or metal alloy. Nowadays, especially their great utilization in high tech applications, such as sensors,[3] polymeric batteries,[4] organic light-emitting diodes (OLEDs) and organic photovoltaic cells (OPVs),[5] and conducting polymers,[6] have been extremely accelerated the development of polymer research and have become the vital study areas of current science. Polymer materials possess various designable properties. These range from toughness, adhesion, barrier properties (e.g., paintability, printability), solvent resistance, miscibility with other polymers to rheological properties.[7] Because of the moderate polymerization conditions and broad monomer tolerance, free radical polymerization is the most frequently utilized method by the chemical industry. However, for current polymer research, how to control the final polymer properties to meet the increasing requirements of the high-tech applications and the daily needs remains a huge challenge. As a well-known classical term said: structures determine the properties. One major factor of the structure determined the final properties originate

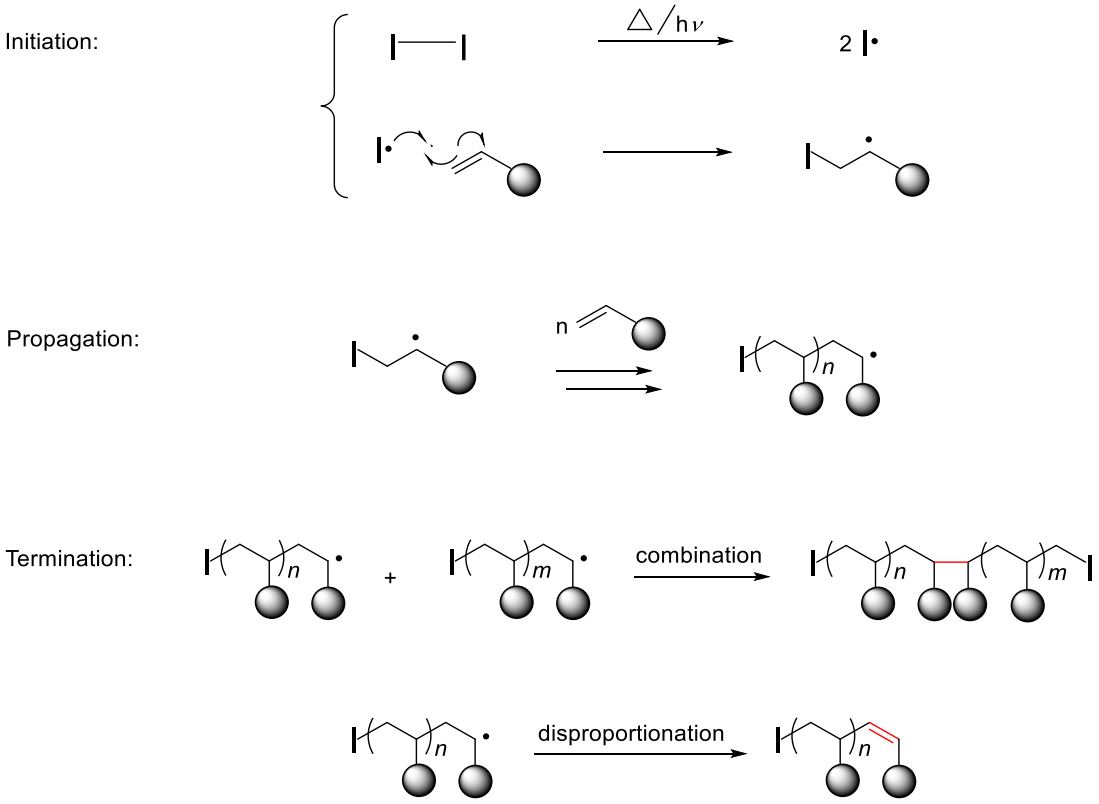
from the structure of the selected monomers and its derivatives included the density of functional groups along a polymer chain, which have an enormous influence on the physical or chemical properties of polymeric materials, i.e., toughness, surface properties, rheological properties, adhesion, and chemical reactivity of a polymer. Additionally, polymerization techniques, i.e., free radical polymerization, living polymerization, or reversible-deactivation radical polymerization (RDRP) is another kind of key element and can determine the final properties of corresponding polymers as well, since the polymerization techniques have a large effect on the molecular weight, the molecular weight distribution and the tacticity of a polymer.

To sum up, the final polymer properties are determined and can be regulated by their inner structures and polymeric techniques. Numerous efforts to discover novel polymers and polymerization methods and improve the existing polymerization methodology have been made.

1.1. Polyethylene derivatives (C2 polymer)—The most vital commercial and industrial polymers

Nowadays, most commercial and industrial polymers are prepared from the polymerization of vinyl monomer compounds. The existing C=C double bonds make the polymerization easier by conventional techniques, such as radical polymerization, cationic or anionic polymerization, and transition-metal catalyzed polymerization. Hence, because of the multiplicity of vinyl monomers and a robust polymerization platform, polyethylenes are the most dominant industrial polymers. The propagation mechanisms for the polymerization of polyethylenes and their functional derivatives are usually the addition of two carbon atoms per propagating step, the so-called C2 polymerization. Polymers produced by free radical polymerization (FRP) represent roughly 40–45% of all industrial polymers, which indicates that FRP is an essential

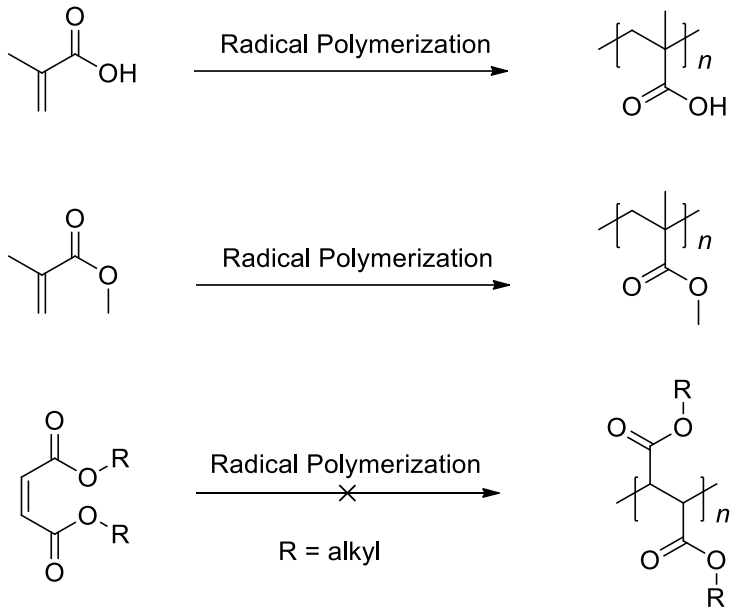
industrial polymerization technique.[8]



Scheme 1.1. Mechanism of C2 polymerization for the synthesis of polyethylene and its derivatives.

The dominant position of FRP polymerization in industry originates from several unique characteristics, such as the high tolerance of protic solvents and trace impurities (oxygen or monomer stabilizers), diverse monomers. Furthermore, the FRP polymerization is relatively easier to operate, and the polymerization conditions are mild. The mechanism of FRP polymerization mainly consists of three steps—initiation, propagation, and termination. The radicals capable of propagating are generated; the initiation step usually involves the thermally or photochemically induced homolytic bond cleavage of a radical initiator and a combination of the just generated radical initiator with one monomer unit. Afterward, the newly generated radical complex in the initiation step (including radical initiator and one monomer unit) continuously attacks

the other monomers accompanying the propagation of polymer chains until all the monomer is consumed or the chain is terminated. FRP is ideally terminated via two radicals' combination or disproportionation between two propagating chains (Scheme 1).

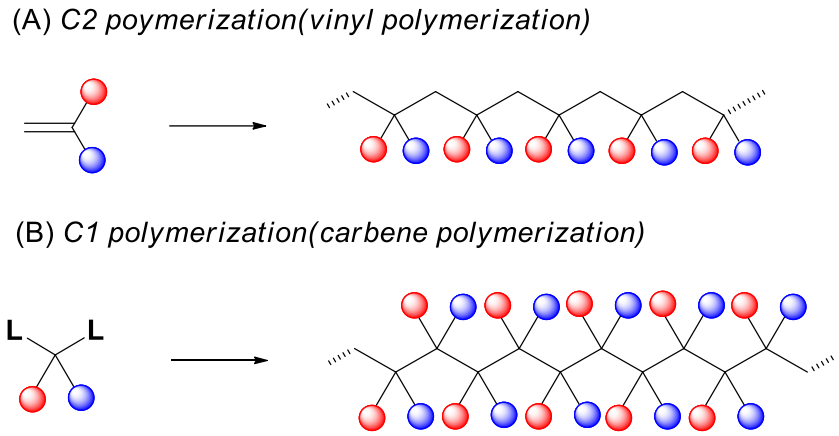


Scheme 1.2. The limitation for the radical polymerization of multiple polar groups tethered on the double bond. It is feasible to polymerize methacrylic acid and methyl methacrylate via conventional radical polymerization, while radical polymerization of the dialkyl maleate remains impossible.

Noteworthy, many polar vinyl monomers are not compatible with the conventional C2 polymerization approaches. Though it is possible to transfer methyl methacrylate (MMA) to poly(methyl methacrylate) (PMMA) and methacrylic acid to poly(methacrylic acid) via conventional radical polymerization; however, dialkyl maleates do not polymerize at all under the conventional radical polymerization (Scheme 1.2). Furthermore, though transition-metal catalyzed polymerization of polar functional vinyl compounds is an alternative approach, it often suffers from catalyst poisoning and only generates oligomers.[7b, 9] Considering the defect of conventional

polymerization techniques and the critical impact of high-polar functional groups on the properties of the final polymers,[10] it is essential to discover novel prospective polymerization techniques tolerated to distinct kinds of monomers or find alternative concepts such as post-polymerization modification.

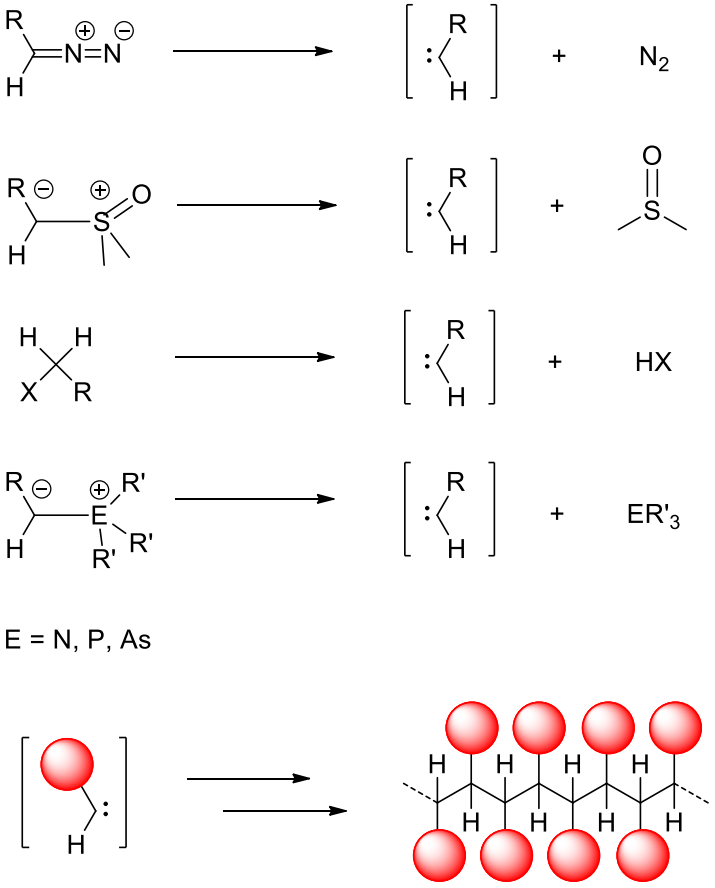
1.2. Common Approaches—For the Synthesis of Functional Polymethylenes via C1 Polymerization



Scheme 1.3. Schematic diagram between C2 polymerization and C1 polymerization.

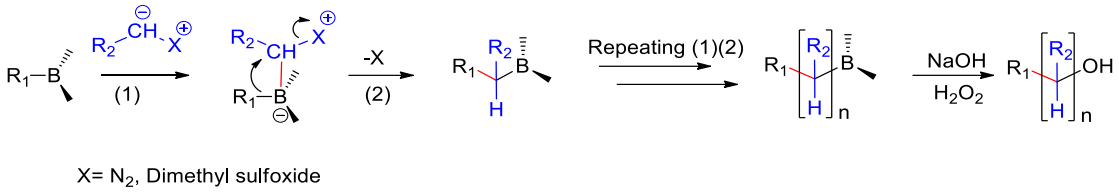
Polymethylenes are the structural analogs of polyethylenes. Compared to C2 polymerization, in the case of C1 polymerization, it involves the propagation of polymers delivering one functionalized carbon atom at each chain-growth step (Scheme 1.3). In 1898, polymerization of polymethylenes via the thermal decomposition of diazomethane was the first reported C1 polymerization - being explosive and unsafe.[11] In the last century, safer and milder methods of C1 polymerization via the use of carbenoid and carbine precursors or carbine equivalents have been developed (Scheme 1.4).[7b] The novel C1 polymerization techniques termed 'polyhomologation,' 'poly(substituted) methylene synthesis,' 'polymerization of (substituted) diazo compounds,' and 'carbene (insertion) polymerization' is regarded as a promising

technique for the synthesis of well-defined polymethylene derivatives. In all these C1 polymerization methods, *Lewis* acid and transition metals such as rhodium and palladium are commonly used as the catalyst, and the carbine precursor such as sulfoxonium ylides and diazo compounds are utilized as the monomer (Scheme 1.4).



Scheme 1.4. Carbene precursors such as diazo acetates and sulfoxonium ylides are utilized for the C1 polymerization. This approach can be utilized for preparing functional polymethylenes.

1.2.1. *Lewis* acid—Boron mediated C1 Polymerization



Scheme 1.5. The proposed addition-migration mechanism of borane mediated C1 polymerization to prepare substituted alkanes. Altered from references.[7b, 12]

Lewis acid such as boron, aluminum, and silicon are all investigated to promote the C1 polymerization; however, the most frequently utilized so far are boron catalysts. In 1966, *Tufariello* and *Lee* developed a method for the homologation of organoboranes.[13] Meanwhile, an addition-migration mechanism was proposed for a single insertion. Soon in 1967, *Kubota* and *Morawetz* reported *Lewis* acid—boron (contained in vacuum grease) mediated polymerization of diazomethane to generate highly crystalline polymethylenes with molecular weight up to 3 million Da.[14] Inspired by the work of *Tufariello* and *Lee* in 1997, *Shea* developed a method for the 'polyhomologation' of alkylboranes by reaction with sulfoxonium ylides. They obtained the linear polymethylenes with molecular weight up to 500 kDa and narrow molecular distribution (polydispersity between 1.01 to 1.20).[15]

The mechanism contains the complexation between the monomer and the boron catalysts, the subsequent 1,2-migration insertion with the elimination of one molecular nitrogen or dimethyl sulfoxide, and the final oxidation-hydrolysis to generate the ultimate polymer (Scheme 1.5). Initially, the carbon anions of the monomer (diazo alkane or sulfoxide ylides) coordinate with the boron catalyst to generate the boron complexes. Then one of the three alkyl substituents on the borane undergoes 1,2-migration to the methylene group accompanying by generating newly homologated boranes and eliminating one molecule of dimethyl sulfoxide or nitrogen. The polymethylene chain is propagated along with the repetition of these two steps. Till all

the monomers are consumed, the propagation is done; subsequently, after oxidation-hydrolysis, the ultimately substituted polymethylenes are obtained. However, one main drawback is that borane-mediated C1 polymerizations are only available for monomer diazoalkanes and polar functional monomer such as ethyl 2-diazoacetate[16] ; only oligomers are obtained.

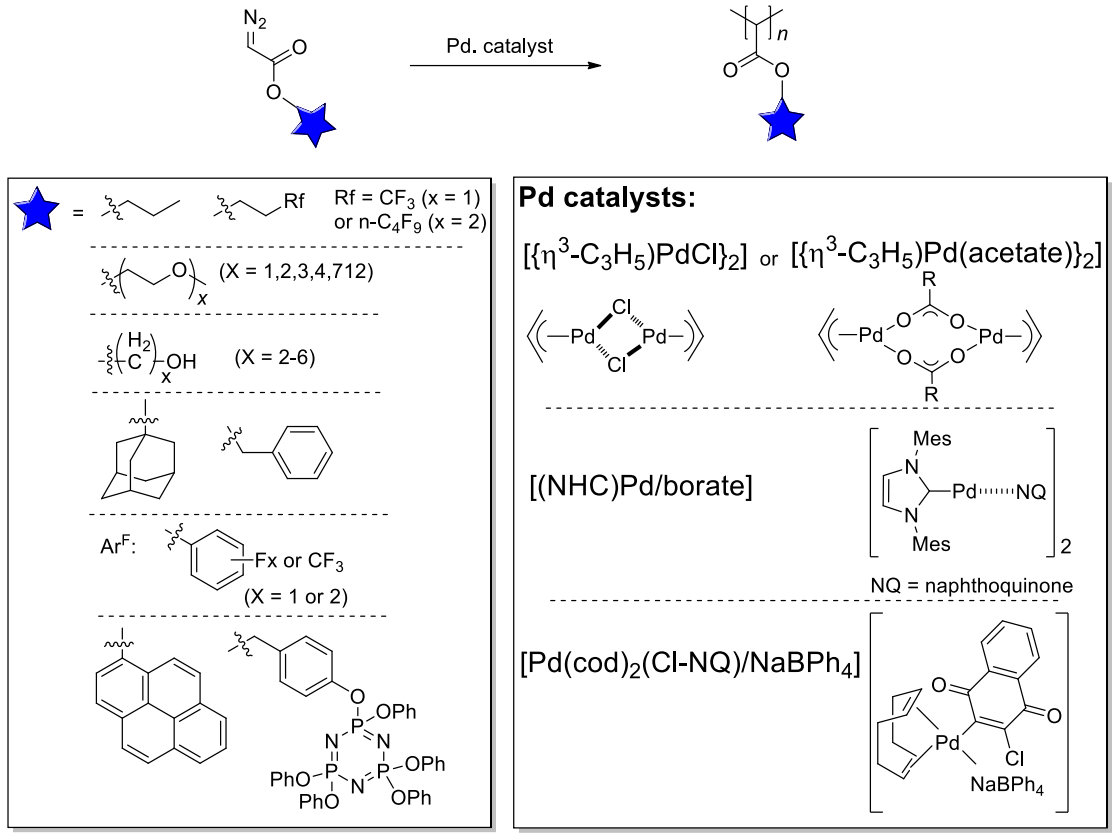
1.2.2. Transition-Metal Mediated Polymerization of C1 polymers

1.2.2.1. Homogeneous C1 Polymerization of Diazoalkanes

Catalysts such as transition metal gold[17] and copper[18] utilized in the studies of polymerization of C1 monomer diazoalkanes were reported early. Compared to the borane catalyst, transition metal gold- or copper-mediated C1 polymerization of diazomethane affords almost quantitative yields of polymethylenes. Many other heterogeneous metals can also prompt the C1 polymerization of polymethylene from diazomethane, and the details can be found in the review by *de Bruin et al.*[7b] However, compared to C1 polymerization of polyalkanes, polymerization of high polar functional monomers such as ethyl 2-diazoacetate, which are much safer than diazo alkanes, are still a challenging task because of the stability delivered by the existence of the carbonyl group adjacent to the diazo bearing carbon atom. In 2002, *Liu* and co-workers reported copper-powder mediated C1 polymerization of poly(allyl 2-ylidene-acetate) from allyl-diazoacetate, and the molecular weight of the resulted polymer reach up to 3000 Da. Shortly after this, the palladium(II) catalyzed C1 polymerization of various diazo compounds such as ethyl 2-diazoacetate or methyl 2-diazoacetate to afford polymethylene derivatives were disclosed by *Ihara* and co-workers. These are two very successful examples for the C1 polymerization of polar functional alkyl diazo compounds to generate the substituted polymethylenes. Significant progress has been made along with the synthesis of high molecular weight polymers, stereospecific

polymers, and functionalized polymers. However, among all of the polymerization methods[19], transition metal palladium[20] and rhodium[7b, 10, 21] are the most frequently utilized catalysts for the promotion of C1 polymerization of polar functional monomer—2-diazo carbonyl compounds.

1.2.2.2. Transition metal palladium-catalyzed C1 Polymerization of 2-Diazo carbonyl compounds



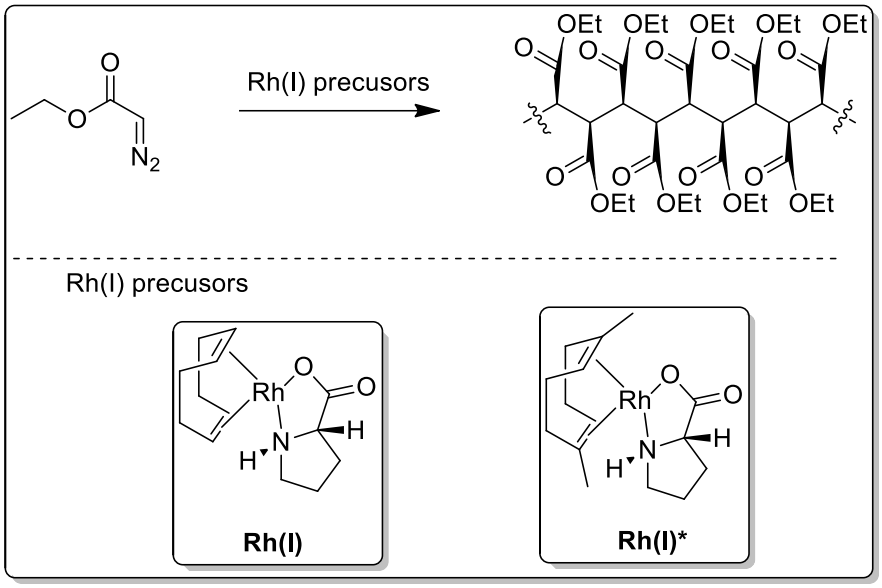
Scheme 1.6. The monomers of diazo-carbonyl compounds have been utilized in the palladium-catalyzed C1 polymerization and the commonly used palladium catalytic system.

Ihara and co-workers have done systematic studies on the development of palladium-catalyzed C1 polymerization of 2-diazo carbonyl compounds in the last twenty years.

Polymerization of distinct functional groups, such as hydroxyl group, ethylene, and polyethylene glycol, decorated polymethylenes with high yield, was reported shorter after this. Meanwhile, polymethylenes obtained by Pd(II) catalytic system are atactic. Among of all of the reported publication on C1 polymerization, Pd(II) complexes are the most frequently utilized catalysts, [allylPdCl], [allylPdCl/$NaBPh_4$] or [(NHC)Pd/Borate], *etc.,* The relevant results are concluded in Scheme 1.6.

Polymerizations of high hindered 1-adamantyl diazoacetate, pyrene-1-ylmethyl 2-diazoacetate, and cyclotriphosphazene-substituted diazoacetate were all feasible in the palladium catalysis system (Scheme 1.6). For example, in the [(NHC)Pd(II)/borate] system, controlling polymerization of cyclotriphosphazene-containing polymethylenes with high molecular weight (20600 Da) and narrow distributions (1.11) was achieved for the first time by *Ihara*. Numerous studies on the mechanism have been reported so far; however, the specific mechanism is still unclear.[20c, 20e, 20h, 22] Usually, Pd(II) species were assumed to be the critical active catalysts reported by *Ihara, Toast*.[20h, 22b] For instance, here ethyl diazoacetate (EDA) was utilized as a representative monomer to depict the mechanism: (1) generation of [L-Pd(II)-R]$^+$ active initiating species, (2) insertion of EDA into the [L-Pd(II)-R]$^+$ along with releasing of N_2, (3) termination via β-H elimination accompanying with the generation of Pd(II)-H species and the resulting polymer.[20e] The step—EDA coordinate with the Pd catalyst is the determining step. Recently, a dinuclear Pd(II) complex catalyzed mechanism in C1 polymerization was reported by *Toste* and co-workers, which showed a lower transition energy state calculated via density-functional theory (DFT) compared to the single molecular Pd(II) catalytic pathway. With the addition of naphthoquinones (nq), syndiotactic C1 polymers were first captured in Pd(nq)-based initiating system by *Ihara* and coworkers. With the use of chiral ligand, *Wu* and co-workers realized high effectively living helix-sense-selective C1 polymerization of diazoacetates.[23] The molecular weight of the obtained polymers is up to 14.8 kDa, and the narrow dispersity is 1.16.

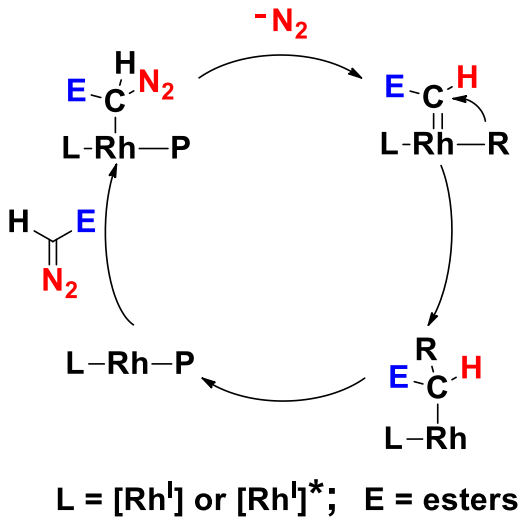
1.2.2.3. Rhodium-Catalyzed Stereoselective C1 Polymerization



Scheme 1.7. Homogeneous rhodium-mediated C1 polymerization of EDA, the obtained polymers are syndiotactic. Tow common utilized rhodium(I) precursors, such as [(*L*-prolinate)Rh^{I}(1,5-cyclooctadiene)] (Rh^{I}) and [(*L*-prolinate)Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] (Rh^{I})* are described as well.

In 2006, *Reek* and *de Bruin* reported the rhodium-catalyzed high stereoselective polymerization of EDA for the first time. In contrast to the palladium-initiating system, the obtained polymethylene derivatives via the rhodium catalysis system showed high molecular weights (up to 190 kDa) and broad dispersity (not less than 2). Notably, given the stereoregularity, the obtained polymethylenes resulting from the rhodium catalysis system are syndiotactic, shown in Scheme 1.7. Polymer yields and molecular weights highly rely on the structure of catalysts and the selected monomers. Though how the real steric effects determine the process of polymerization is not very clear so far, from the results of their experiments, it can be seen that if the monomers if the monomers mismatch with the rhodium catalysts, the subsequent yield will be very low, mostly

because the propagation steps terminate at the resting state along with the generation of oligomers such as dimers, trimers, and tetramers.[21e]



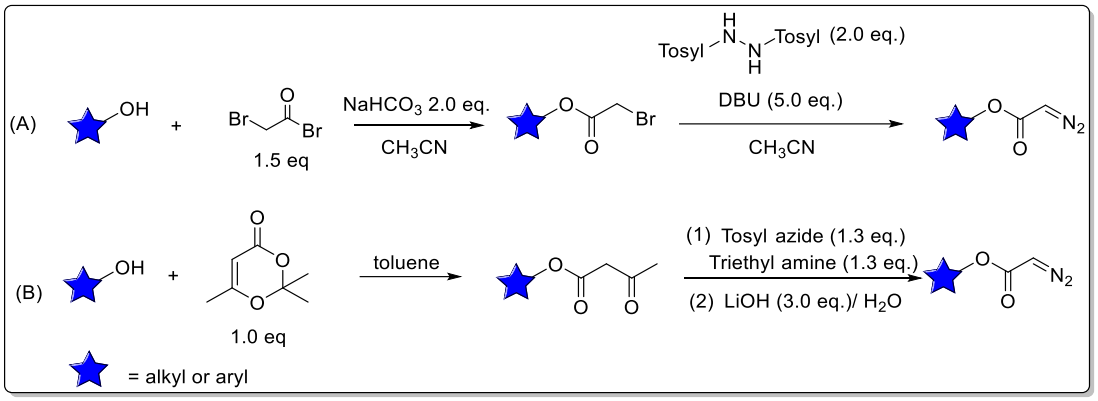
Scheme. 1.8. A schematic diagram of the proposed mechanism on the rhodium-catalyzed C1 polymerization. It involves the insertion-migration process.[24]

Diene ligands and *N,O*-ligands coordinated rhodium precursors were primarily utilized in the rhodium mediated C1 polymerization studies.[21e] The used *N,O*-ligands show sole influences on the polymer yields and no influence on the polymer properties, which is assumed that *N,O*-ligands are dissociated from the rhodium precursors in the initiating step, and they only affect the kinetics of initiation; however, the diene ligands are the rhodium-supporting ligands of the catalytically active species during the propagation steps, which determines the molecular weights and dispersity or tacticity of the target polymers.

The preliminary research on the kinetics of C1 polymerization was done by supervising amounts of releasing nitrogen gas to determine the reaction rate.[24] *Liu* discovered the more specific details on the kinetics studies of Pd- and Rh- mediated C1 polymerization using real-time FT-IR.[25] The Rh-mediated C1 polymerization of EDA showed the

first-order reaction, and the coordination between the Rh-catalyst and EDA and nitrogen-releasing was assumed as the rate-determining step. However, for the Pd-catalyzed C1 polymerization of EDA, zero-order was found, and the rate-determining step was suggested as the formation of EDA-Pd transition state through the coordination of Pd with EDA.

1.2.3. Monomers Mostly Utilized for C1 Polymerization—Diazocarbonyl Compounds

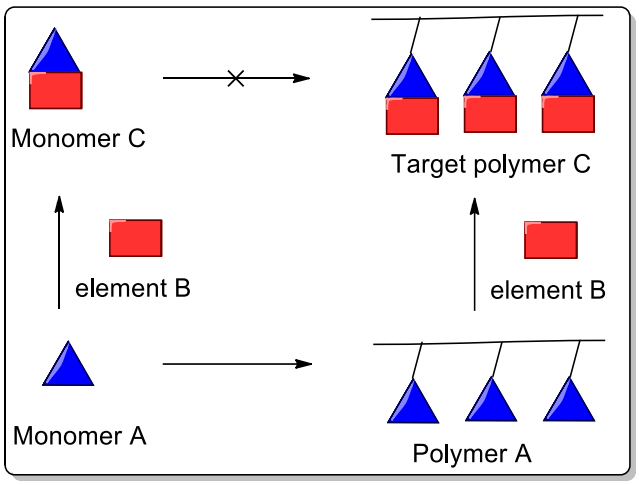


Scheme 1.9. The two most utilized procedures for the synthesis of diazo carbonyl compounds.

Though various carbene precursors can be utilized as the monomers for the C1 polymerization, the most frequently used carbene precursors are diazocarbonyl compounds, a more stable and safer compound than the other carbenes or carbene precursors. The conjugation between the carbonyl and diazo group delocalizes the π-electron of the nitrogen and increases the stability of the diazocarbonyl compounds. Since ethyl diazoacetate was first synthesized by *Curtius* [26], it opens the gate for the studies of ethyl diazoacetate. Especially because of their good compatibility with transition metals, numerous transition metal-catalyzed carbene insertion reactions were reported recently.[27] Different methodologies have been developed to synthesize

diazocarbonyl compounds, especially two of the most commonly used methods of owning the mild preparation conditions and high yields described in Scheme 1.9.[28]

1.3. Post-polymerization Modification

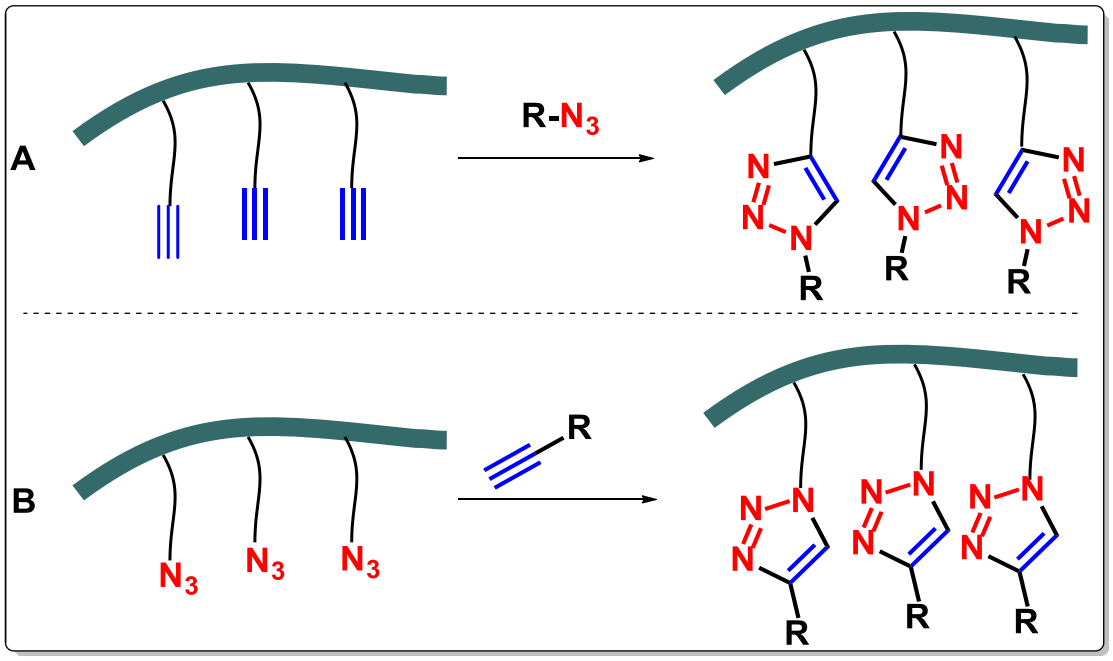


Scheme 1.10. Schematic illustration of the post-polymerization modification pathway.

Since *Serniuk* reported the functionalization of butadiene polymers with aliphatic thiols via thiol-ene addition in 1948,[29] post-polymerization modification has been evidenced as a powerful tool to engineer synthetic polymers along with the preparation of multiple polymers that cannot be synthesized by direct polymerization. Hence, post-polymerization modification provides an alternative concept and complementary pathway for the preparation of polymers compared to direct polymerization. One sketch is taken to talk about the process of post-polymerization modification. As shown in Scheme 1.10, if we intend to synthesize functionalized polymer C, two paths can be chosen. The first one is the synthesis of its corresponding monomer and thus direct polymerization of the obtained monomer C. However, usually the more complicated structure the monomers own, the harder the corresponding polymerizations will be. An alternative precursor, polymer A is selected as an anchor. This can be easily polymerized by a relatively less complicated and active monomer A. Element B reacts with the active

elements of polymer A to obtain the target polymer C. Though numerous approaches have been developed and reported for the post-modification of polymers, only are a few reactions most frequently used because the majority of them cannot result in quantitative and selective conversion at mild reaction conditions so far.[30]

1.3.1. Copper-Catalyzed Azide-Alkyne Cycloaddition reactions (CuAAC)

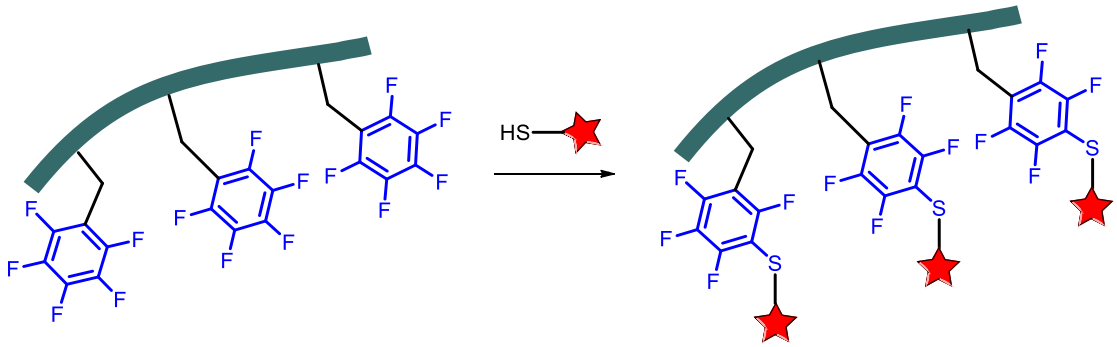


Scheme 1.11. Schematic diagram on the two possible paths of CuAAC post-modification reaction.

The azide-alkyne reaction is one kind of 1,3-dipolar cycloaddition reaction that occurred between azide and alkyne reported by *Huisgen* and co-workers in 1953, and usually, a mixture of 1,4-adduct and 1,5-adduct are obtained.[31] Later, in 2002 the copper(I)-catalyzed azide-alkyne cycloaddition reaction (CuAAC) was reported by *Sharpless* and co-workers [32], which regard as an origin point of 'Click Chemistry'. With the addition of copper, the sole regioselective 1,4-adducts were obtained, and

various functional groups, such as hydroxyl, carboxyl, amine, and hetero-rings, can be tolerated in this reaction. Interestingly, usually quantitative yields were obtained for CuAAC both in aqueous and organic solvents under moderate conditions. Although there's a drawback that the removal of copper catalysts is essential, due to excellent selectivity, quantitative yields, and mild reaction conditions, CuAAC is still one of the most frequently utilized tools in the fields of post-polymerization modification. Whether azide group or terminal alkyne tethered on the precursor polymer, the subsequent post-polymerization modification via CuAAC reaction can be performed smoothly under mild reaction conditions (Scheme 1.11).

1.3.2. Para-Fluoro-Thiol reaction (PFTR)



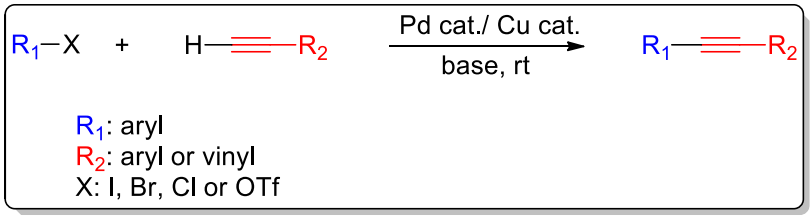
Scheme 1.12. Schematic illustration on the post-polymerization modification via Para-Fluoro-Thiol Reaction (PFTR).

The nucleophilic aromatic substitution on the perfluorinated aryl compounds can date back to the 1950s, when hexafluorobenzene and alkali methoxide or hydroxide was employed to prepare pentafluoroanisol or pentafluorophenol, respectively.[33] After that, the nucleophiles' scope for the nucleophilic substitution of perfluorinated aryl compounds was broadened to alcohols, amines, and thiols.[34] Interestingly, as to the pentafluorophenyl motifs, the substitution can only regioselectively occur on the *para*-position.[34a, 35] Compared to alcohols and amines, thiols can react with

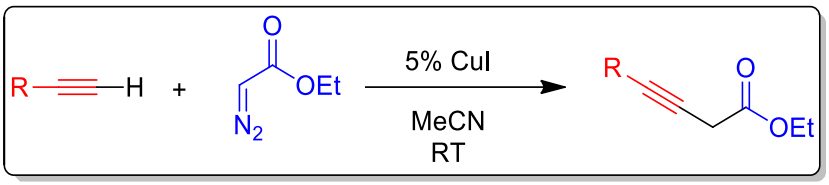
pentafluorophenyl motifs under even milder reaction conditions due to higher acidity and nucleophilicity.[36] Noteworthy, until 2010, the tetrahedral S_N2 mechanism of PFRR was verified by *Král* and co-workers through the theoretical study of transition states. In recent years, due to the quantitative conversion, excellent regioselectivity, and mild reaction conditions, the PFTR has been drawing more attention for the application in polymer chemistry, as it can be employed as a highly efficient and versatile tool for the post-polymerization of polymers (Scheme 1.12).[36-37]

1.3.3. Transition metal-catalyzed coupling reaction

In 1975, the palladium-catalyzed cross-coupling of aryl halide and terminal alkyne was reported by *Sonogashira* and co-workers (Scheme 1.13).[38] Since then, transition metal-catalyzed cross-coupling reactions of terminal alkyne have attracted more attention, and numerous works have been reported, as they can directly construct a C–C bond with high yields and under mild conditions compared to other strategies.[39] The post-modification of polymers with tethered alkynes or aryl halides has been investigated extensively. However, the recently developed copper-catalyzed carbene insertion reaction attracted our interest, as they can directly build up various functional motifs under moderate reaction conditions, such as allene (Scheme 1. 14),[40] 3-alkynoates,[41] or furan.[42]



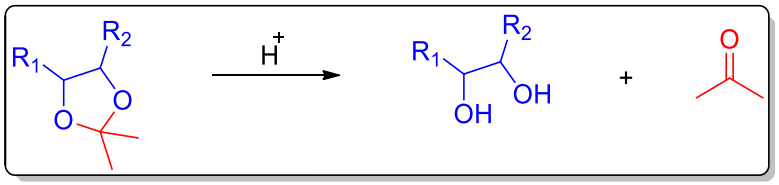
Scheme 1.13. Schematic illustration of *Sonogashira* reaction.



Scheme 1.14. The copper(I)-catalyzed reaction between a terminal alkyne and ethyl diazoacetate to synthesize 3-alkynoates directly.

1.3.4. Hydrolysis of 1,3-dioxolane—one easy way to generate two vicinal hydroxyls

Glycols or, more specific 1,2-diols are fundamental functional groups in organic synthesis and polymer or materials synthesis.[43] For example, they have strong binding ability with boronic acids, which can be utilized to prepare the self-healing borax-diol hydrogels.[43a] However, as to the high activity of the vicinal hydroxyls, usually the 1,2-diols are protected as cyclic ketals after they react with a ketone, which is stable to bases, nucleophiles, organometallics, catalytic hydrogenation, and oxidizing reagents. Meanwhile, the protecting group can be easily removed under mild reaction conditions with aqueous HCl, acetic acid, or PTSA.[44]

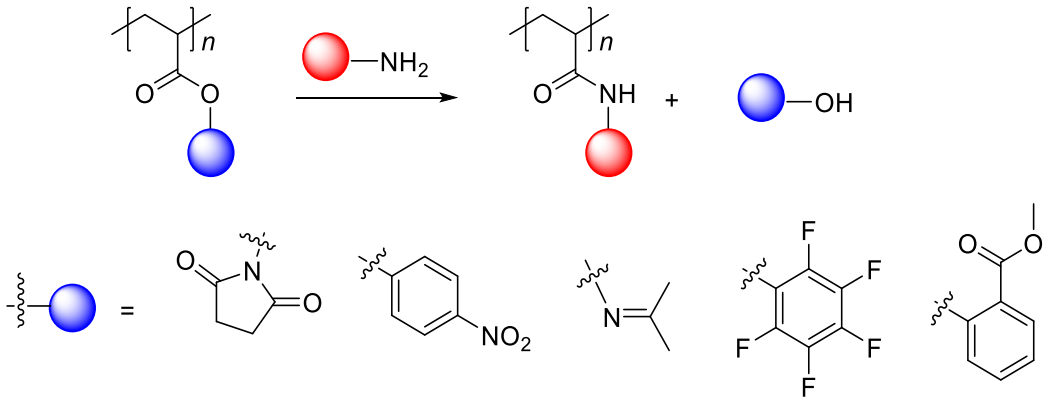


Scheme 1.15. Depicts the hydrolysis of 1,3-dioxolane to generate high active 1,2-diols.

1.3.5. Amidation or Transesterifications

Amidations or transesterifications have been proved as an efficient organic reaction in organic synthesis. These reactions need to be conducted for ordinary esters under harsh conditions, which extremely suppresses its application. In 1972, *Ferruti* and *Ringsdorf*

separately reported the post-modification of active ester contained polymer precursors via transesterification. The mainly utilized active esters include pentafluorophenol,[45] 4-nitrophenol,[46] *N*-hydroxysuccinimide (NHS),[47] acetone oxime,[48] and methyl salicylate acrylate (MSA) ester.[49]



Scheme 1.16. Aminations for the post-modification of active esters.

These active esters shown in Scheme 1.16 can go through quantitative amidation's reaction under mild conditions, which have been confirmed as valuable tools for the preparation of functional polymers.

2. Concept and Motivation

Radical polymerizations (C2 polymerizations) of vinyl compounds remain challenging if the monomers' C=C double bond is tethered with more than one polar functional group. Fortunately, rhodium-catalyzed C1 polymerization of carbene precursors (diazocarbonyl compounds) is available for the preparation of polymethylenes and provides good access to highly functional polymethylenes. However, the monomer scope suitable for C1 polymerization is still quite limited. Monomers of themselves, are unstable usually sensitizing to temperature and light. Furthermore, although the reason is not so apparent, the polar side functional groups attached to the monomers show the enormous impact on the C1 polymerization, such as yield, molecular weight, and polydispersity. Post-polymerization modification provides an alternative route to overcome these limitations and quickly and efficiently broaden the diversity of polymethylenes. The inherent highly polar side group density of functional polymethylenes becomes another critical factor that can hinder their ligating chemistry compared to their structural analogs—polyethylenes.

The project mainly focuses on broadening the scope of carbene precursors suitable for C1 polymerization and disclosing the influence of polymer's side group density on post-polymerization modification. Similarities and differences concerning the conversion efficiency of the post-modified functional polymethylenes compared with corresponding analogous polyethylenes were explicitly discussed and demonstrated using the same post-polymerization modification reaction conditions. It is well-known that the final polymer properties can be determined by the grafted side functional groups.[10] Additionally, it can be seen from the literature that the final polymer properties could be impacted by their grafted side group density [21i, 50], and the grafted side group density can influence the pathways of the post-modification as well.[20b, 21j,

[21s, 51] Hence, it is essential to conduct a specific study on the functional polymethylenes originating from the densely grafted side groups in the post-polymerization modification process.

It is indispensable to prepare suitable functional polymethylenes tethered with reactive groups that can access post-modification in the first step. The introduced reactive groups are going to be screened by the use of known and extensive post-modification techniques. The previously reported rhodium-catalyzed C1 polymerization is preferred, as it can prepare polymethylenes featuring relatively high molecule weights and perfect stereoregularity. Additionally, diazocarbonyl compounds utilized as the monomer for the rhodium-catalyzed C1 polymerization are relatively less sensitive and active than other functional ylides available for the other C1 polymerization techniques, e.g., *Lewis* acid (boron or aluminum) mediated C1 polymerization. Hence, a systematic study on the preparation of functional polymethylenes suitable for ligation chemistry and the corresponding post-modification of the obtained polymethylenes is conducted and presented.

Another project aims at discovering novel post-modification methods to enrich the current ligation techniques. Although post-modification is a robust and highly efficient method to prepare novel polymers, the organic reactions utilized for post-modification are still somewhat limited. Hence, the discovery of highly efficient and mild methodologies for the post-modification of polymers via currently developed organic reactions, such as cross-coupling reactions or carbon-hydrogen bond activation (C–H bond activation), are also important and meaningful. They can enrich the toolbox of post-polymerization modification and be promising to prepare a large amount of novel polymeric materials quickly and efficiently. Hence, the copper-catalyzed reaction between a terminal alkyne and various diazo compounds will be utilized as an example to conduct this project, as attributes of this reaction system are efficiency, mildness, and simplicity. Specifically, copper-catalyzed reactions between poly(propargyl acrylate)

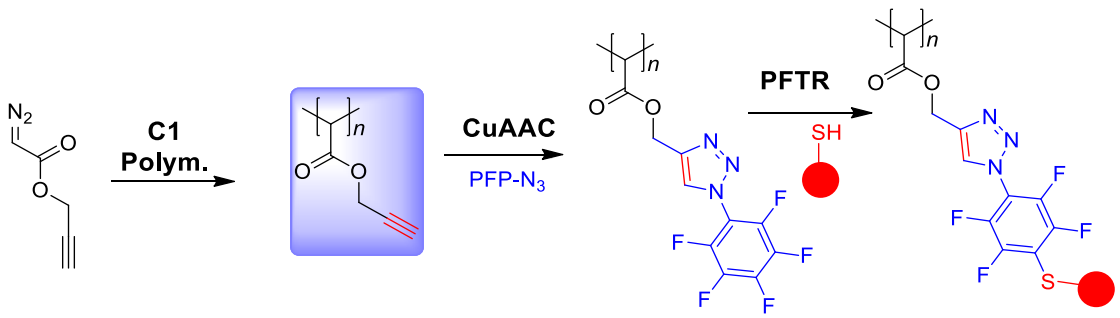
(PPA) and various diazo compounds are presented and discussed in this dissertation.

3. Results and Discussions

The following parts will cover all the results and achievements during my doctoral research. The initial approach was managed to get access to synthesize functional polymethylenes. After that, a series of functional diazo compounds were synthesized and subsequently investigated the feasibility of rhodium-catalyzed C1 polymerization. The next goal is to get access to the synthesis of various novel functional polymethylenes based on the obtained polymethylenes precursors, which can conduct post-polymerization modification facilely and efficiently.

Graphical Overview of the Works

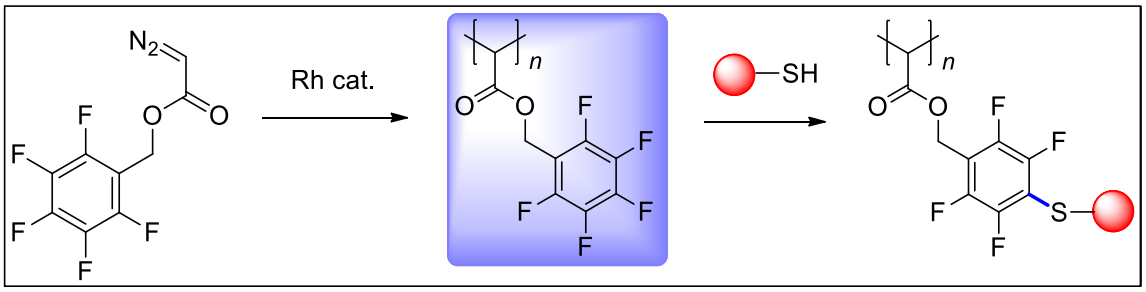
Chapter 3.1 selectively synthesizes poly(propargyl 2-ylidene-acetate) (PPA) and discusses the results of comparative research between poly(propargyl 2-ylidene-acetate) (PPA) and poly(propargyl acrylate) (PPAc) to explain the general feasibility of post-polymerization modification on functional polymethylenes via copper-catalyzed alkyne-azide cycloaddition reaction (CuAAC). Noteworthy, one consecutive post-polymerization modification was realized when pentafluorophenyl azide reacted with PPA (Scheme 3.1).



Scheme 3.1. Schematic graphical illustration of the work discussed in chapter 3.1

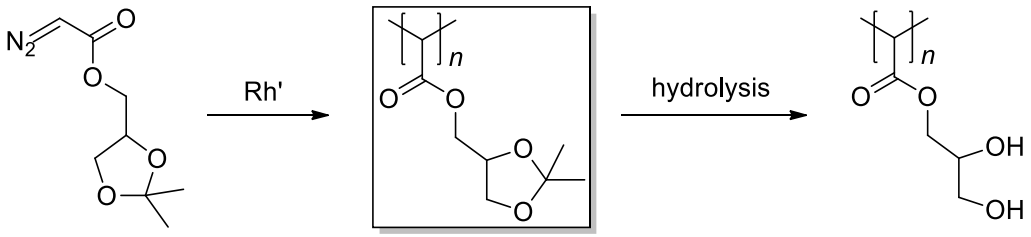
In Chapter 3.2. a first approach towards the synthesis of functional polymethylene is

described as suitable for a mild post-modification. In this part, poly(pentafluorobenzyl 2-ylidene-acetate) was firstly synthesized, and its corresponding post-polymerization modifications via Para-Fluoro-Thiol reactions (PFTR) were investigated as well (Scheme 3.2).



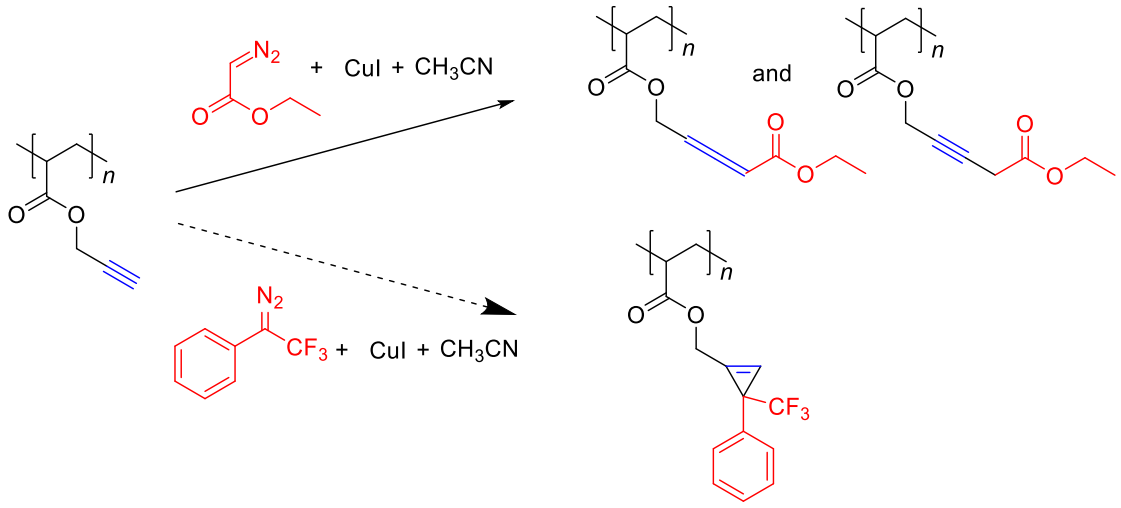
Scheme 3.2. Schematic illustration of the work discussed in chapter 3.2

Chapter 3.3 highlights poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-ylidene-acetate] as a most versatile functional polymethylene for a facile post-modification (Scheme 3.3).



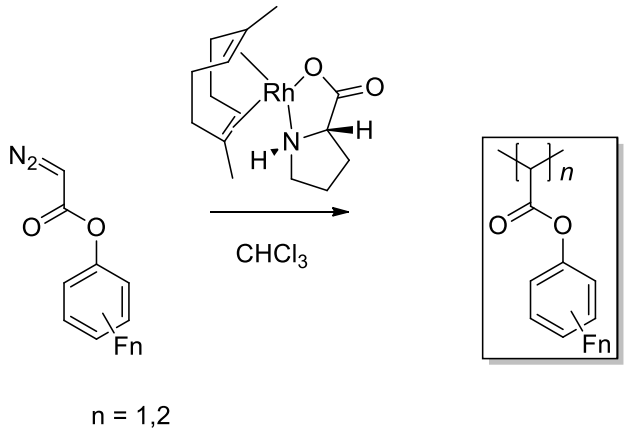
Scheme 3.3. Schematic illustration of the work discussed in chapter 3.3

Chapter 3.4 discusses the new post-polymerization modification methodology of terminal alkyne tethered polymers via copper-catalyzed reactions with diazo carbonyl and diazo alkanes (Scheme 3.4).



Scheme 3.4. Schematic illustration of the work discussed in chapter 3.4

Chapter 3.5 discusses a possible approach towards the synthesis of poly(low fluorinated phenyl 2-ylidene-acetate) (Scheme 3.5).



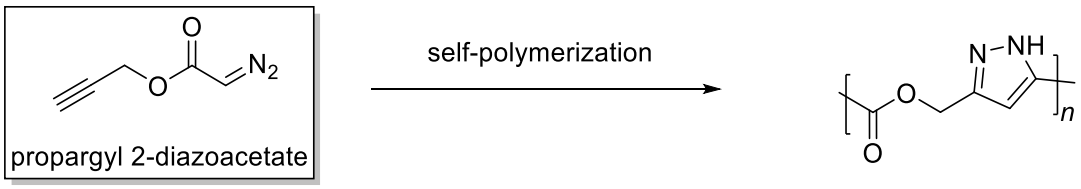
Scheme 3.5. Schematic illustration of the work discussed in chapter 3.5

3.1. Synthesis and Post-modification of Poly(propargyl 2-ylidene-acetate)

The main part of this chapter is adapted from my paper: Synthesis and post-polymerization modification of poly(propargyl 2-ylidene-acetate).

3.1.1. Introduction

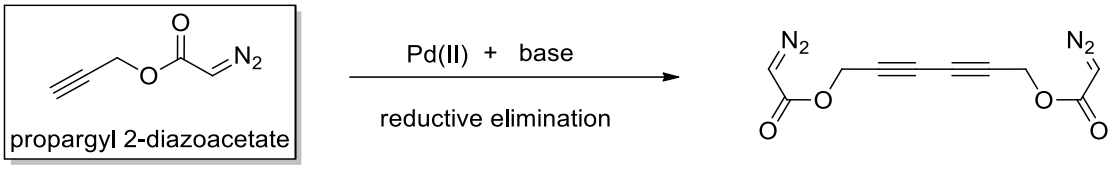
Because of the high branching density, the high polar functional group decorated polymethylene derivatives are desirable to prepare novel materials, such as polymeric electrolyte, organic light-emitting diodes (OLED), conducting polymers, and sensors. In the past decades, few samples for the synthesis of polymethylene derivatives with diverse functional groups such as epoxide, hydroxyl, alkene, and ethylene glycol have been reported.[20j, 21i, 21s] However, currently, we face such vital challenges in future polymer synthesis, which need to develop novel monomers or polymerization methodologies to synthesize polymethylenes enabling for corresponding efficient and facile post-modifications. Because the concept of post-polymerization modifications assists the broad accessibility of functional polymethylenes tremendously.



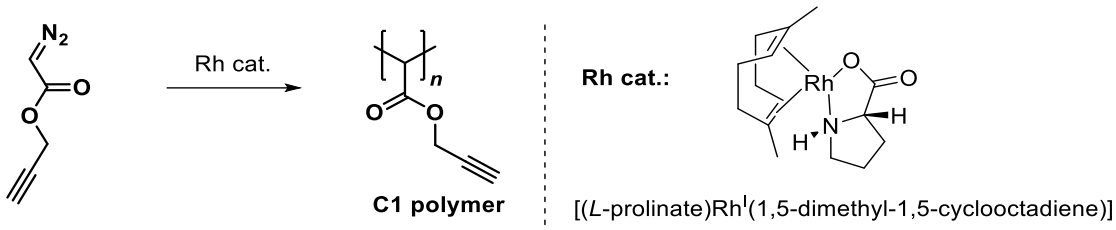
Scheme 3.6. Self-polymerization process of monomer propargyl 2- diazoacetate.

As a highly active functional group, terminal alkyne has been widely utilized in the polymer synthesis and post-polymerization modification of polymers.[52] Thus, to further enrich the toolboxes of functional polymethylenes, we intended to explore the

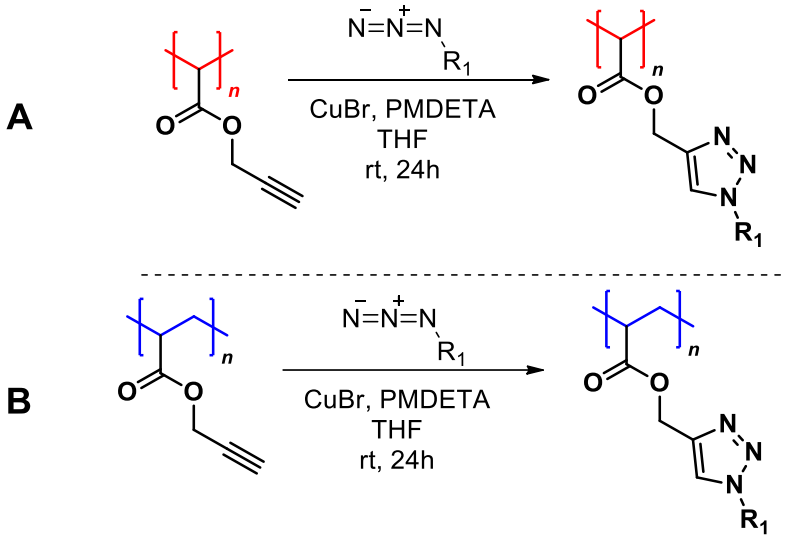
C1 polymerization of one *α*-diazo carbonyl monomer possessing terminal alkyne, i.e., propargyl 2-diazoacetate. Among the enormously reported approaches for post-polymerization modifications, only a few approaches result in quantitative and selective conversion under mild and facile reaction conditions. Hence, we aimed to utilize the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) for a post-polymerization modification. However, propargyl 2-diazoacetate possesses two active groups, the diazo and the terminal alkyne, which need to be controlled to realize an efficient C1 polymerization selectively. For example, *Legros* and colleagues reported the catalyst-free, terminal alkyne-induced self-polymerization via 1,3-dipolar cycloaddition of the diazo group to the alkyne, as shown in Scheme 3.6.[53] Further, propargyl 2-diazoacetate can also occur as a base-mediated reductive elimination to yield the diacetylene derivatives in the existence of transition-metal such as Pd(II) (Scheme 3.7), despite its potential to promote the C1 polymerization of α-diazocarbonyl monomers.[20c, 23, 54] The method of choice could be the low valance rhodium-mediated C1 polymerization (Scheme 1.7), as it allows for high molecular weight and stereoregular polymers. Furthermore, the utilization of low valance Rhodium(I) catalysts can successfully prevent reductive elimination of monomers occurring in the Palladium(II) catalyst system. Hence, we proposed the synthesis of propargyl 2-diazoacetate and its subsequent C1 polymerization in the mediation of low valance Rh-catalyst (e.g., [(*L*-prolinate)Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] to prepare well-defined polymethylenes (Scheme 3.8). Additionally, the polymers containing densely packed alkyne side groups shall be efficiently post-modified via copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) (Scheme 3.9 A). In comparison, the post-modification of polymethylenes and their corresponding structural C2 analogs derived from poly(propargyl acrylate) utilizing the same reaction conditions are investigated as well (Scheme 3.9 B).



Scheme 3.7. Reductive elimination of Pd(II) accompanied by the homo-coupling of the alkyne unit of the monomer propargyl 2-diazoacetate.



Scheme 3.8. The Rh-mediated C1 polymerization of propargyl 2-diazoacetate to yield C1 polymer, i.e., poly(propargyl 2-ylidene-acetate).



Scheme 3.9. Post-polymerization modification of PPA and PPAc via Copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reactions under mild conditions.

3.1.2. Synthesis and Characterization of Propargyl 2-Diazoacetate

The monomer propargyl 2-diazoacetate was synthesized according to Scheme 1.9 B. Propargyl alcohol reacted with 2,2,6-trimethyl-4H-1,3-dioxin-4-one to yield propargyl acetoacetate, which was subsequently utilized for the reaction with tosyl azide to yield propargyl 2-diazoacetate as a yellow liquid in a reasonable yield (46%). The structure of 2-diazoacetate was characterized by ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), and Fourier transform infrared spectroscopy (FT-IR, Bruker vertex 80). Detailed information is illustrated in Figure 3.1–3.3.

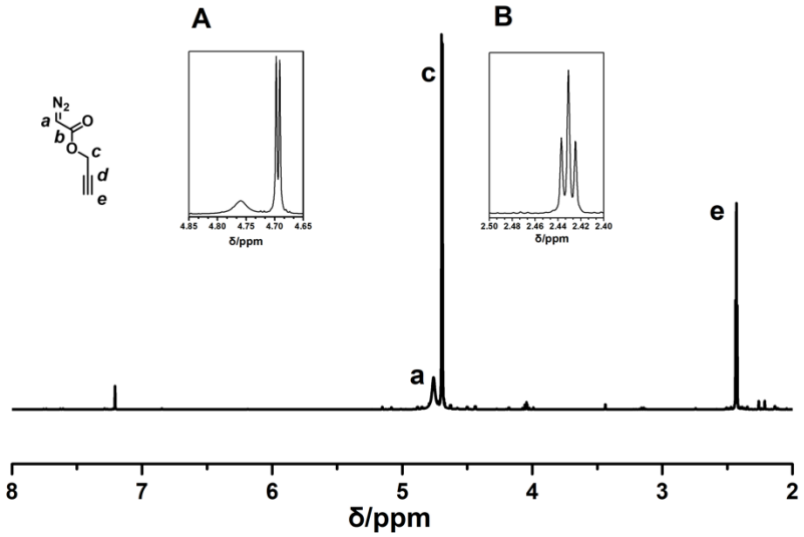


Figure 3.1. ^{1}H NMR of propargyl 2-diazoacetate in $CDCl_3$ (400 MHz); (A), The magnified spectrum at chemical shift between 4.85 to 4.65 ppm; (B), The magnified spectrum at chemical shift between 2.5 and 2.4 ppm.

The ^{1}H NMR spectrum illustrated in Figure 3.1 shows a triplet signal at 2.42 ppm, which is assigned as the proton of acetylene. The peak exhibited a small signal at 4.76 ppm arises from the proton of the $N_2C\mathit{H}$ group. Furthermore, the methylene $\mathit{C^cH_2}$ gives rise to a signal at 4.75 ppm.

The monomer was identified in the ^{13}C NMR spectrum as well (Figure 3.2). The observed peaks at 52 ppm and 46 ppm are assigned for the methylene C^c and backbone carbon C^a and the $N_2C\mathit{H}$ group. Furthermore, the peaks of triple bond carbon atom C^d and C^e are located at 77.5 ppm and 75.7 ppm.

Another noticeable feature of the diazo compound is the strong N_2 vibration band in the FT-IR spectrum (Figure 3.3). For propargyl 2-diazoacetate, the diazo group exhibits a strong signal at 2212 cm^{-1} along with a weak band at 3112 cm^{-1} originating from the proton of the $N_2C\mathit{H}$ group. Though the intense stretch of N_2 vibration hides the vibration of the triple-band, the C–H stretch of the acetylene group can be observed at 3290 cm^{-1}.

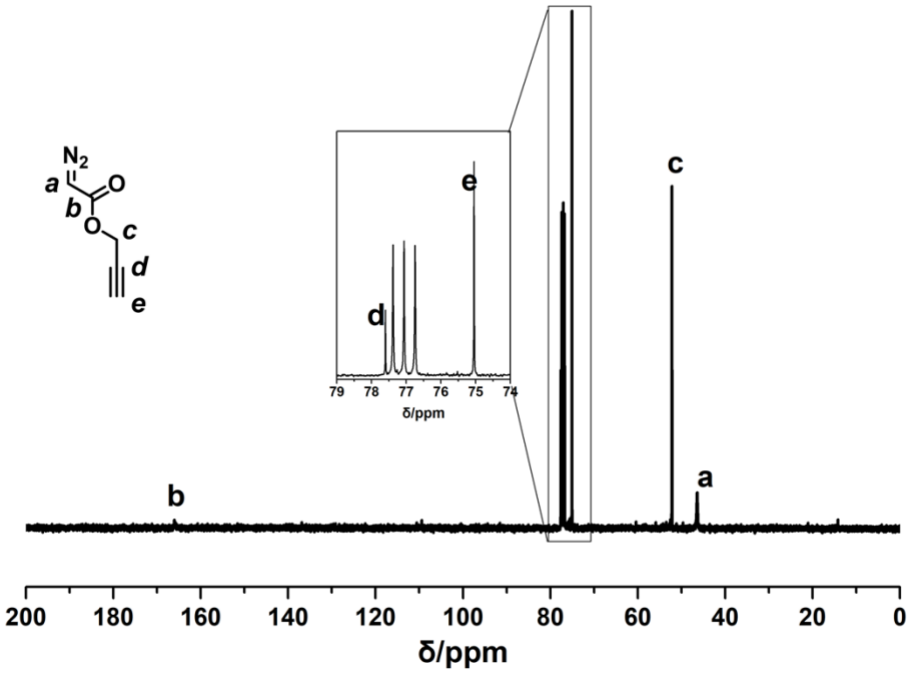


Figure 3.2. ^{13}C NMR of propargyl 2-diazoacetate in $CDCl_3$ (101 MHz).

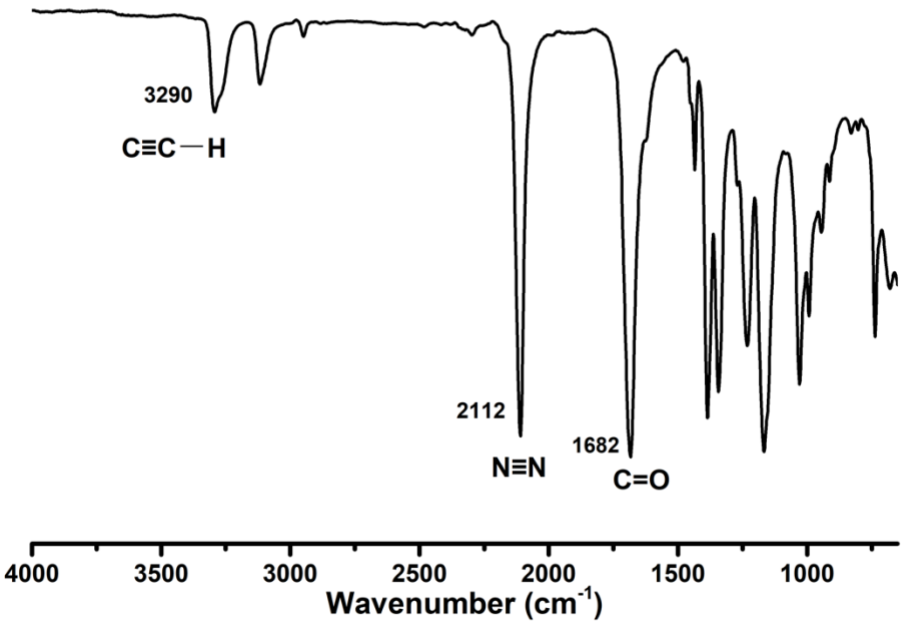


Figure 3.3. FT-IR (ATR mode) spectrum of propargyl 2-diazoacetate.

3.1.3. Synthesis and Characterization of Poly(propargyl 2-ylidene-acetate) and Poly(propargyl acrylate) (PPAc).

The synthesis of poly(propargyl 2-ylidene-acetate) (PPA) via rhodium-mediated C1 polymerization was inspired by the synthesis procedure described in the literature.[21f, 21i, 21j, 21s] Fortunately, the triple bond did not interfere with the rhodium catalyst. Thereby, the catalyst did not get poisoned, and the selective C1 polymerization was not hampered. Ultimately, PPA was obtained in moderate yield (35%). The average molecular weights (M_n = 3290 g/mol, M_w = 9250 g/mol) were determined by gel permeation chromatography (GPC) calibrated by polystyrene standards with DMAC as eluent (Figure 3.4). Furthermore, PPA was also fully characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR. The details are shown in Figure 3.5, 3.7–3.8.

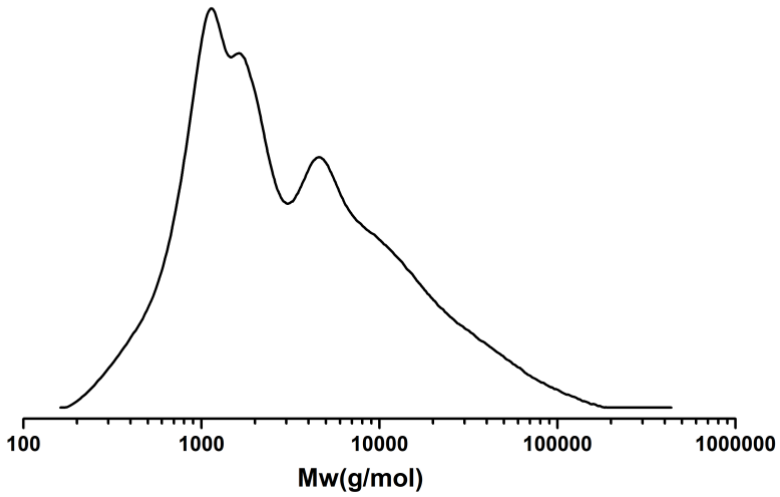


Figure. 3.4. GPC data of poly(propargyl 2-ylidene-acetate) (PPA). DMAC was utilized as eluent.

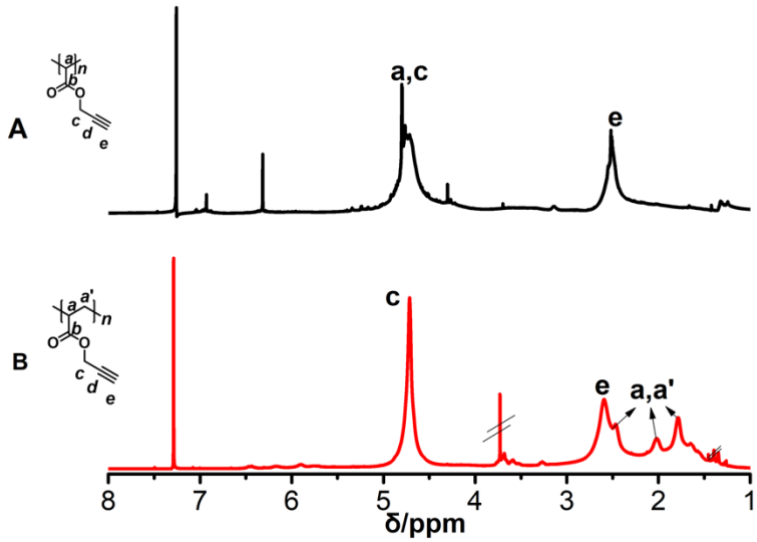


Figure 3.5. Comparison of the ^{1}H NMR spectra obtained from poly(propargyl 2-ylidene-acetate) (PPA) and poly(propargyl acrylate) (PPAc). The spectra were measured in $CDCl_3$ (400 MHz).

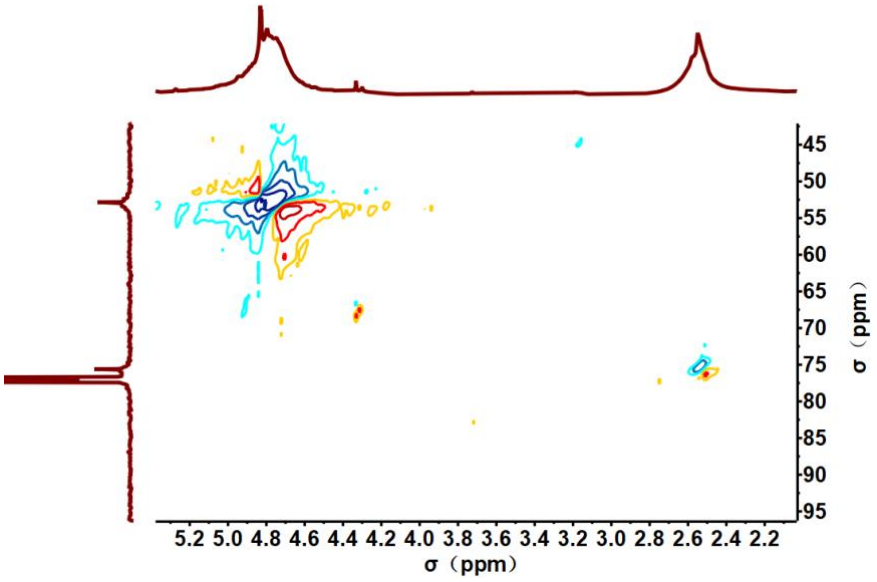


Figure 3.6. ^{1}H -^{13}C HSQC NMR spectrum of poly(propargyl 2-ylidene-acetate) (PPA). The spectrum was measured in $CDCl_3$ (400 MHz).

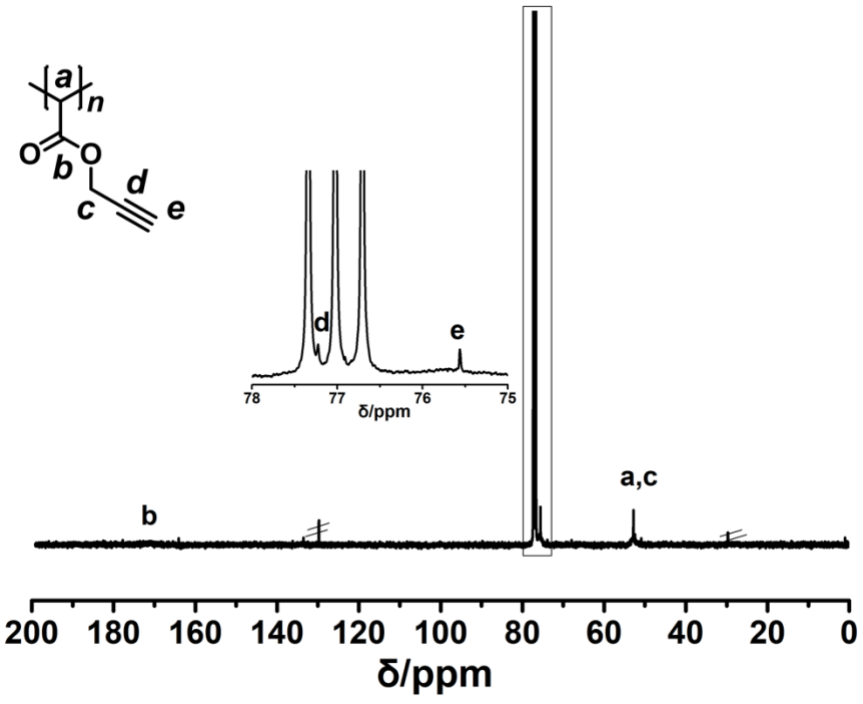


Figure 3.7. The ^{13}C NMR spectrum of poly(propargyl 2-ylidene-acetate) (PPA). The spectrum was measured in $CDCl_3$ (400 MHz).

Figure 3.5 shows the ^{1}H NMR spectra of PPA and PPAc. As shown in Figure 3.5 A, the signal of acetylene proton ***e*** located at 2.52 ppm remains intact. However, the methylene CH_2 and backbone CH peak are overlapped, confirmed by HSQC (Figure 3.6). Compared to the spectrum of C2 polymer PPAc**,** it also verifies the successful polymerization of PPA indirectly.

It is noteworthy that, in the ^{13}C NMR spectrum of Figure 3.7, the signal of the backbone carbon C^{a} is not observed, which results from the signal overlapping with the methylene carbon C^{c} at 52.4 ppm. The ^{1}H-^{13}C HSQC spectrum confirms the overlap in Figure 3.6.

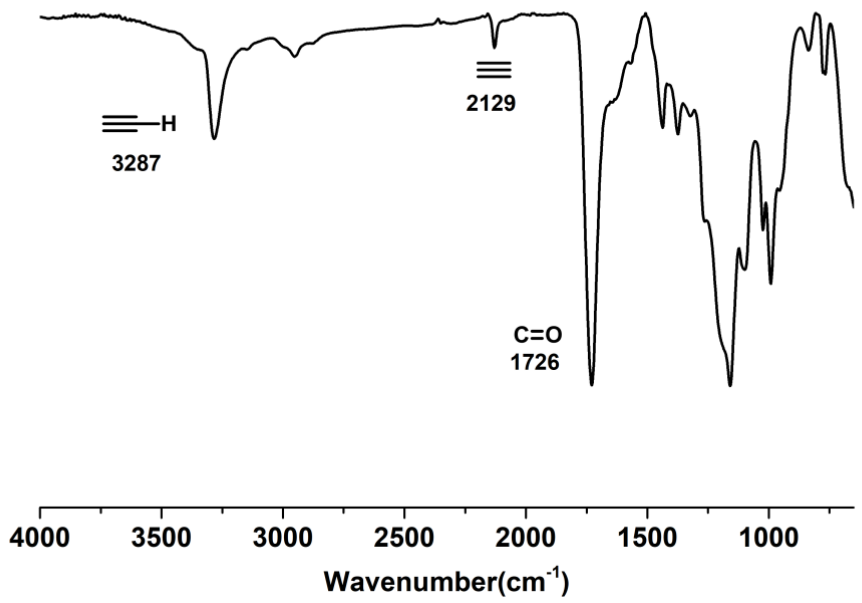


Figure 3.8. FT-IR (ATR mode) spectrum of poly(propargyl 2-ylidene-acetate) (PPA)**.**

The FT-IR spectrum in Figure 3.8 shows a weak stretch vibration at 2129 cm^{-1} and a moderate band at 3287 cm^{-1}, which arises from the triple bond stretch and the acetylene C–H bond, respectively. Furthermore, the intense vibration located at 1726 cm^{-1} confirms the existence of the carbonyl group, which indicates that the ester groups

remain intact after the C1 polymerization. Nevertheless, the strong vibration of the N–N triple bond disappeared, which also confirms the successful C1 polymerization.

As a structural analog, poly(propargyl acrylate) (PPAc) was prepared from propargyl acrylate in 1,4-dioxane at 80 ℃ for 16 h, which was utilized to investigate the branch density on the influence of the post-polymerization reaction.

3.1.4. Post-modification of Poly(propargyl 2-ylidene-acetate) (PPA) and poly(propargyl acrylate) (PPAc).

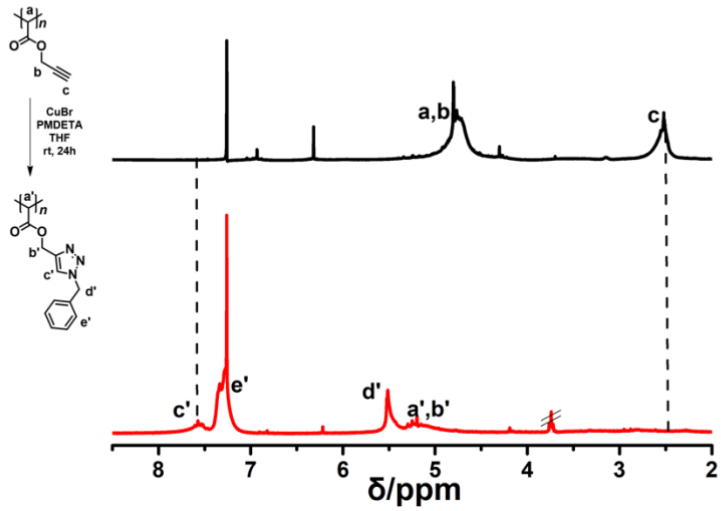
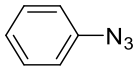
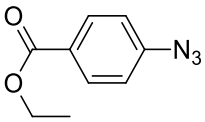
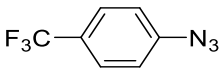
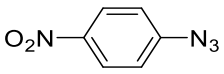
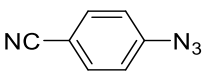


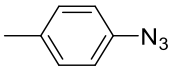
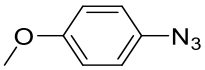
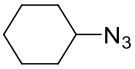
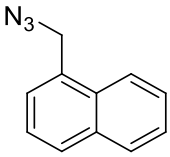
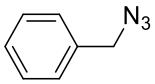
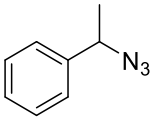
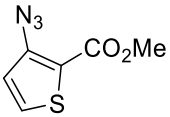
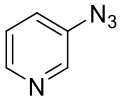
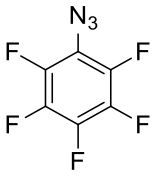
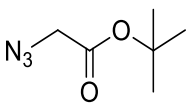
Figure 3.9. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of PPA before and after post-modification with benzyl azide via CuAAC reaction.

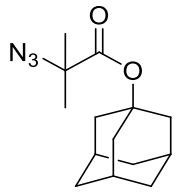
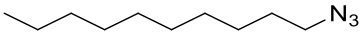
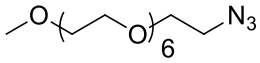
Terminal alkyne can quickly go through a copper-catalyzed alkyne-azide cycloaddition reaction (CuAAC) with benzyl azide (Figure 3.9). The cycloaddition reactions with various azides enrich the functional group diversity of polymethylene derivatives. The reactivity of aromatic and aliphatic azides utilized for the CuAAC was investigated as

well. As shown in Table 3.1, the substituents of the aromatic azides tend to influence the conversion of CuAAC, with a strong electron-donating methoxy group suppressing the reaction. In contrast, electron-withdrawing groups and modestly electron-donating methyl groups do not harm the conversions of post-modification reactions. Compared to the conversion of corresponding C2 polymer (Table 3.1, Entry 15 & 16), the steric hindrance of the *tert*-butyl 2-azidoacetate and adamantan-1-yl 2-azido-2-methylpropanoate and the high branching density of PPA seems not to influence the conversion of CuAAC post-modifications.

Table 3.1. Substrates Scope of various Azides for Post-modification of the C2 polymer PPAc and C1 polymer PPA via CuAAC Reaction.

Azido compound (1.2 equiv)	**Entry**	**Conversion of C2 polymer via ^{1}H NMR[c]**	**Entry**	**Conversion of C1 polymer via ^{1}H NMR[c]**
	**1**	**3a; >99%**	**19**	**3a'; >99%**
	**2**	**3b; >99%**	**20**	**3b'; >99%**
	**3**	**3c; >99%**	**21**	**3c'; >99%**
	**4**	**3d; >99%[b]**	**22**	**3d'; >99%[b]**
	**5**	**3e; >99%**	**23**	**3e'; >99%**

	**6**	**3f; >99%**	**24**	**3f'; >99%**
	**7**	**3g; 53%**	**25**	**3g'; 46%**
	**8**	**3h; >99%**	**26**	**3h'; >99%**
	**9**	**3i; >99%**	**27**	**3i'; >99%**
	**10**	**3j; >99%**	**28**	**3j'; >99%**
	**11**	**3k; >99%**	**29**	**3k'; 0**
	**12**	**3l; >99%**	**30**	**3l'; 73%**
	**13**	**3m; >99%**	**31**	**3m'; >99%**
	**14**	**3n; >99%**	**32**	**3n'; >99%**
	**15**	**3o; >99%**	**33**	**3o'; >99%**

	**16**	**3p; >99%**	**34**	**3p'; >99%**
	**17**	**3q; >99%**	**35**	**3q'; >99%**
	**18**	**3r; >99%**	**36**	**3r'; >99%**

[a] With regard to 1 equiv. of PPAc and PPA repeating unit, polymer (40 mg, 0.29 mmol, 1 equiv.); CuBr (2.05 mg, 0.15 mmol, 0.05 equiv.), PMDETA (3.46 mg, 0.02 mmol, 0.07 equiv.) and azido compounds (1.2 equiv.) in 2.0 mL THF. [b] As the solubility in $CDCl_3$ is not good, the conversion was confirmed via FT-IR spectroscopy. [c] Without a further note, all the samples were dissolved in $CDCl_3$ for the ^1H NMR (400 MHz) measurements.

Interestingly, as to the polar oxygen atom (owing to a chelating ability) aggregated PEG chains, it can also be ligated smoothly with polymethylene (C1 polymer) and polyethylene (C2 polymer) via CuAAC post-modification.

Last but not least, when aromatic azide 1-azido-2,3,4,5,6-pentafluorobenzene (Table 3.1, entry 14 & 32) was utilized as the substrates for the post-modification of both PPA and PPAc, quantitative conversions of both were realized, which is confirmed via ^1H NMR and FT-IR (Figure 3.10) as is well-known that the PFP motif can react with thiol via Para-Fluoro-Thiol reaction (PFTR). Hence, the cascade post-modifications of PPA and PPAc via PFTR were investigated to introduce the PFP motif.

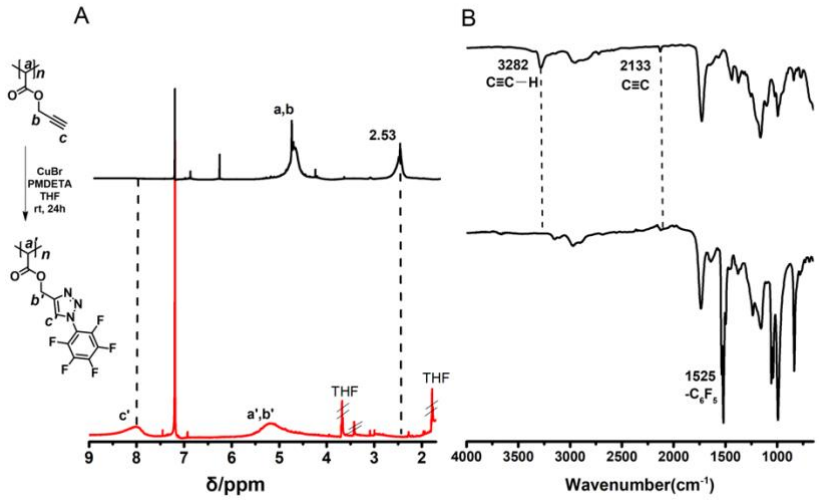


Figure. 3.10. (A), ^{1}H NMR spectra ($CDCl_3$, 400 MHz) and (B), FT-IR (ATR mode) spectrum of **PPA** before and after CuAAC with 1-azido-2,3,4,5,6-pentafluorobenzene.

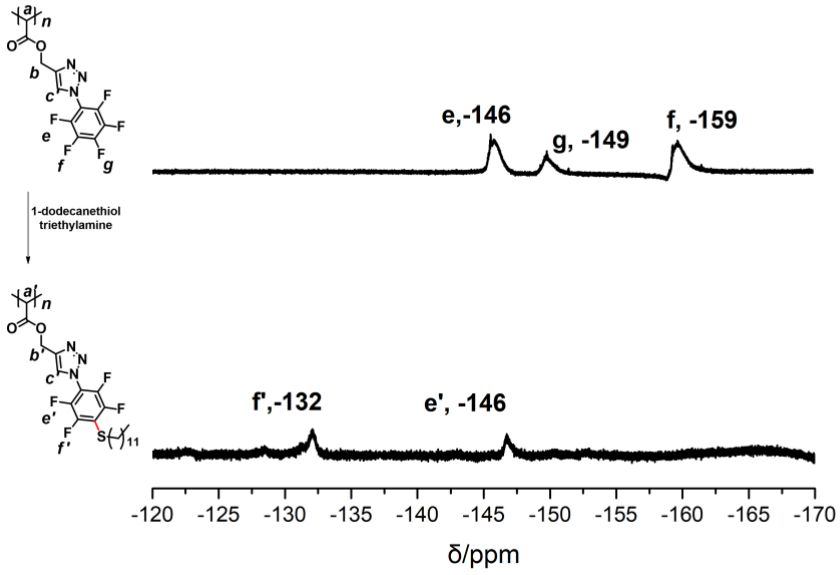


Figure. 3.11. ^{19}F NMR (377 MHz, $CDCl_3$) spectra before and after post-modification of polymethylene derivatives 3n' via Para-Fluro-Thiol reaction (PFTR).

Indeed, the continuous post-modification via PFTR was also consistent with prediction. When 3n' reacted with 1-dodecanethiol, the quantitative conversion was obtained, characterized by ^{19}F NMR. From the ^{19}F NMR spectrum of Figure 3.11, the signal of *para*-fluoride located at -149 ppm was disappeared along with the downfield shift of the adjacent *meta*-fluorides by approximately 27 ppm to roughly -132 ppm.

Additionally, from the ^{1}H NMR spectrum, it can be seen that the triazole groups remain intact, which is verified by the proton of triazole located at 8.08 ppm (Figure 3.12). Furthermore, it can be found that the complex structures of 3n', included ester, and triazole, do not inhibit the conversion of PFTR post-modification.

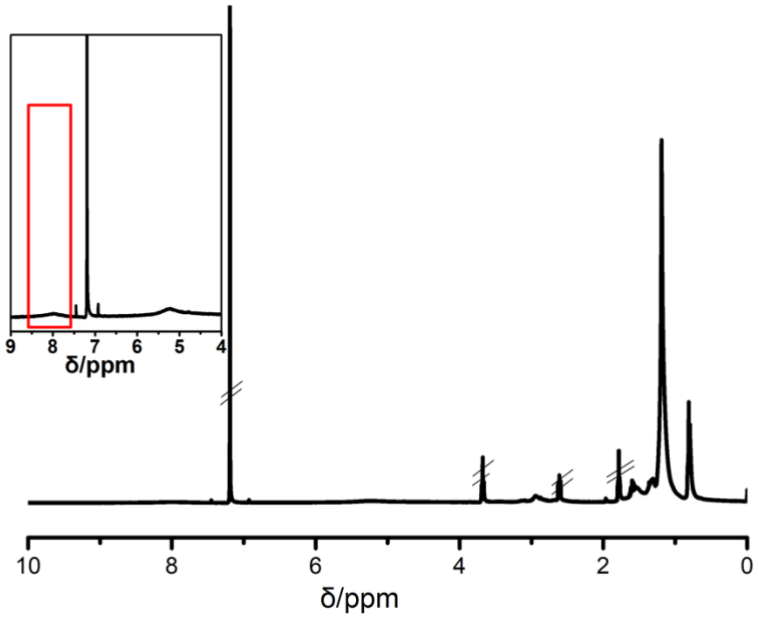


Figure 3.12. The ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the product was obtained after PFTR post-modification of polymethylene derivatives 3n'.

3.1.5. Conclusion

The successful synthesis of poly(propargyl 2-ylidene-acetate) (PPA) and its highly efficient post-modification via CuAAC and PFTR are described. Further, with the use of low valence Rh complexes, the selective C1 polymerization was achieved, which could successfully overcome the self-polymerization of propargyl 2-diazoacetate. Various azido compounds, such as aromatic azides, aliphatic azides, and PEG azide, were utilized for primary post-modification, which did not show apparent repression on the conversion. As a comparison, post-modification of poly(propargyl acrylate) (PPA) was also investigated, and quantitative conversions were obtained. As to the conversion of CuAAC with various azides, no apparent differences were found for both C2 polymer PPAc and C1 polymer PPA. Notably, cascade post-modification via CuAAC and PFTR was realized for the first time, which enriches the toolbox of synthesis of diverse polymethylene derivatives. Overall, poly(propargyl 2-ylidene-acetate) (PPAc) has been proved to be the best choice for a broad range of distinct ligation reactions, promising to prepare diverse novel polymeric materials.

3.2. Synthesis and Post-modification of Poly(pentafluorobenzyl 2-ylidene-acetate) (pPFBDA)

This chapter is reorganized from the paper: Poly(pentafluorobenzyl 2-ylidene-acetate): Polymerization and Post-Polymerization Modification.

3.2.1. Introduction

Chapter 3.2 exhibited the successful synthesis of poly(propargyl 2-ylidene-acetate) and its subsequent efficient post-polymerization modification. In this part, pentafluorobenzyl (PFB**)** attracts our interests while they can efficiently go through Para-Fluoro-Thiol reaction (PFTR) under mild conditions. If the PFTR post-modification was intended to be achieved, the PFB tethered polymethylene derivatives should be synthesized at first. Additionally, the high polar functional element fluorine is introduced into polymethylene simultaneously, which greatly enriches the diversity of C1 chemistry. Pentafluorobenzyl methacrylate can be easily polymerized to poly(pentafluorobenzyl methacrylate) (pPFBMA) via free radical polymerization. The *para*-fluoro substitution with thiols and amines has been systematically investigated.[36] However, the polymerization and post-modification of its analog C1 polymer—poly(pentafluorobenzyl 2-ylidene-acetate) (pPFBDA) have not been reported yet. Hence, in this chapter, the polymerization of pPFBDA and its post-modification via PFTR is described for the first time.

3.2.2. Synthesis and Characterization of Pentafluorobenzyl 2-Diazoacetate.

The monomer synthesis of pentafluorobenzyl 2-diazoacetate was conducted according to procedure B in Scheme 1.9. Pentafluorobenzyl alcohol was reacted with 2,2,6-

trimethyl-4H-1,3-dioxin-4-one to yield pentafluorobenzyl acetoacetate, which was subsequently utilized for the reaction with tosyl azide under the mediation of triethylamine and then treated with lithium hydroxide to yield the monomer as a yellow liquid in a good yield (78%). The structure of pentafluorobenzyl 2-diazoacetate was fully characterized by ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectroscopy. To the best of our knowledge, the synthesis of pentafluorobenzyl 2-diazoacetate has been reported for the first time. Detailed spectral information is depicted in Figure 3.13–3.14, Figure S20.

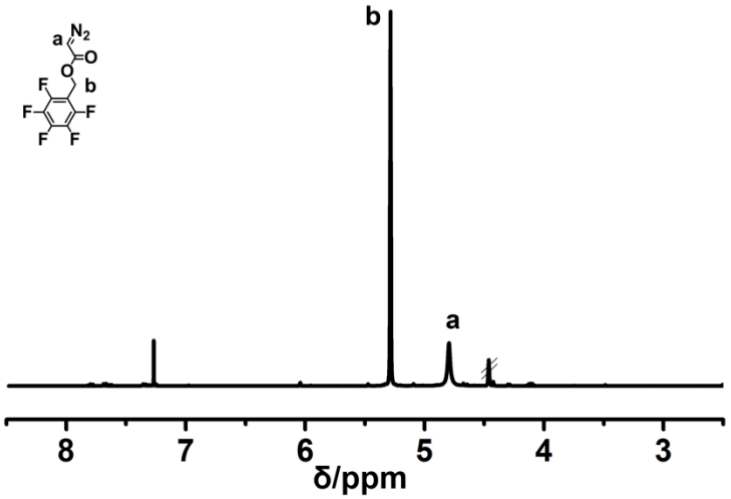


Figure 3.13. ^{1}H NMR spectrum of pentafluorobenzyl 2-diazoacetate measured in $CDCl_3$ (400 MHz).

As shown in Figure 3.13, the small peak located at 4.73 ppm is assigned to the proton of the $N_2C\mathit{H}$ group *a*. The sharp and intensive peak located at 5.20 ppm attributes from the proton of methylene *b*. Furthermore, in the ^{19}F NMR spectrum (Figure 3.14), three classic peaks are observed, verifying the successful synthesis of pentafluorobenzyl 2-diazoacetate. For instance, the peak at -143 ppm results from the two *ortho*-fluorine *c*, the para-fluorine *e* shows a peak at -153 ppm, and the peak at -162 ppm arises from the two *meta*-fluorine *d*.

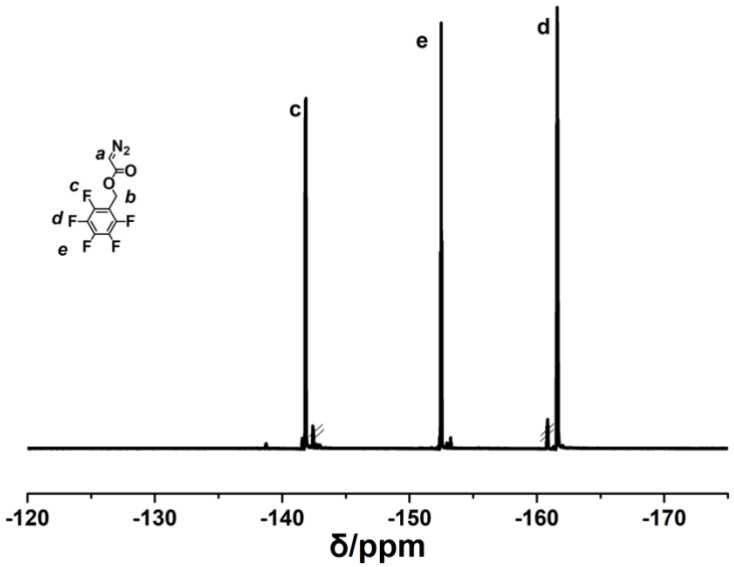
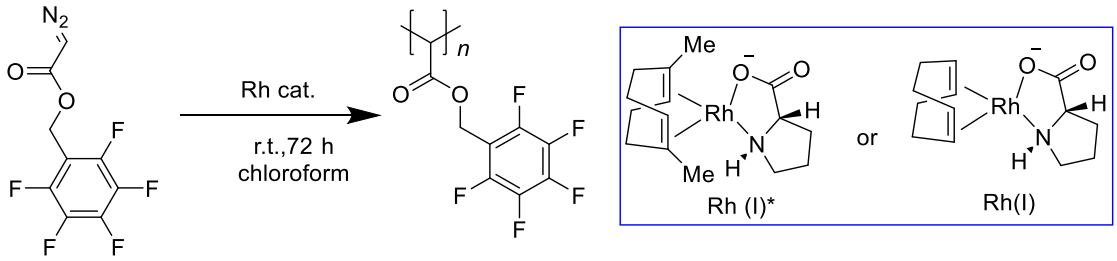


Figure 3.14. ^{19}F NMR spectrum of pentafluorobenzyl 2-diazoacetate measured in $CDCl_3$ (377 MHz).

3.2.3. Synthesis and Characterization of Poly(pentafluorobenzyl 2-diazoacetate) (pPFBDA)



Scheme 3.10. Rhodium-catalyzed C1 polymerization of pentafluorobenzyl 2-diazoacetate yielding poly(pentafluorobenzyl 2-ylidene-acetate) (pPFBDA).

To prepare poly(pentafluorobenzyl 2-diazoacetate), the rhodium complexes Rh(I)* and Rh(I) (Scheme 3.10) were utilized for the C1 polymerization. The obtained polymer pPFBDA was fully characterized by Gel Permeation Chromatography (GPC),

Thermogravimetric Analysis (TGA), ^{1}H NMR, ^{19}F NMR, and FT-IR.

Table 3.2 can be seen, the catalyst Rh(I)* shows us a slightly better yield compared to the catalyst Rh(I) though the molecular weight and dispersity are nearly the same. Diene ligands act as a supporting ligand to the active rhodium center during the propagation steps, which indicates 1,5-dimethyl-1,5-cyclooctadiene coordinated Rh intermediates are much more active during the propagation of the monomer. *N,O*-ligands are involved in the initiation steps and hence influence the polymer yields, which indicates the dissociation of prolinate from [(*L*-prolinate)Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] is more accessible due to the more significant steric hindrance of 1,5-dimethyl-1,5-cyclooctadiene.

Table 3.2. Screening of the polymerization of pentafluorobenzyl 2-diazoacetate

run	monomer	catalyst	solvent	yield[a]	M_n[b]	$Đ$
1	**PFBDA**	Rh(I)*	$CDCl_3$	10-16%	3410	1.26
2	**PFBDA**	Rh(I)	$CDCl_3$	7%	3580	1.19

The solubility of pPFBDA is not very high in common solvents. After screening various deuterated solvents, the best NMR spectra of pPFBDA were obtained in toluene-*d*8, as is shown in Figure 3.15. It can be seen from Figure 3.15, the signal of backbone proton *a* located at 3.2–3.8 ppm, and the signal of the *CH_2 (b)* on the side chains appeared at 4.5–6.0 ppm, respectively. According to the literature, the backbone proton's peak is so broad, which indicates the products are probably atactic.[21p] Additionally, from the ^{19}F NMR spectrum (Figure 3.16), the three typical peaks of pentafluorophenyl appear at -143, -153, and -162 ppm, respectively, which is similar to the reported methacrylic analog poly(pentafluorobenzyl methacrylate) (pPFBMA).[36] From the FT-IR

spectrum of Figure 3.17, the vibration of the carbonyl group located at 1743 cm^{-1} can be observed. Furthermore, the strong stretch band of C_6F_5 appears at 1504 cm^{-1}, revealing that the pentafluorophenyl group remains intact after the polymerization.

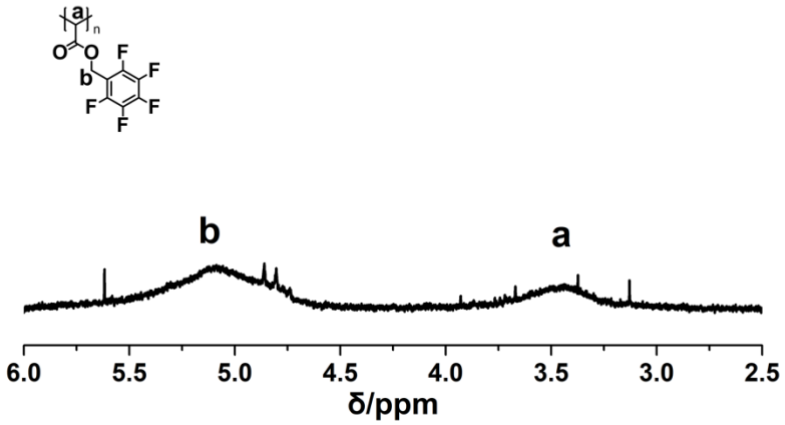


Figure 3.15. ^{1}H NMR of pPFBDA was measured in *d*8-toluene (400 MHz).

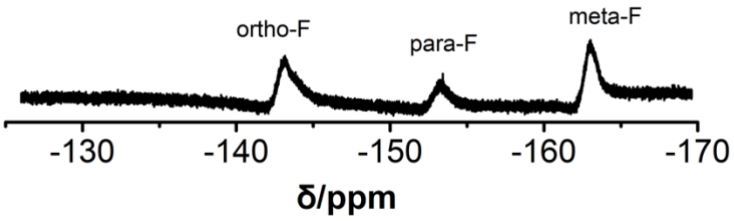


Figure 3.16. ^{19}F NMR of pPFBDA was measured in *d*8-toluene (377 MHz).

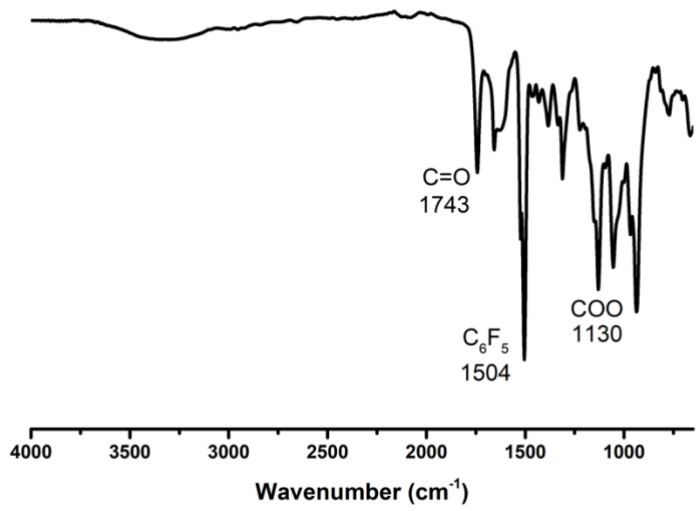


Figure 3.17. FT-IR spectrum of pPFBDA.

Next, pPFBDA was also characterized by thermogravimetric analysis (TGA) (Figure 3.18), which showed that the onset temperature for thermal decomposition of pPFBDA is 270 ℃.

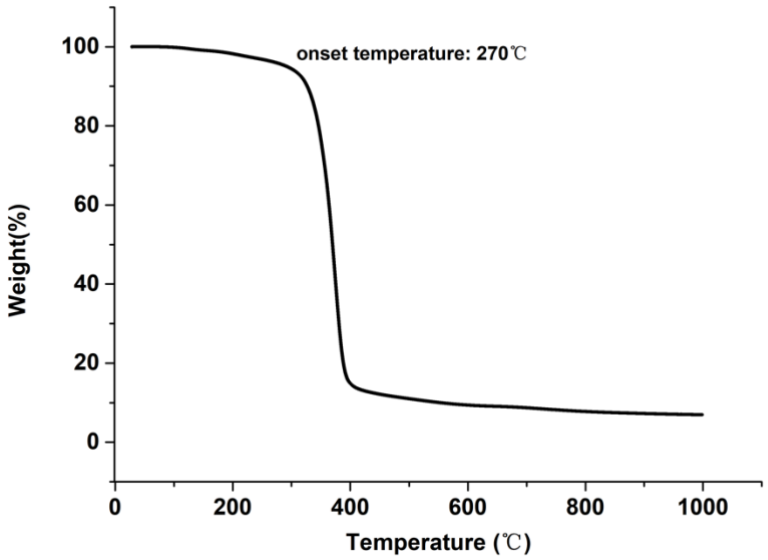


Figure 3.18. TGA paragraph of pPFBDA.

From Figure 3.19, the DSC analysis shows that the glass transition temperature (T_g) of

pPFBDA is -18 ℃, which is much lower than the glass transition temperature of the methacrylate analog pPFBMA (T_g = 65 ℃)[36] and poly(2,3,4,5,6-pentafluorostyrene) (T_g = 95 ℃)[55].

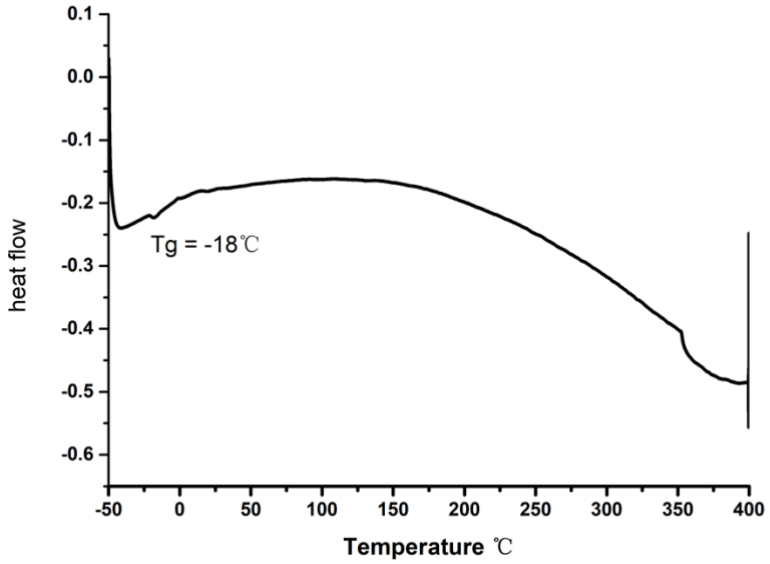


Figure 3.19. DSC analysis of pPFBDA.

Noteworthy, the NMR measurement disclosed that pPFBDA does not have good solubility in many common solvents. Thus, the solubility of pPFBDA was investigated at ambient temperature as well, which is depicted in Table 3.3, and the reported solubility of pPFBMA is also included. Compared to the solubility of pPFBDA with its C2 analog—pPFBMA, differences in solubility can be found. Of all screened solvents, pPFBDA was soluble in toluene, dichloromethane, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, and tetrahydrofuran but insoluble in *n*-hexane, methanol, benzene, and water. Interestingly, pPFBDA was partially soluble in chloroform, acetonitrile, and 1,4-dioxane, while its C2 analog pPFBMA was found to be soluble in various solvents such as chloroform, DMAC, DMSO, acetonitrile, anisole, diethyl ether, pyridine, and 2,2,2-trifluoroethanol.

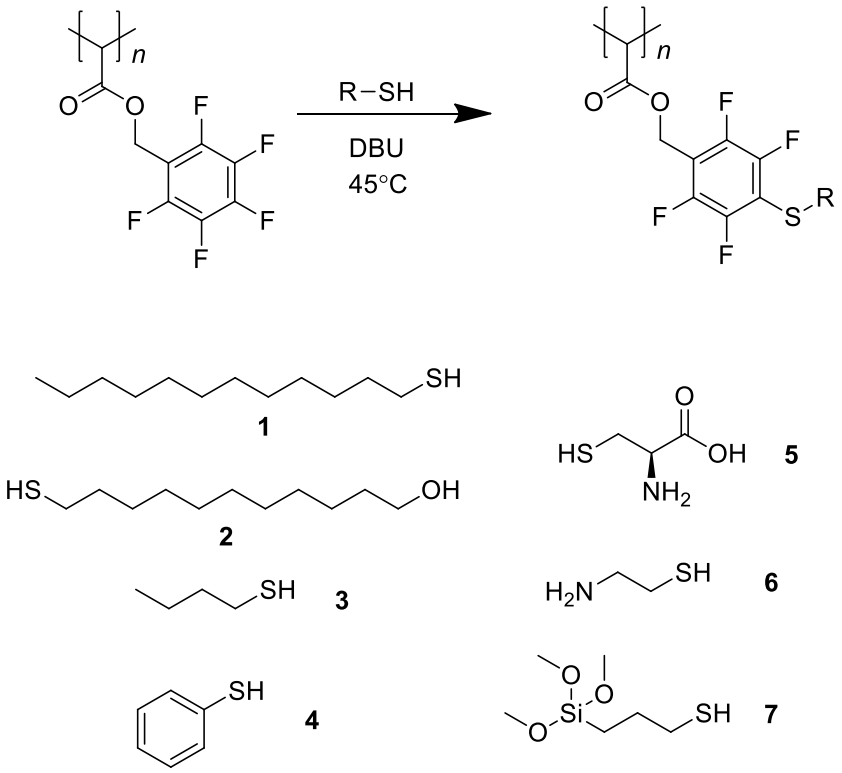
Table 3.3. Solubility of polymer poly(pentafluorobenzyl 2-yildene-acetate) (pPFBDA) and poly(2,3,4,5,6-pentafluorobenzyl methacrylate) (pPFBMA).

solvent	Solubility of pPFBDA	Solubility of pPFBMA[b]	solvent	Solubility of pPFBDA	Solubility of pPFBMA[b]
water	−	−	CH_3CN	±	+
THF	+	+	CH_2Cl_2	+	—
DMSO	±	+	toluene	+	—
CH_3OH	−	−	*n*-hexane	−	−
$CHCl_3$	±	+	DMF	+	+
dioxane	±	—	DMAC	+	+
benzene	−	—			

[a]Symbols: "+": soluble; "-": insoluble; "±": partly soluble; "—": no comparative literature data; [b]data about the solubility of pPFBMA was referred to the literature;[36] Picture of the solubility data can be found in supporting information. 1.5 mg samples were dispersed in 1 mL for the check of solubility.

3.2.4. Post-modification of Poly(pentafluorobenzyl 2-ylidene-acetate) (pPFBDA) via PFTR.

As is known that the PFB motif can go through PFTR reaction quickly. Thus, the post-modification of pPFBDA via the PFTR reaction was investigated as well. It was found that using DBU as a base at 45 ℃ can get a complete conversion within 2 hours. Noteworthy, the solubility of the post-modified product improved apparently. Various aliphatic nucleophilic thiols, including the hydrophobic and hydrophilic thiols and aromatic nucleophilic thiol—thiophenol, were tested for the post-modification (Scheme 3.11). Good results were obtained from the characterization by ^{19}F NMR or FT-IR, shown in Figures 3.20&3.21.



Scheme 3.11. Para-Fluoro-Thiol post-modification of pPFBDA with various thiols.

Figure 3.20 A and Figure 3.20 B, complete conversion of the PFTR post-modification of pPFBDA can be determined by the peak's absence of the *para*-fluoride located at -153 ppm for and a downfield shift about 29 ppm of the adjacent *meta*-fluoride to roughly -135 ppm. Note: In few samples, the sharp peaks originate from the existence of tricky separated oligomers of PFBDA. The signal at about δ/ppm = -123 was related to the DBU hydrofluoride generated during the reaction. Compared to the reported conversion of pPFBMA with thiols, no apparent inhibition on the conversion resulting from the densely packing side groups of pPFBDA was observed.

Notably, (3-mercaptopropyl)trimethoxysilane was also tested in the PFTR post-modification reaction under the customary reaction conditions, resulting in an insoluble product. However, from the IR spectroscopy Figure 3.21, it can be seen that the carbonyl bond remains intact, and the new generated band located at 2927cm^{-1} and 1115 cm^{-1} indicates the successful ligation between the polymer pPFBDA and (3-

mercaptopropyl)trimethoxysilane. Additionally, the C_6F_5 band moves from 1504 cm^{-1} to 1478 $cm^{-1,}$ revealing that the PFTR reaction completes.

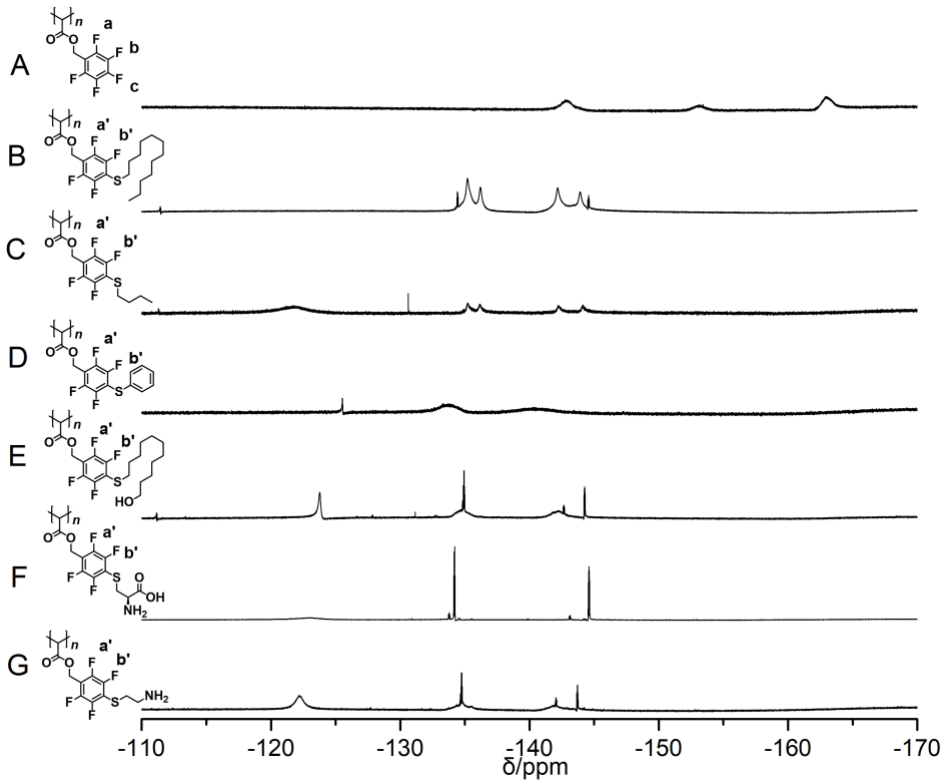


Figure 3.20. Conversions of PFTR reactions investigated for post-polymerization modification of pPFBDA, as determined by ^{19}F NMR in $CDCl_3$ except for A, measured in d8-toluene.

3.2.5. Conclusion

A novel reactive polymethylene derivative poly(pentafluorobenzyl 2-ylidene-acetate) (pPFBDA) was successfully synthesized by Rh-catalyzed C1 polymerization, and the post-modification of pPFBDA via PFTR reaction was revealed as well. Noteworthy, pPFBDA shows differences in solubility in comparison to its analogous C2 polymer pPFBMA. The post-modification of pPFBDA with aliphatic and aromatic thiols can proceed quantitatively, confirmed by ^{19}F NMR or FT-IR. Thus, this reaction enriches the post-modification toolbox for the efficient functionalization of polymethylenes.

Last but not least, compared to pPFBMA, it can be found that the density of functional grafted groups on the backbone does not have an apparent influence on the modification efficiency.

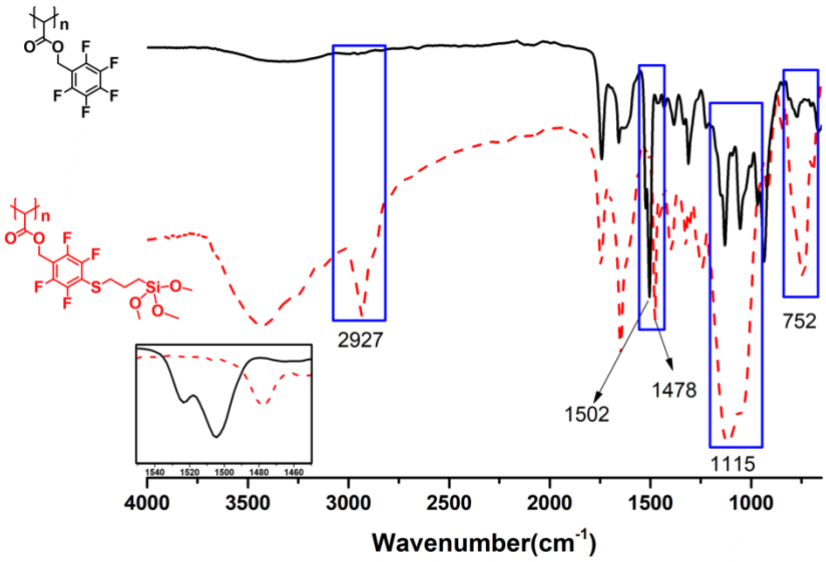


Figure 3.21. IR graph of (3-mercaptopropyl)trimethoxysilane before and after post-modification.

3.3. Synthesis of Poly[(±)(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-ylidene-acetate] and its hydrolysis to generate corresponding poly[((±)2,3-dihydroxypropyl) 2-ylidene-acetate] (pDDMDA)

1,2-diols are one kind of very high active functional group which is widely used in modern organic synthesis. Namely, it can go through pinacol rearrangement to generate its corresponding ketone derivatives. Further, it also can easily bind with boric acid to generate the borax hydrogels.[34a] However, due to its high activity, direct polymerization to obtain the 1,2-diols tethered polymethylene derivatives is infeasible. With the use of cyclic ketals, poly[(±)(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-ylidene-acetate] was successfully synthesized, and after hydrolysis, the high active 1,2-diols was introduced into polymethylenes, which can enrich the post-modification tools of C1 chemistry.

3.3.1. Synthesis and Characterization of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate

The monomer (2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate was prepared by synthetic route B as shown in Scheme 1.9. The monomer was obtained as a yellow liquid in a 27% yield. As the inherent high activity of α-diazocarbonyl compounds, the obtained yields are usually very low. The obtained products were successfully characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, as shown in Figures 3.22 and 3.23. Figure 3.22, it can be seen that the signal of the N_2CH proton is located at 4.75 ppm, and the peak located at 4.36 ppm and 1.30 ppm is assigned to the di-methyl group $^{g}CH_3$. The peaks located between 3.6 to 4.2 ppm belong to the peaks of $^{c}CH_2$ and $^{e}CH_2$, and because of the splitting, these peaks are overlapped together. The multiple peaks

located at 4.25 ppm are assigned to ^{d}CH. From the ^{13}C spectrum, the carbon of the N_2CH group located at 46 ppm can be seen obviously. Further, the peaks of cyclic ketals are assigned clearly, and the results can be found in Figure 3.23.

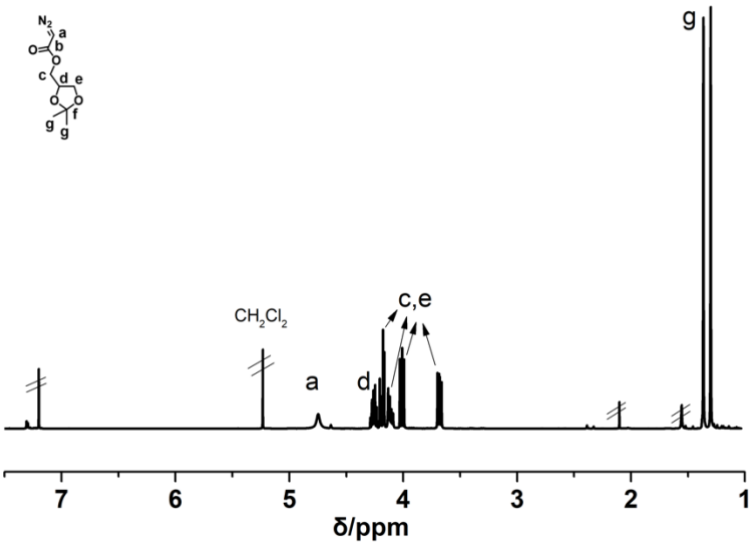


Figure 3.22. ^{1}H NMR of monomer (±)(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate measured in $CDCl_3$ (400 MHz).

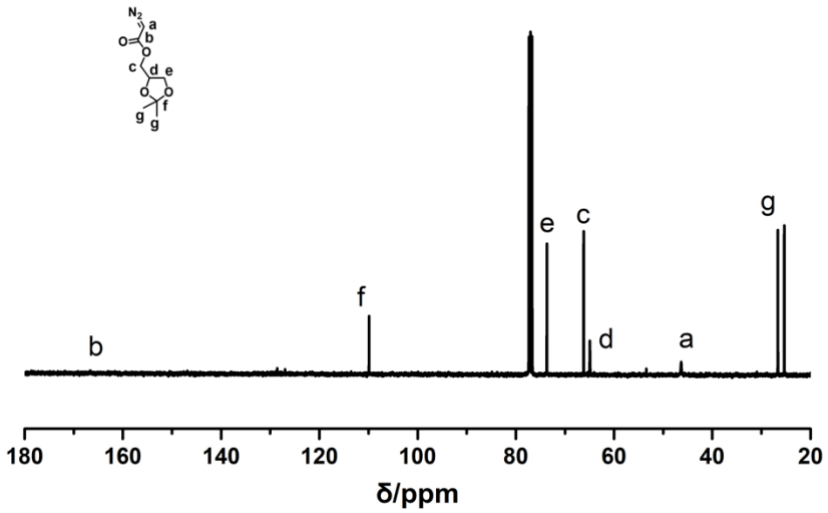


Figure 3.23. ^{13}C NMR of monomer (±)(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate measured in $CDCl_3$ (101 MHz).

3.3.2. Synthesis and Characterization of Poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate] (pDDMDA)

First, (2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate was polymerized via rhodium-mediated C1 polymerization in chloroform at room temperature for 22 h. Two distinct rhodium catalysts [(*L*-prolinate)Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] and [(*L*-prolinate)Rh^{I}(1,5-cyclooctadiene)] were both tested for the polymerization.

The reaction was conducted at room temperature in chloroform and proceeded for 22 hrs. when the solution turned a little bit turbid. The polymer was obtained after rapid precipitation and lyophilization from 1,4-dioxane. After lyophilization, the polymer was obtained in 17% yields. Noteworthy, nearly the same yields were obtained when two different rhodium catalysts were screened for polymerization (Table 3.4). The polymer was fully characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, and GPC.

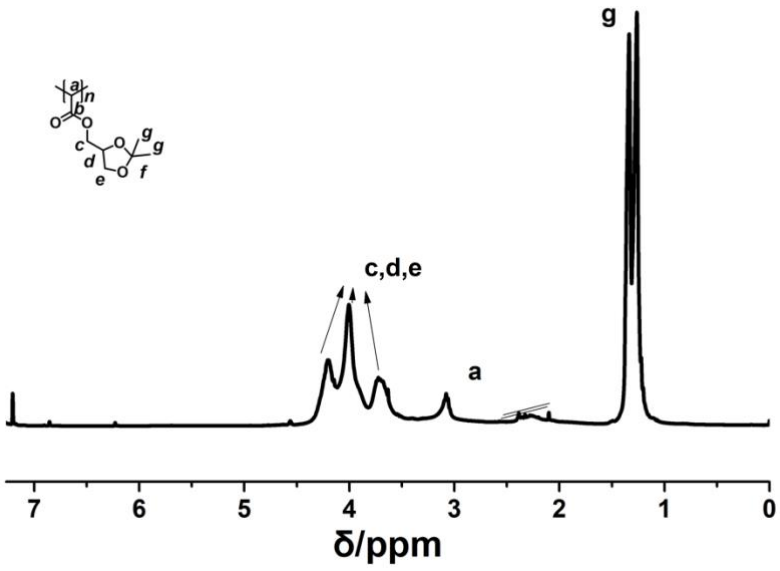


Figure 3.24. ^{1}H NMR spectrum of polymer poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate] (pDDMDA) measured in $CDCl_3$ (400 MHz).

From the ^{1}H NMR spectrum of pDDMDA in Figure 3.24, it can be seen that the peak

located at 3.10 ppm is assigned to the backbone proton, and due to the splitting, the peak of carbon is labeled as C^c, C^d, and C^e are overlapped together.

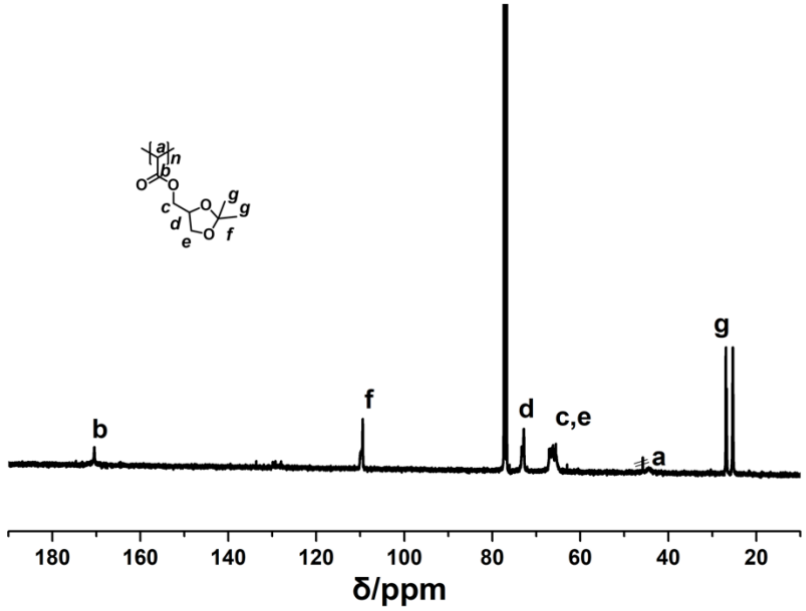


Figure 3.25. ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of polymer poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate] (pDDMDA).

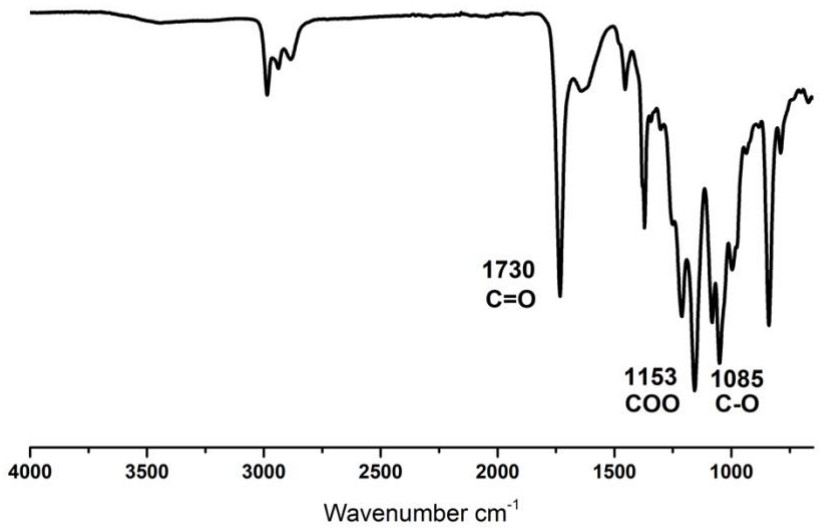


Figure 3.26. FT-IR spectrum of polymer poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate] (pDDMDA).

From the ^{13}C NMR spectrum of pDDMDA in Figure 3.25, the small peak located at 46 ppm attributes from the backbone carbon, and the peak at 170 ppm indicated the carbonyl group remains intact in the polymer. The peak at 110 ppm results from quaternary carbon signed f. The peak located at 68 ppm comes from $^{e}CH_2$ and $^{e}CH_2$.

Table 3.4. Screening of the catalyst for the polymerization of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate.

Entry	Cat. Rh	Yields	Mw/Da	*Đ*
1	Rh(I)*	20%	6300	7.00
2	Rh(I)	17%	9100	8.30

Additionally, from the FT-IR spectrum of pDDMDA (Figure 3.26), the strong vibration of carbonyl located at 1730 cm^{-1} can be observed clearly, and the band at 1153 cm^{-1} and 1085 cm^{-1} are assigned to *COO* and *C–O* stretch, respectively. Further, the band located at 2998 cm^{-1} arises from the dimethyl group. The GPC (DMAC as eluent) shows that the molecular weight of pDDMDA can reach up to 9100 Da under the mediation of Rh(I) catalyst, though the polydispersity is not very good (Figure 3.28).

3.3.3. Hydrolysis of polymer Poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate] (pDDMDA)

The post-modification of pDDMDA via hydrolysis was performed in THF with 1 N HCl for 2 hours. Then after removal of the solvent, the product was obtained after lyophilization. Figure 3.27, it can be seen that the newly generated O–H stretch appears at 3440 cm^{-1}, and the band of O–C–O located at 1053 cm^{-1} disappears. Additionally, the signal of the carbonyl group at 1734 cm^{-1} indicates that the ester group remains intact. In Figure 3.28 of the GPC graph, after post-modification, the molecular weight

decreased, suggesting successful hydrolysis.

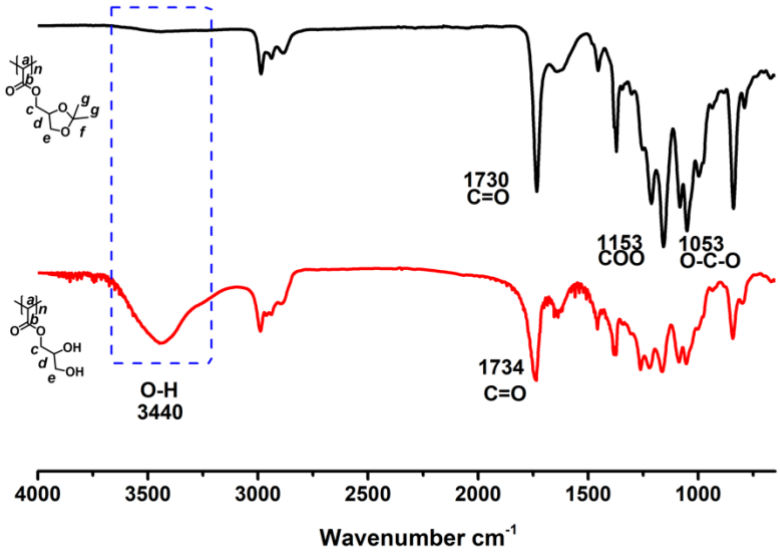


Figure 3.27. FT-IR graph of pDDMDA before and after post-modification via hydrolysis.

3.3.4. Conclusion

The successful synthesis of poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate] (pDDMDA) via rhodium-mediated C1 polymerization is presented here. Further, after the post-modification reaction via hydrolysis, the 1,2-diols functional group was quantitatively obtained under mild conditions. It is well known that 1,2-diols can easily bind with boric acid to generated borax-hydrogels. This could be made possible not only to be promising to prepare novel borax-hydrogels possessing special properties but also to investigate the backbone structure (polymethylene or polyethylene derivatives) on the influence of novel prepared borax-hydrogel properties. Additionally, as a highly active functional group, hydroxyl can be treated as an initiator for ethylene oxide or lactide polymerization. Thus, two-branched side chains can be easily introduced into the polymethylenes, which incredibly enriches functional tools for modifying polymethylenes.

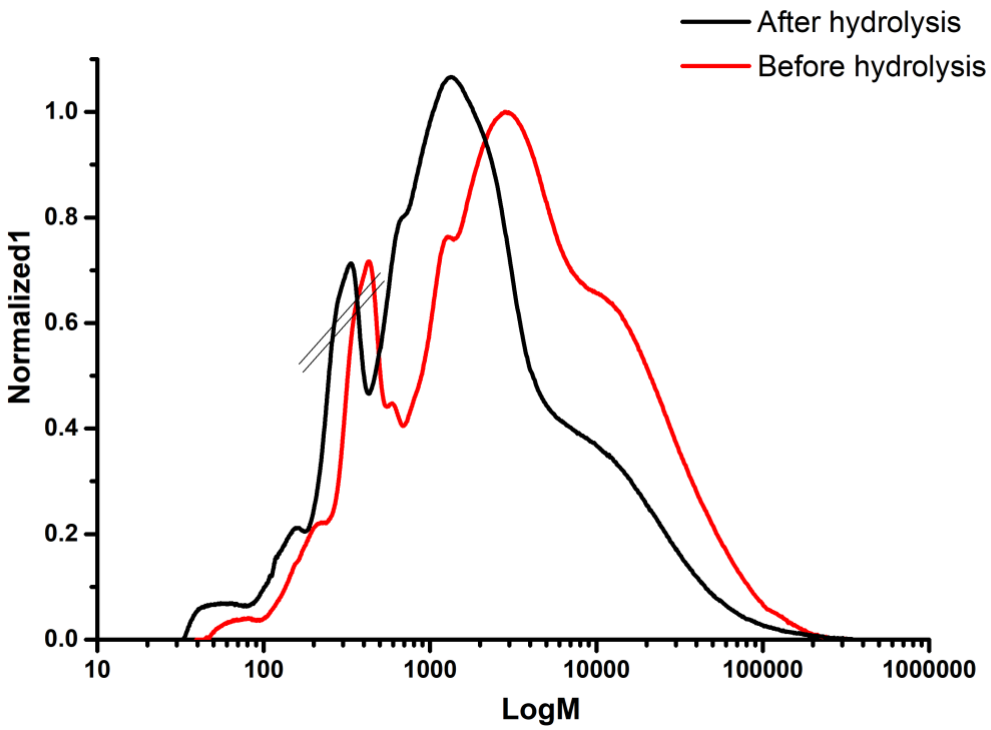
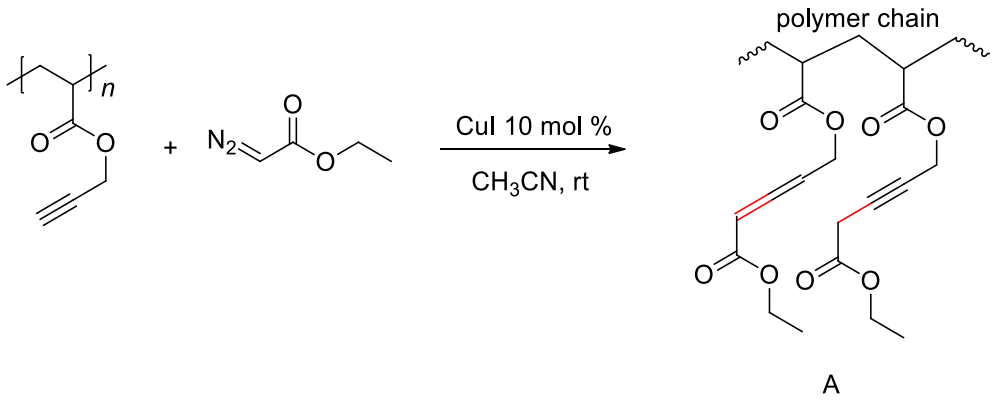


Figure 3.28. GPC graph (DMAC as eluent) of polymer poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate] (pDDMDA).

3.4. Post-modification of polyethylene derivatives via copper-catalyzed reactions

Transition metal-catalyzed reactions or C–H bond activation reactions provided an efficient way to prepare multiple novel compounds, which draw the scientist much more attention in the last decades. Although thousands of organic reactions have been developed for the post-modification of polymers, there are still not enough tools, and hence, the traditional 'click' reaction is the most frequently utilized method. Most reactions need harsh reaction conditions, miscellaneous and abundant additives, and intricate purification procedures, which inhibit their applications for the post-modification of polymers. Here, our motivation is intended to discover or utilize the newly developed transition metal-catalyzed reaction or C–H bond activation reaction for the post-modification of the polymer.

3.4.1. Post-modification and characterization of terminal alkyne tethered polymer.



Scheme 3.12. The copper-catalyzed reaction between polymer poly(propargyl acrylate) and ethyl 2-diazoacetate.

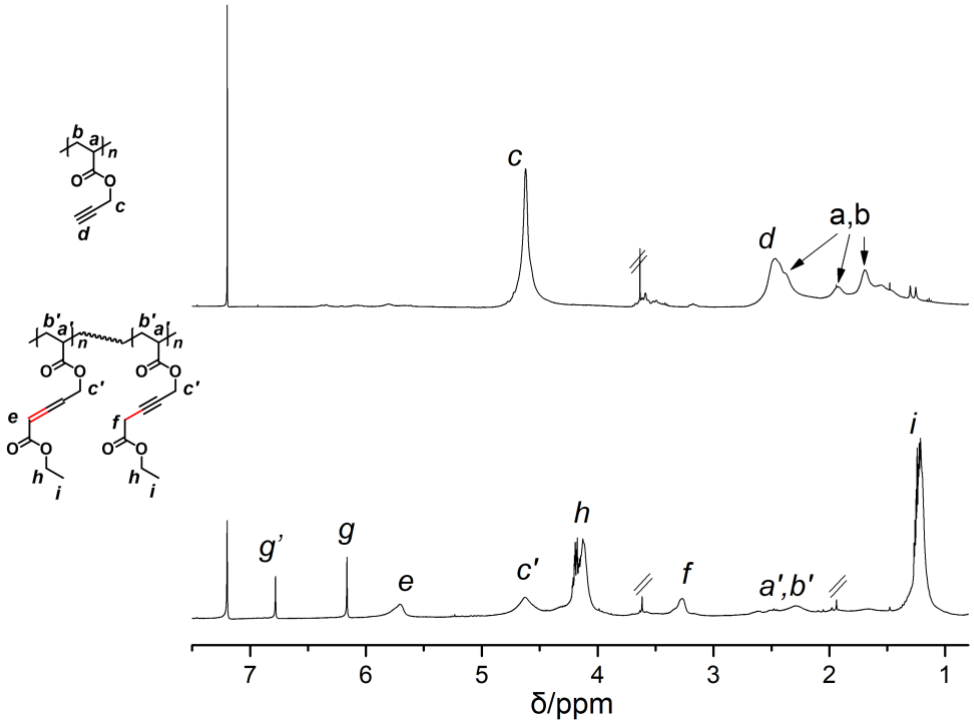
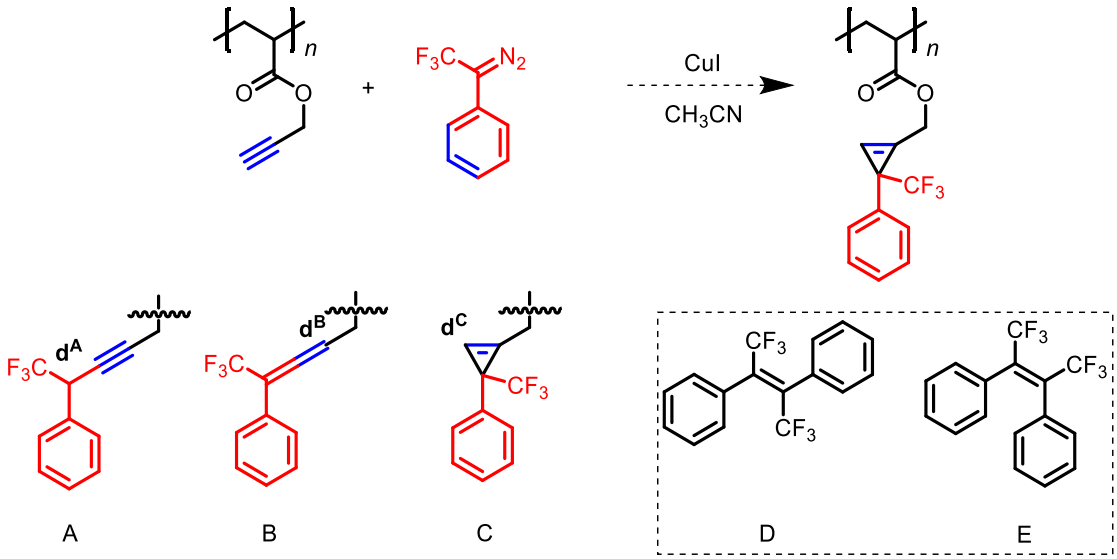


Figure. 3.29. ^{1}H NMR spectra of poly(propargyl acrylate) and the product after reaction with ethyl diazoacetate.

As rhodium and iridium are high expensive transition metals, the cheaper copper was chosen as the utilized catalyst. *Fu* and co-workers reported the copper-catalyzed reaction between a terminal alkyne and ethyl diazoacetate towards the preparation of 3-alkynoates. In their work, only a trace amount of allene isomer (<8%) was obtained.[41] Inspired by their work, we intended to explore the differences of the same reaction between the substrates of small molecules and polymers and tried to utilize it as one new post-modification methodology. Initially, poly(propargyl acrylates) was utilized as the standard polymer to investigate the reaction with ethyl diazoacetate (Scheme 3.12). Surprisingly, from the ^{1}H NMR spectrum (Figure 3.29), the post-modified polymers containing allene isomers are observed, the ratio between the 3-alkynoate and allene isomers is nearly 5:6, and the conversion is quantitative. However, a reason for the ratio is not known so far. In the ^{1}H NMR spectrum, the signal ***e*** of allene proton locates at

5.71 ppm, and the $^{f}CH_2$ of 3-alkynoate isomer locates at 3.26 ppm, which can be seen clearly in Figure 3.29. Further, the peak at 4.13 ppm and 1.2 ppm are assigned to ethyl $^{h}CH_2$ and $^{i}CH_3$, respectively. The peak at 6.78 ppm and 6.16 ppm result from diethyl fumarate and diethyl maleate, which are generated by the homo-coupling of ethyl diazoacetate. The percentage of the generated diethyl fumarate and diethyl maleate is 3% and 6%, respectively.

Subsequently, the more active diazoalkanes were also tested as the unsubstituted diazo alkanes are not stable and could not be used directly. Usually, the diazoalkanes are replaced by their corresponding hydrazones or tosyl hydrazones, which can generate diazoalkanes in situ during the reaction. However, in 2004 *Gouverneur* and co-workers reported the successful synthesis of 1-(diazo-2,2,2-trifluoroethyl)arenes which can be purified by column chromatography.



Scheme 3.13. Copper-catalyzed reaction between poly(propargyl acrylate) and (1-diazo-2,2,2-trifluoroethyl)benzene and the possible products.

Hence, the diazo alkane (1-diazo-2,2,2-trifluoroethyl)benzene was prepared and utilized for the copper-catalyzed reaction with poly(propargyl acrylate) (PPAc). As the

product is quite reactive, purification by precipitation is impossible. It's worth noting that the newly generated products seem to be crystalline when the solvent is removed, and the solubility is also not good. Hence, proton NMR was directly used for the characterization of the products after removing the volatiles.

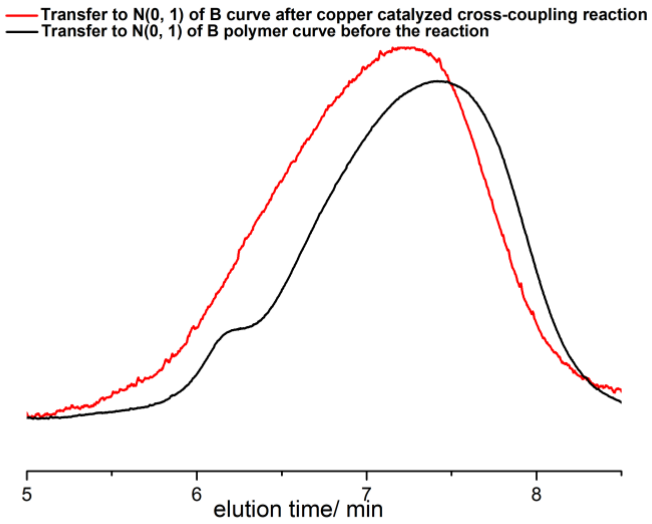


Figure 3.30. GPC graph before and after the reaction between poly(propargyl acrylate) and (1-diazo-2,2,2-trifluoroethyl)benzene.

From the ^{1}H NMR spectroscopy, the 3-alkynoate and allene isomers were not obtained; at first sight, from the ^{1}H NMR spectrum (Figure 3.32), we thought the cyclopropene derivatives (C) or allene derivatives (B) were obtained seeing in Scheme 3.13. From the GPC chromatography Figure 3.30, the molecular weight shifts before and after reaction can also be seen clearly. In the ^{1}H NMR spectrum (Figure 3.32), despite the peak at 2.53 ppm is overlapped with the backbone peak, the intensity of the acetylene peak decreases. Additionally, the ratio between peak *d'* and *e'* in Figure 3.32 is 1:2, and the same results were obtained after repeating several times. In the ^{1}H-^{1}H COSY spectrum (Figure 3.33), there is a correlation between the peak of *d'* and *c'*, which reveals that the obtained products are not a mixture of the unreacted PPAc and

homocoupling product of (1-diazo-2,2,2-trifluoroethyl)arenes (D, E, Scheme 3.13). The obtained product was also characterized by FT-IR, ^{13}C NMR, ^{19}F NMR, and ^{1}H-^{13}C HSQC (Figure 3.31, 3.34–3.36). However, after careful analysis via the data obtained by FT-IR, ^{13}C NMR spectrum and HSQC, all the possible structure is excluded and the specific structure of this post-modified product is still not determined by the presently obtained data, yet. A detailed explanation is showing in the following.

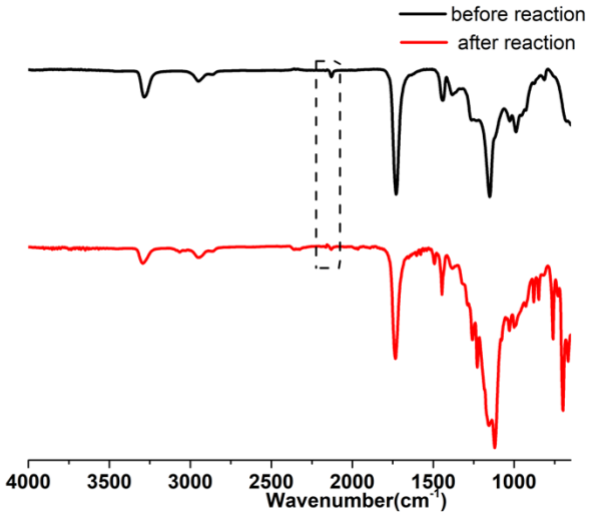


Figure 3.31. IR spectra before and after the reaction between poly(propargyl acrylate) and (1-diazo-2,2,2-trifluoroethyl)benzene.

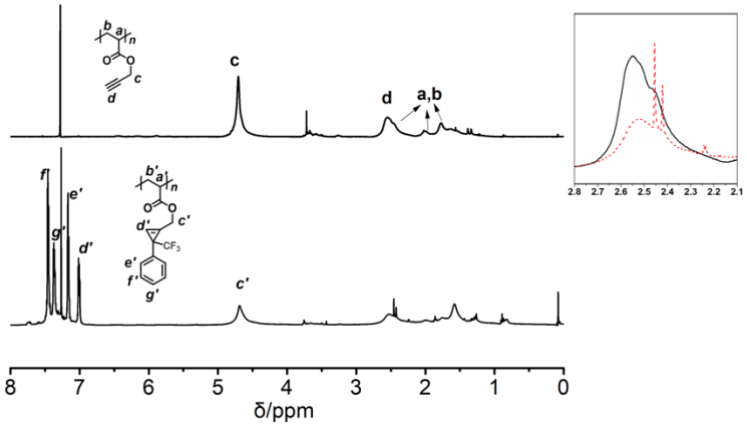


Figure 3.32. ^{1}H NMR spectra of poly(propargyl acrylate) and the ^{1}H NMR spectrum of the product after the reaction between poly(propargyl acrylate) and (1-diazo-2,2,2-

trifluoroethyl)benzene.

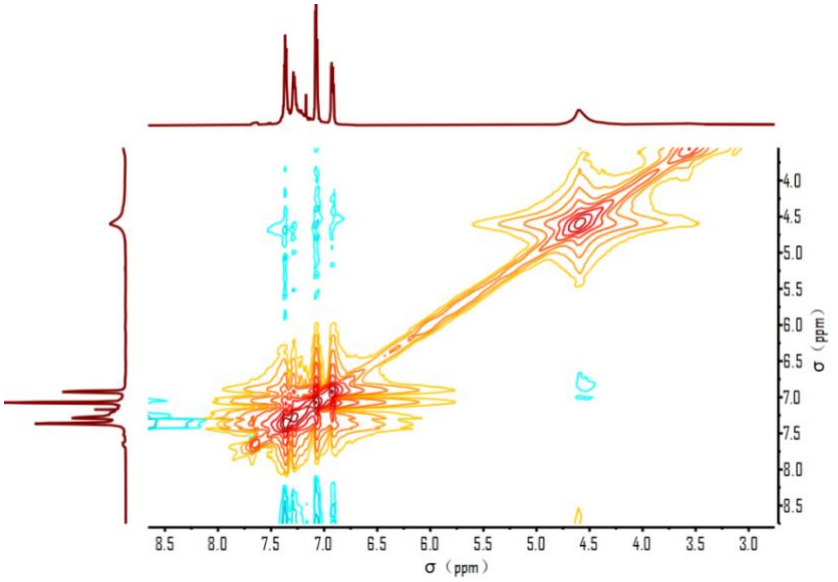


Figure 3.33. ^{1}H-^{1}H HSQC (^{1}H NMR 400 MHz, ^{1}H NMR 400 MHz, $CDCl_3$) spectrum of the product after the reaction between poly(propargyl acrylate) and (1-diazo-2,2,2-trifluoroethyl)benzene.

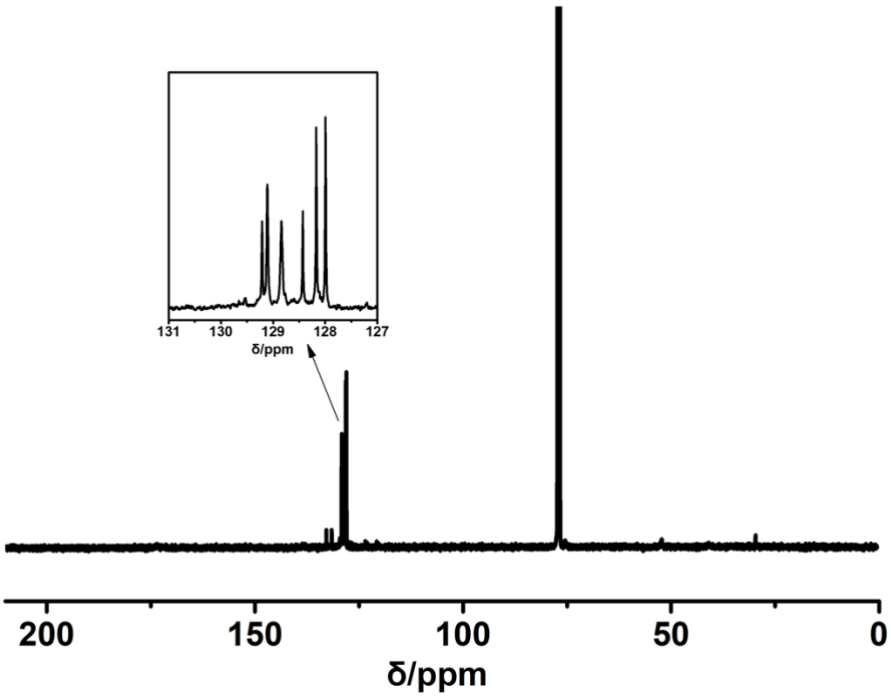


Figure 3.34. The ^{13}C NMR spectrum of the product after the reaction between

poly(propargyl acrylate) and (1-diazo-2,2,2-trifluoroethyl)benzene.

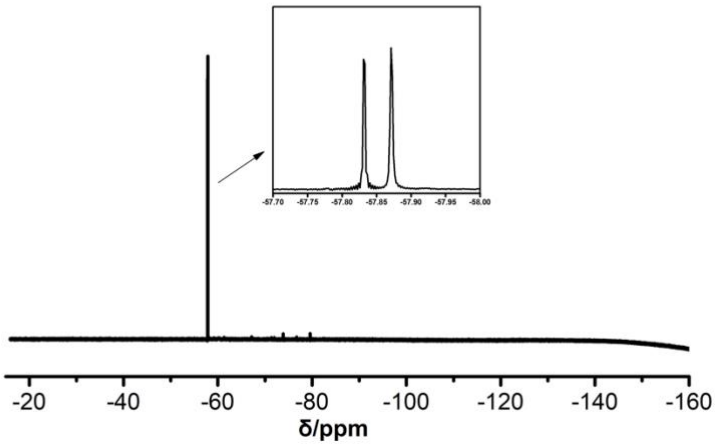


Figure 3.35. ^{19}F NMR ($CDCl_3$, 377 MHz) spectrum of the product after the reaction between poly(propargyl acrylate) and (1-diazo-2,2,2-trifluoroethyl)benzene.

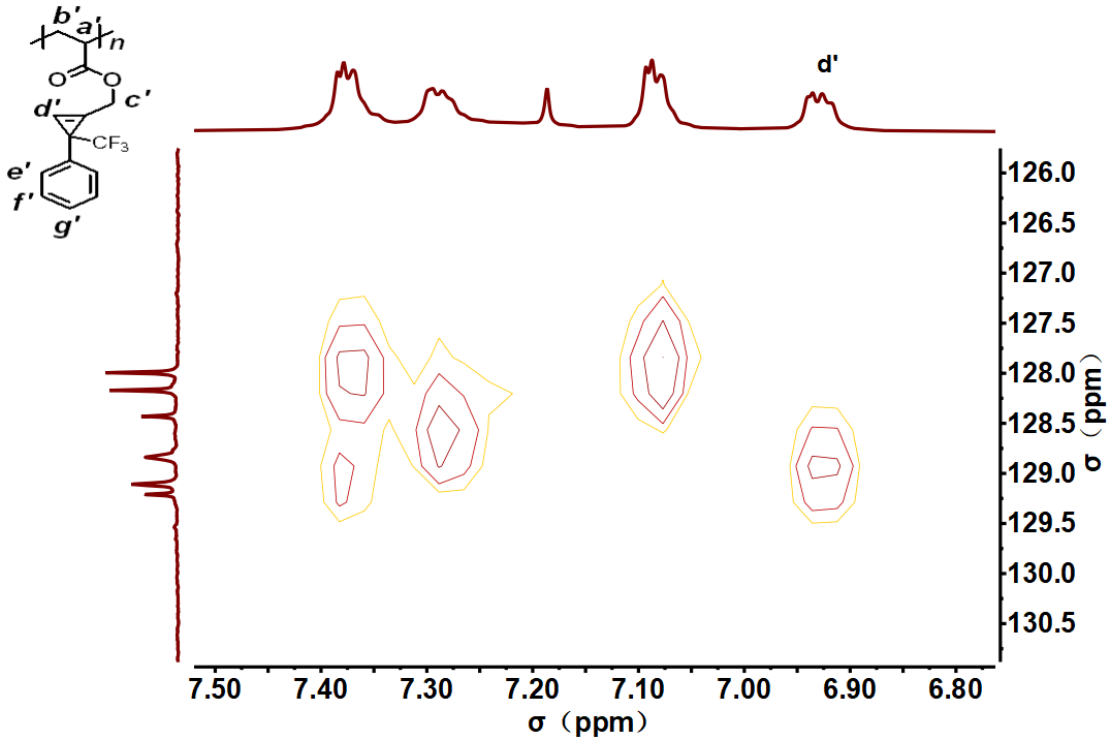


Figure. 3.36. ^{1}H-^{13}C HSQC (^{1}H NMR 400 MHz, ^{13}C NMR 101 MHz, $CDCl_3$) spectrum of the product after the reaction between poly(propargyl acrylate) and (1-diazo-2,2,2-

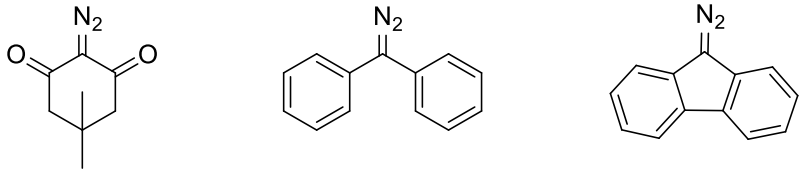
trifluoroethyl)benzene.

Actually, from the theoretical analysis, there are three potential structures of the final generated product: 3-alkynoate types (A), allene types (B), and cyclopropene (C). In the ^{1}H NMR spectrum (Figure 3.32), the peak *d'* located at 6.99 ppm indicates an olefinic peak, and hence the structure A is excluded. Given that it is structure B, in ^{1}H NMR, the peak of proton d^{B} should appear at about 6 ppm, and in the ^{13}C NMR spectrum (Figure 3.34), the peak of carbon d^{B} should locate at 90–100 ppm.[56] However, in Figure 3.36, the peak at 6.99 ppm correlates with the carbon at 129 ppm, which indicates this proton is not attributed to the allenic proton. Further, if it is structure B, in the ^{13}C NMR spectrum (Figure 3.34), there should have one peak located at 200 ppm arisen from the tertiary carbon as well. Hence, structure B precludes it as well. Then the structure C is considered. The peak located at 6.93 ppm is consistent with proton d^{C}. However, from the HSQC spectrum in Figure 3.36, this peak correlates with the carbon located at 129 ppm, not around 100 ppm. Thus, the spectrum of the obtained product does not belong to structure C.[57]

According to the 19F NMR spectroscopy data on the reference[58], the two sharp peaks at -57.82 and -57.85 ppm probably could be assigned as the structures D and E. However, the results obtained from ^{19}F NMR contradict the data obtained from ^{1}H NMR, GPC, and IR above.

After careful analysis and exclusion one by one, the specific structure of the obtained product after the reaction between poly(propargyl acrylate)and (1-diazo-2,2,2-trifluoroethyl)benzene is still not determined yet.

Subsequently, the other diazo compounds, which are less active than (1-diazo-2,2,2-trifluoroethyl)benzene, seeing in Scheme 3.14, were also tested. However, the reaction doesn't work, and the only unreacted PPAc was recovered.



Scheme 3.14. The other investigated diazo compounds.

3.4.2. Conclusion

In this part, various diazo compounds utilized for the reaction with poly(propargyl acrylate) were investigated. Compared to the reaction of corresponding small molecules, for the copper-catalyzed reaction between ethyl 2-diazoacetate and poly(propargyl acrylate), the mixture of 3-alkynoate and allene isomers were obtained, and the ratio is 5:6. After the reaction, the utilized polymer conversed completely. Further, as it is known that the allene group is quite reactive, perhaps the purification ways can influence the ratio of the obtained two isomers. Hence, different purification conditions were also investigated; however, the ratio did not get improved. In light of the mild reaction condition and high conversion, it can be treated as one novel post-modification way to introduce the allene group or 3-alkynoates into the polymer.

3.5. Rhodium-catalyzed C1 polymerization of fluorinated polymethylenes.

3.5.1. Introduction

Due to the unique properties, the fluorine-containing polymer has been developed and utilized as one important functional polymeric material.[59] As is known from the reported examples, the R^f-containing polymers exhibit a very low critical surface tension, good transparency, low refractive index, which is resulted from the R^f-groups on the side chains. Additionally, F-containing phenyl (Ph^F) group tethered polymers can be utilized as precursor polymers for the post-modification with various nucleophilic reagents, for example, amine and alcohol. Rhodium-catalyzed C1 polymerization of diazocarbonyl compounds can afford high molecular weight polymers.[21p] Our group has already reported the post-polymerization modification of poly(benzyl 2-ylidene-acetate), where the formation of five-membered cyclic imide was found.[21j] Though a very high conversion was achieved, quantitative conversion has not been realized. We believe that the Ph^F-containing phenoxy-tethered polymethylenes are a more active precursor polymer, which could obtain a quantitative conversion, as Ph^F-containing phenoxy is more active than the phenoxy group. Hence, we intended to utilize the rhodium-mediated C1 polymerization to prepare high molecular weight F-containing polymethylenes derivatives and expected to investigate their potential possibility for the subsequent post-modification.

3.5.2. Synthesis and Characterization of Ph^F containing monomers.

Ph^F-phenoxy diazoacetate, e.g., 3,5-difluorophenyl 2-diazoacetate, 4-fluorophenyl 2-diazoacetate, was prepared according to the synthesis route as shown in Figure 1.9A. The monomer 3,5-difluorophenyl 2-diazoacetate was obtained as a pale-yellow liquid in a 31% yield. It was fully characterized by ^{1}H NMR and ^{19}F NMR spectroscopy, which is consistent with the reference. It can be seen from Figure 3.37, the multiple peaks located at 6.6–6.7 ppm are assigned to aromatic protons *b*, *c*, and the broad peak at 4.9 ppm results from the α proton H^a of the diazo group. Additionally, from the ^{19}F NMR spectroscopy (Figure 3.38), one single peak originated from the fluorine locates at -109 ppm.

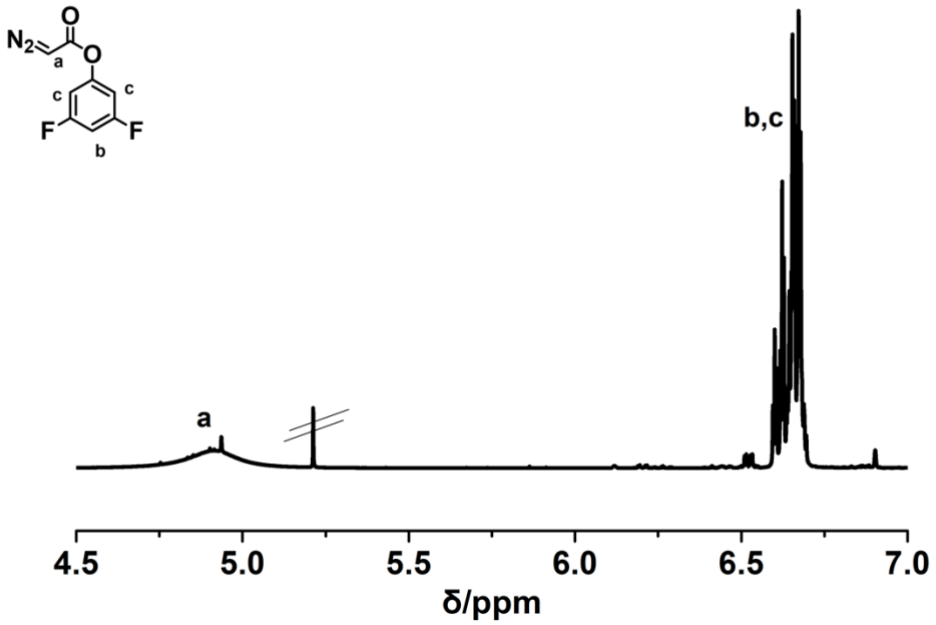


Figure 3.37. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of 3,5-difluorophenyl 2-diazoacetate.

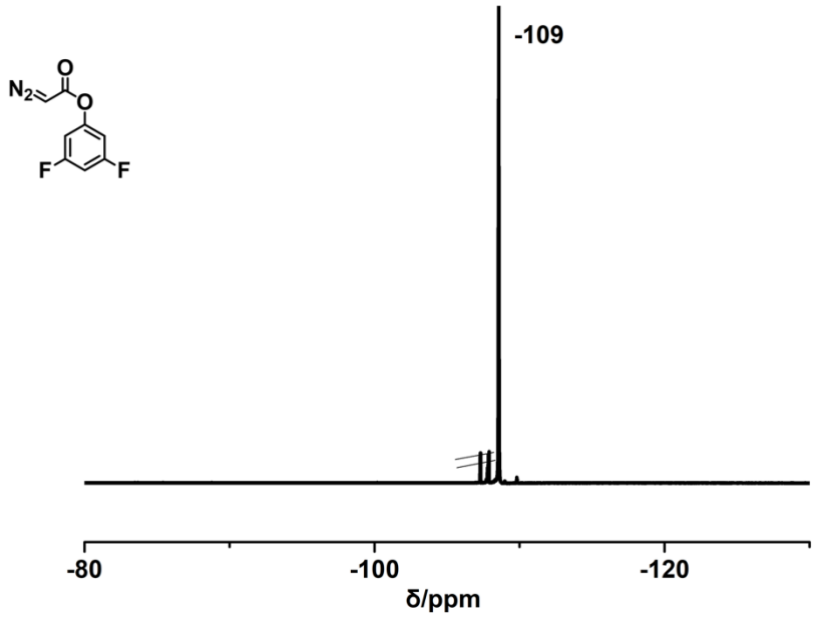


Figure 3.38. ^{19}F NMR ($CDCl_3$, 377 MHz) spectrum of 3,5-difluorophenyl 2-diazoacetate.

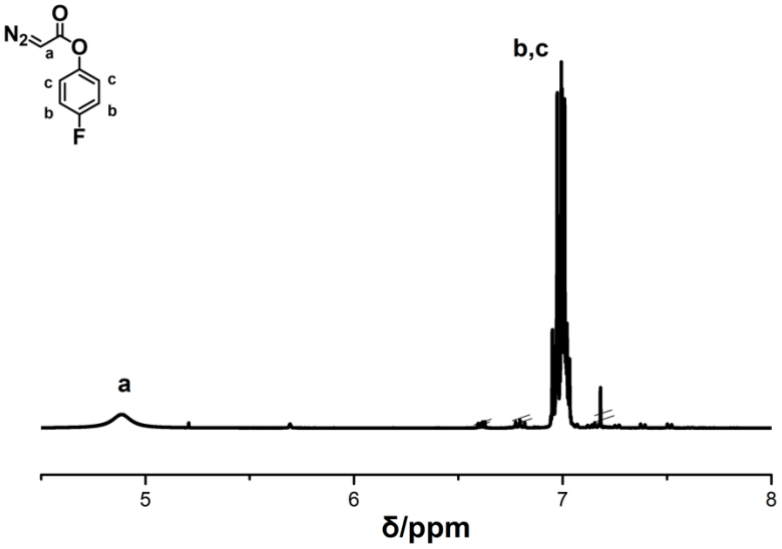


Figure 3.39. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of 4-fluorophenyl 2-diazoacetate.

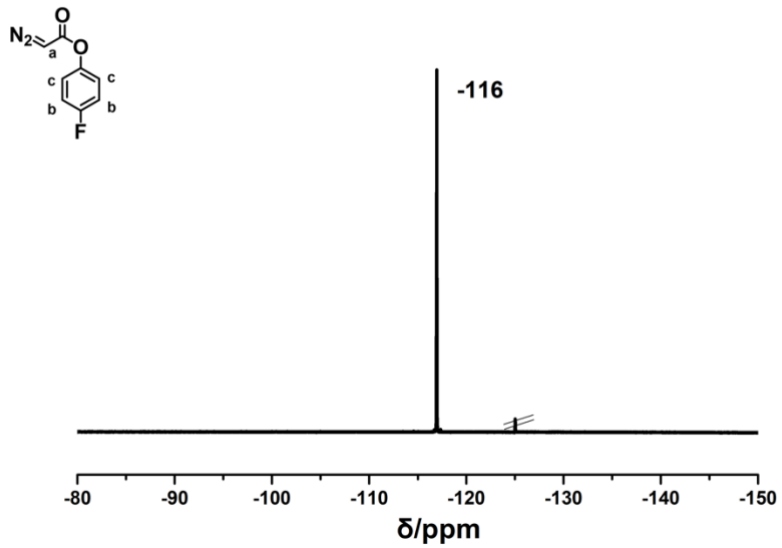


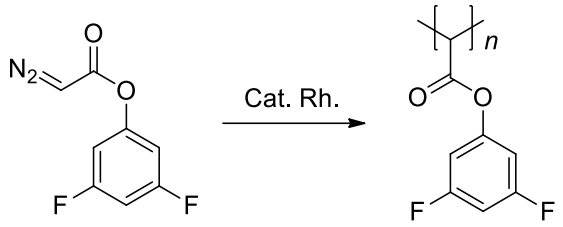
Figure 3.40. ^{19}F NMR ($CDCl_3$, 377 MHz) spectrum of 4-fluorophenyl 2-diazoacetate.

The monomer 4-fluorophenyl 2-diazoacetate was obtained as a pale-yellow liquid, and the separation yield is 34%. The product is confirmed by ^{1}H NMR and ^{19}F NMR spectroscopy, which is consistent with the reference. It can be seen from Figure 3.39, the multiple peaks located at 6.9–7.2 ppm are assigned to the aromatic proton H^b, H^c, and the broad peak at 4.9 ppm comes from the proton H^a of the N_2CH group. Further, in the ^{19}F NMR spectrum of Figure 3.40, the signal of *para*-fluoride results in one single peak located at -116 ppm.

3.5.3. Synthesis and Characterization of Ph^F containing polymethylenes.

Polymerization of the fluorinated diazoacetates was conducted in chloroform at room temperature mediated by rhodium catalysts, following the procedure reported by *de Bruin et al.* Specifically, 3,5-difluorophenyl 2-diazoacetate was polymerized in chloroform for 22 h (Scheme 3.15), via the catalysis of [(*L*-prolinate)Rh^I(1,5-dimethyl-

1,5-cyclooctadiene)] (Rh*) and [(*L*-prolinate)Rh^{I}(1,5-cyclooctadiene)] (Rh), respectively. From table 3.5, it can be seen that catalyst [(*L*-prolinate)Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] shows a relatively better result, and 10% yield was obtained, compared to [(*L*-prolinate)Rh^{I}(1,5-cyclooctadiene)], only 5% yield was obtained.



Scheme 3.15. Rhodium catalysts for the catalyzed C1 polymerization of 3,5-difluorophenyl 2-diazoacetate.

Table 3.5. Screening of the catalysts for the polymerization of 3,5-difluorophenyl 2-diazoacetate.

Entry	cat. Rh.	Yields
1	[(*L*-prolinate)Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] (Rh*)	10%
2	[(*L*-prolinate)Rh^{I}(1,5-cyclooctadiene)] (Rh)	5%

The obtained polymer poly(3,5-difluorophenyl 2-ylidene-acetate) was fully characterized by ^{1}H NMR, ^{19}F NMR, and GPC chromatography. It can be seen from Figure 3.41, the signal of aromatic protons H^{b}, H^{c} on the side chains locate at 6.2–6.9 ppm, and the peak of the backbone proton H^{a} shows a broad peak and locates at about 4.1 ppm. Additionally, from the ^{19}F NMR spectrum in Figure 3.42, the signal of meta-fluoro presents a single peak at -109 ppm.

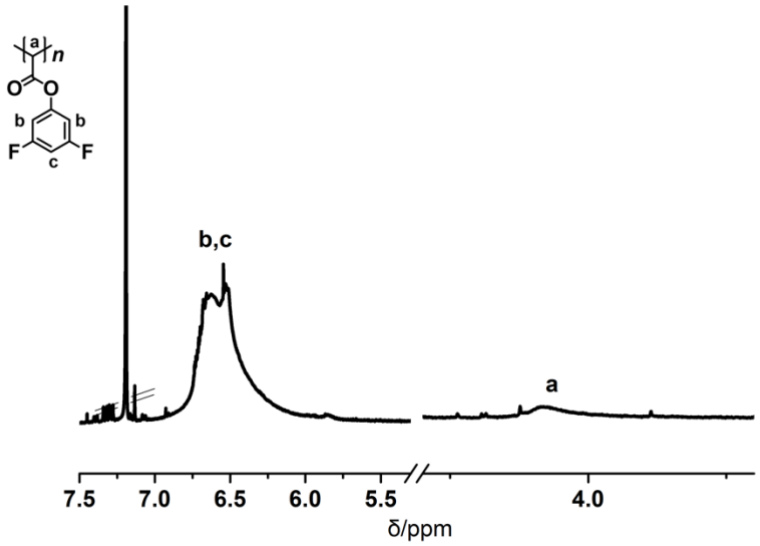


Figure 3.41. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of poly(3,5-difluorophenyl 2-ylidene-acetate).

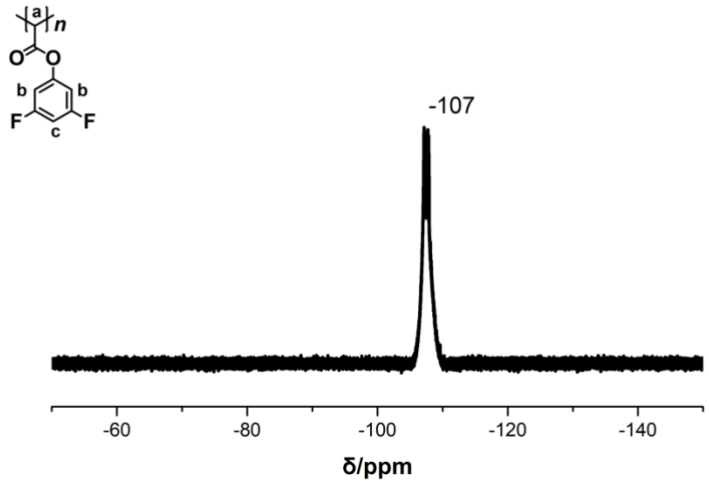


Figure 3.42. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of poly(3,5-difluorophenyl 2-ylidene-acetate).

Two different catalysts were investigated for the polymerization of monomer 3,5-difluorophenyl 2-diazoacetate. From the GPC results in Figure 3.43, Rh* shows a

relatively better molecular weight, but the PDI doesn't show a noticeable difference (1.25–1.36).

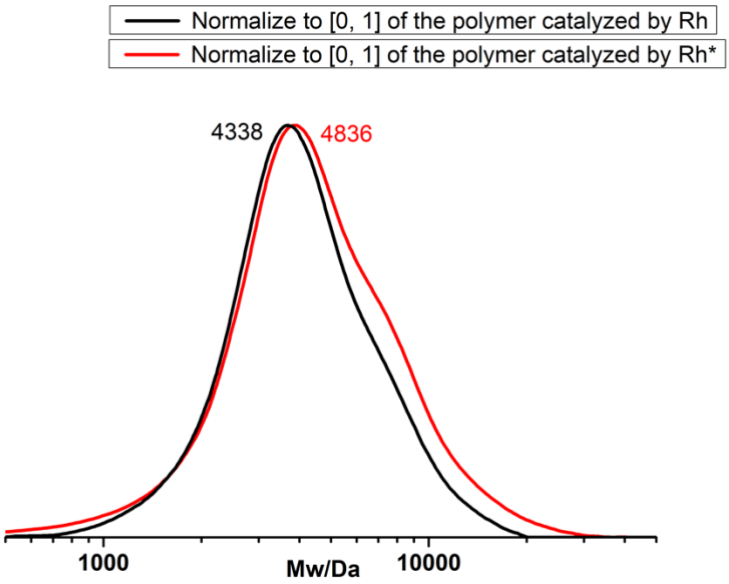
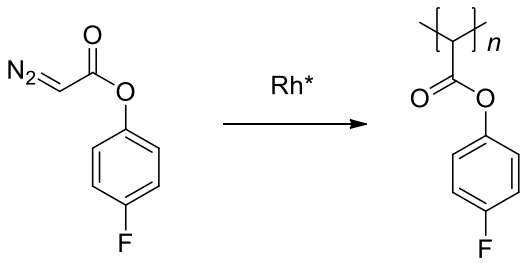


Figure 3.43. GPC graph of poly(3,5-difluorophenyl 2-ylidene-acetate) polymerized by catalysts Rh and Rh*, DMAC as eluent.



Scheme. 3.16. Rh* catalyzed polymerization of 4-fluorophenyl diazoacetate.

Rh* catalyzed C1 polymerization of 4-fluorophenyl diazoacetate was also realized at ambient temperature in chloroform (Scheme 3.16). Poly(4-fluorophenyl 2-ylidene-acetate) was obtained in 13% yield. The molecular weight is 17260 Da, but the PDI is 3.9 (Figure 3.44).

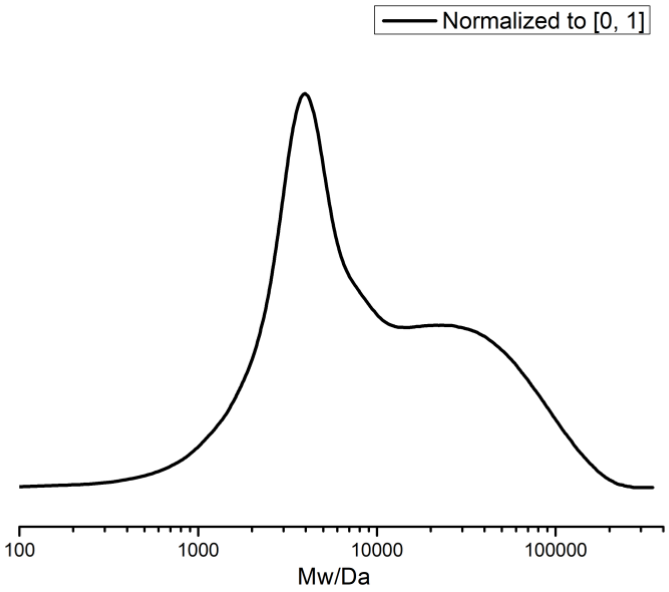


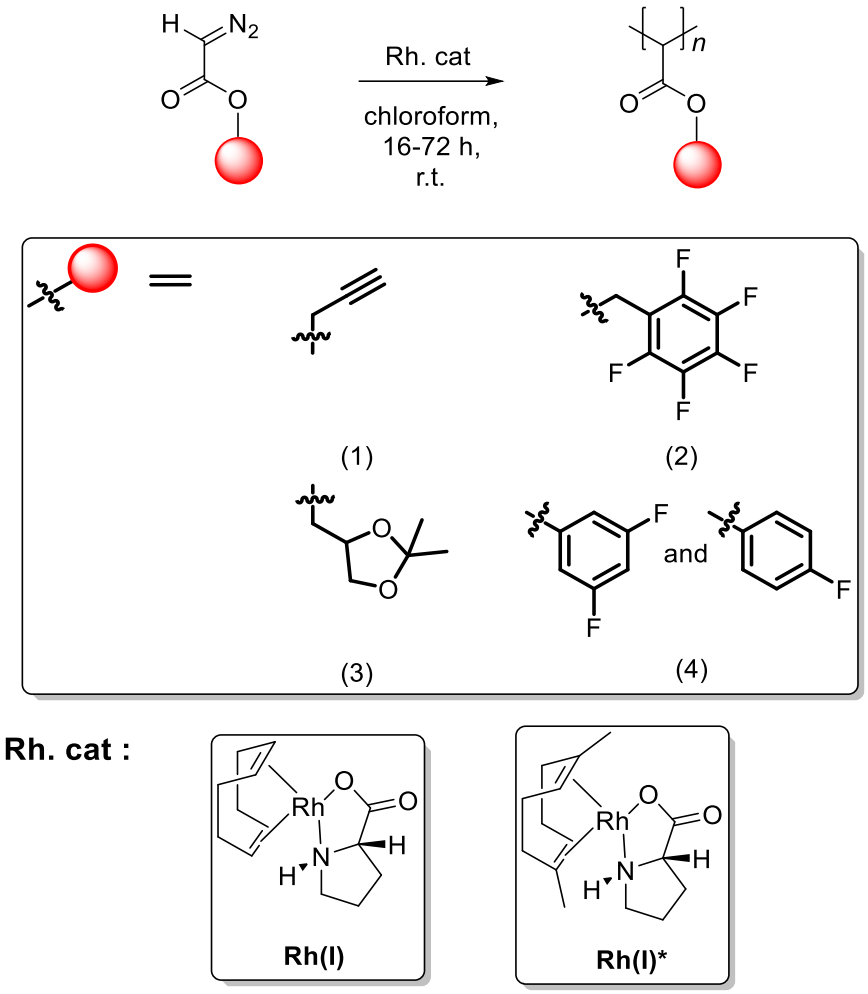
Figure 3.44. GPC graph of poly(4-fluorophenyl 2-ylidene-acetate), DMAc as eluent.

3.5.4. Conclusion

Two kinds of Ph^F containing phenoxy group tethered polymethylenes were prepared by rhodium-catalyzed carbene polymerization under mild reaction conditions in 5%–10% yields. As to the investigation for poly(3,5-difluorophenyl 2-ylidene-acetate) polymerization, though the molecular weights are not very high, PDI is very small (1.25–1.36). Additionally, polymerization of poly(4-fluorophenyl 2-ylidene-acetate) was also realized via the mediation of Rh* in 13% yields. The obtained poly(4-fluorophenyl 2-ylidene-acetate) molecular weight is 17270 Da, but the PDI is quite large (3.9). Transesterification is an efficient way for the post-modification of polymer and has been widely utilized in the post-modification of polymers. Though the reported esterification of poly(benzyl 2-ylidene-acetate) shows high conversions, they still have not realized the quantitative conversion. It is well known that the phenoxy group is an excellent leaving group, and the introduction of a high electron-withdrawing group F atom can accelerate the leaving ability of the phenoxy group. Hence, the Ph^F containing polymethylenes could make the quantitative esterification of polymethylene derivatives

come true. This work still needs to be done further.

4. Summary and Outlook



Scheme 4.1. Rhodium-catalyzed C1 polymerization to prepare various functional polymethylenes with catalysts Rh(I) and Rh(I)*.

Rhodium-mediated C1 polymerizations of functional diazoacetates to prepare various polymethylenes were investigated, which can be utilized for the subsequent post-polymerization modifications. Furthermore, the feasibility of the post-modification of the newly synthesized polymethylenes was studied as well. Nevertheless, the post-modification of polymers with the recently developed organic reaction, e.g., transition-meal catalyzed reaction or C–H bond activation reactions, was explored as well.

Specifically, the copper-catalyzed reaction between terminal alkynes and diazo compounds is quite efficient and easy-performed. Hence, it would be valuable and meaningful to utilize it for the post-modification of terminal alkyne tethered polymers. Scheme 4.1 depicts the selected functional polymethylenes that were synthesized and explored, and Scheme 4.2 illustrates the exploration of the new post-modification ways via copper-catalyzed reaction.

The successful preparation of functional polymethylenes with a high density of branching groups is depicted in Scheme 4.1.1. Specifically, poly(propargyl 2-ylidene-acetate), one kind of highly active group—alkyne decorated polymethylene, was selectively prepared, which successfully overcome the own 1,3-dipolar cycloaddition of propargyl 2-diazoacetate. Notably, the obtained polymers were subjected to CuAAC reactions with diverse azides under mild reaction conditions with the quantitative conversion. Additionally, the compared ligation reactions with its analog poly(propargyl acrylate) were smoothly completed. Noteworthily, compared to the quantitative conversion of poly(propargyl acrylate), for (1-azidoethyl)benzene, no conversion of poly(propargyl 2-ylidene-acetate) was observed, which indicates that the side density can inhibit the conversion of post-modification somehow.

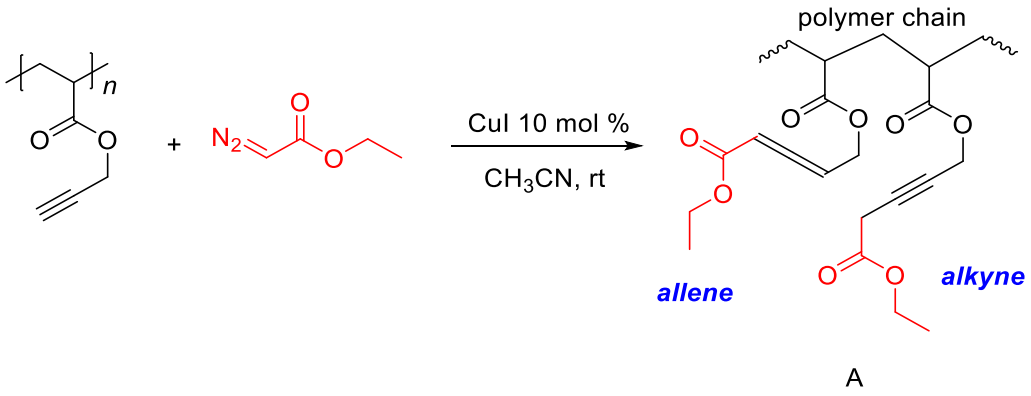
Regarding the specific reason how the side chain's density affects the conversion of CuAAC, it is still not clear so far. The substituents on aromatic azides can also influence the conversion of the CuAAC reaction. As to substrate 1-azido-4-methoxybenzene, for both poly(propargyl 2-ylidene-acetate) and poly(propargyl acrylate), only moderate conversions were obtained compared to quantitative conversions of the other substrates. Based on the literature,[60] the mechanism was proposed that the strong electron-donating effect of the methoxy group strengthens coordinating ability between the copper center and the N^- of the azide; however, suppresses the dissociation between each other so that the obtained yields of the final products were relatively lower. Last

but not least, when 1-azido-2,3,4,5,6-pentafluorobenzene, which can be treated as a linker for the PFTR reaction, was utilized for the CuAAC reaction, the cascade post-modification reaction by PFTR and CuAAC were realized with quantitative conversion, which extremely enriches the toolbox for the post-modification of polymethylene derivatives.

For the first time, poly(pentafluorobenzyl 2-ylidene-acetate) was successfully synthesized, which not only introduced the high-fluoro-substituted pentafluorophenyl group into polymethylenes but also got access to the post-modification of polymethylenes via para-fluoro-thiol reaction (PFTR). Diverse substituents tethered thiol substrates can smoothly go through the PFTR reaction with quantitative conversion, from polar groups such as amino and hydroxy to an aromatic phenyl group, which does not show pronounced inhibition to PFTR. Importantly, poly(pentafluorobenzyl 2-ylidene-acetate) shows the difference in the solubility of various solvents compared to its C2 analog poly(pentafluorobenzyl acrylate) attributed to the side density on the backbone.

Poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate] (pDDMDA) was first synthesized under the reaction with a rhodium catalyst, which can introduce two adjacent hydroxy groups after one-step hydrolysis. After screening the performance of different rhodium catalysts, Rh(I) showed a better molecular weight (up to 9100 Da). Notably, the newly generated diols can initiate the polymerization of lactide[61] or ethylene oxide[62] , making it possible to prepare high polar group cumulated polymethylene derivatives. Though we completed the synthesis of poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate] (pDDMDA) for the first time, the polymer weights are still not very perfect, possibly due to the high-sterically hindered side substituents of the monomer. Hence more active catalysts are still essential for the highly efficient synthesis of such kind polymers.

Poly(3,5-difluorophenyl 2-ylidene-acetate) and poly(4-fluorophenyl 2-ylidene-acetate) (Scheme 4.1.4) were also completed by the mediation of [(*L*-prolinate)Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] (Rh*). Compared to the reported polymethylenes mediated by palladium, the polydispersity of polymers prepared by rhodium catalysis is smaller (1.35), even if the yield is not improved. However, as the separation of fluoro-substituted-phenyl 2-diazoacetate is quite tricky, this work still needs to be done furthermore not only to broaden the scope of the side fluoro-substituted phenol but also to investigate the polymer precursors for the subsequent post-modification.



A

Scheme 4.2. The copper-catalyzed reaction between poly(propargyl acrylate) and ethyl diazoacetate.

A copper-catalyzed reaction between terminal alkyne tethered polymer—poly(propargyl acrylate) and ethyl diazoacetate was discovered for the first time (Scheme 4.2). The methodology features mild reaction conditions (room temperature, no additives, no ligands, and quantitative conversion). Hence, it can be regarded as an efficient way for the post-modification of polymers. Interestingly, the actively allenic motif was first captured in polymers via a post-modification despite a mixture of alkynoates and allenic isomers. Diazoalkanes were utilized for the post-modification of poly(propargyl acrylate) as well. Only the substrate (1-diazo-2,2,2-trifluoroethyl)benzene seems to work under this condition. However, due to the limited

characterization methods of polymer mixtures so far, the specific structure of the final product is still pending. Discovering an efficient way to purify the products deeply is necessary and meaningful for the characterization of the polymer. On the other hand, as the final products are active and unstable, hence NMR grade reaction is also indispensable.

All in all, on the one hand, diversities of functional polymethylene precursors that are accessible for the post-modification reactions were successfully synthesized and utilized for the post-modification reactions, respectively. These projects make them possible for the efficient and precise decorating of polymethylene precursors. Additionally, they also pave the way for subsequent research on discovering the physical properties of the newly prepared materials. On the other hand, the initial work on the post-modification of polymers by the newly developed reaction has been disclosed, which opens the gate for using efficient reactions or C–H bond activation in the post-modification of polymers.

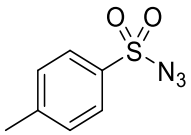
5. Experimental Part

5.1. Methods and Materials

Unless noted otherwise, all chemicals were commercially available and utilized without further purification. Yields refer to isolated and purified products. [(*L*-prolinate)Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] (Rh*) and [(*L*-prolinate)Rh^{I}(1,5-cyclooctadiene)] (Rh) were prepared according to reported literature.[21g] NMR spectral were recorded on a Bruker Ascend III 400 MHz FT-NMR spectrometer in corresponding solvents. Chemical shifts were recorded in ppm (δ) relative to the solvent residual peak added as internal standards. Fourier transform infrared (FT-IR) spectroscopy was measured in a Bruker Vertex 80 FT-IR/NIR Spectrometer. Measurements were conducted via direct transmission method or with an attenuated total reflectance (ATR) attachment. Size Exclusion Chromatography (SEC) analyses were performed on a PL-SEC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 µm bead-size guard column (50 x 7.5 mm) followed by three PLgel 5 µm Mixed C column (300 × 7.5 mm) and a differential Refractive Index (RI) detector. Lithium bromide (LiBr) 0.03 wt% enriched *N*,*N*-dimethylacetamide (DMAC) was used as eluent at an operating temperature of 50 °C and with a flow rate of 1.0 ml min^{-1}. All samples were prepared with a polymer concentration of 0.1 mg/ml, and 100 µL were usually injected into the column. DSC measurements were performed on a TA Instruments Q200 incorporating an RCS90 cooling system. All samples weighing between 10.0 and 14.0 mg were heated from -50 °C to 200 °C twice with a heating ramp of 10.0 K/min. All reported temperature and enthalpy values were given from the second heating ramp curves.

5.2. Synthesis and Characterization of Monomers—2-Diazocarbonyl Compounds and Basic Chemicals related to the Monomers' synthesis

Synthesis of Tosyl azide



Tosyl azide was synthesized according to the following procedure. An Erlenmeyer flask with 100 mL deionized water and 100 mL acetone was loaded with sodium azide (38.02, 600 mmol, 1.1 equiv.). Then, the solution was dumped into another Erlenmeyer flask containing a solution of tosyl chloride (103.25 g, 540 mmol, 1.0 equiv.) dissolved in 250 mL acetone. Afterward, the solution was stirred at room temperature for 4 hours. Subsequently, the solution was poured in 150 mL water, and the organic layer was separated from the aqueous phase, yielding the crude product. The crude product was washed twice with water. Finally, the product was dried with sodium sulfate and then attached to a high vacuum to afford the colorless oil.

Yield: 80.25 g (406 mmol, 75 %).

^{1}H NMR (400 MHz, $CDCl_3$):

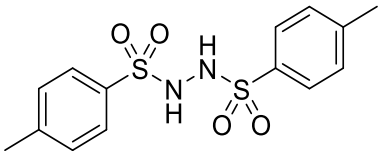
δ(ppm) 7.83 (d, *J* = 8.4 Hz, 2H, CH_{ar}), 7.40 (d, *J* = 7.7 Hz, 2H, CH_{ar}), 2.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) 146.33 (C_{ar}), 135.56 (C_{ar}), 130.37 (C_{ar}), 127.56 (C_{ar}), 21.82 (CH_3).

The analytical data is consistent with the referred literature.[63]

Synthesis of *N,N*-Ditosylhydrazine



p-toluenesulfonyl hydrazide (33.95 g, 182 mmol, 1.0 equiv.) and tosyl chloride (52.13 g, 274 mmol, 1.5 equiv.) were loaded into a dry round bottom flask, and then 150 mL dichloromethane was added. The suspension was stirred at room temperature for 1.5 hours, while pyridine (22.05 mL, 273 mmol, 1.5 equiv.) was added dropwise. The suspension first turned homogeneous and yellow, and then a colorless precipitate was formed a few minutes later. Diethyl ether (350 mL) and water (200 mL) were poured into the solution, and afterward, the solution was stirred for half an hour in the ice bath. The precipitated solids were filtered off and washed with diethyl ether. Finally, the crude product was recrystallized from methanol to afford the product as colorless needles, yield: 47.35 g (139 mmol, 76%).

^{1}H NMR (400 MHz, DMSO-d_6):

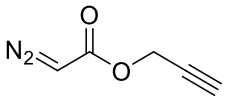
δ(ppm) = 9.59 (s, 2H, *NH*), 7.65 (d, 4H, CH_{ar}), 7.39 (d, 4H, CH_{ar}), 2.40 (s, 6H, CH_3).

^{13}C NMR (101 MHz, DMSO-d_6):

δ(ppm) = 143.40 (2C, C_{ar}), 135.44 (2C, C_{ar}), 129.40 (4C, C_{ar}), 127.76 (2C, C_{ar}), 21.00 (2C, CH_3).

The analytical data is consistent with the referred literature.[28a]

Synthesis of Propargyl 2-diazoacetate



The preparation of propargyl 2-diazoacetate was referred to as the general route B (Scheme 1.9 **B**).

Step A: synthesis of propargyl acetoacetate: Propargyl alcohol (8.40g, 8.80 mL, 150 mmol, 1.0 equiv.) and 2,2,6-trimethyl-4H-1,3-dioxin-4-one (21.30g, 19.90 mL, 150 mmol, 1.0 equiv.) were added into a flask with 50 mL toluene, and then the solution was refluxed overnight. Afterward, the toluene was evaporated, and the crude product was utilized for the synthesis of propargyl 2-diazoacetate without further purification and characterization.

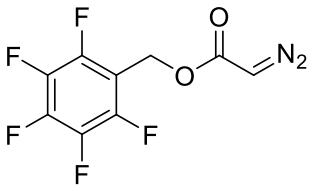
Step B: preparation of propargyl 2-diazoacetate: Tosyl azide (25.48 g, 179 mmol, 1.3 equiv.) dissolved in 30 mL acetonitrile was dropwise added into a solution 80 mL acetonitrile comprising propargyl acetoacetate (19.30 g, 137 mmol, 1.0 equiv.) and triethylamine (21.10 mL, 151 mmol, 1.1 equiv.) over 30 minutes. The reaction mixture was stirred overnight at room temperature. Afterward, lithium hydroxide (9.73 g, 412 mmol, 3.0 equiv.) dissolved in deionized water was poured into the above solution, and then the mixture was stirred for an extra 4 hours at room temperature. Subsequently, the crude product was extracted three times with diethyl ether. All the organic phases were combined and washed with water, and then dried through $MgSO_4$. After evaporating the solvent on the rotavapor, the residual was purified by column chromatography with dichloromethane or ethyl acetate/ petrol ether (1:50 to 1:4) eluent. The pure product was obtained as a yellowish liquid. Yield: 6.7 g (46%)

^{1}H NMR (400 MHz, $CDCl_3$):
δ (ppm) = 4.84 (s, 1H, *CH*COO), 4.77 (s, 2H, *CH$_2$*CCH), 2.50(s, 1H, C*CH*).

^{13}C NMR (100 MHz, $CDCl_3$):
δ (ppm) = 165.75 (*CO*O), 77.59 (*C*–CH), 75.04 (C*CH*), 51.90(*CH$_2$*), 45.82 (*CH*COO).

FT-IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3292, 3117, 2110, 1683, 1386, 1343, 1167, 1029, 993, 737

Synthesis of (pentafluorophenyl)methyl 2-diazoacetate



Step A: The synthesis of pentafluorobenzyl acetoacetate was done by loading pentafluorobenzyl alcohol (25 g, 126 mmol, 1.0 equiv.) and 2,2,6-trimethyl-4H-1,3-dioxin-4-one (17.69 g, 125 mmol, 1.0 equiv.) in a round flask charging with 50 mL toluene. The reaction was heated and refluxed overnight. Subsequently, the solvent was evaporated, and the crude product was utilized for the synthesis of propargyl 2-diazoacetate without further purification and characterization.

Step B: **The synthesis of (pentafluorophenyl)methyl 2-diazoacetate:** tosyl azide (9.09 g, 46 mmol, 1.3 equiv.) in 30 mL acetonitrile was dropwise added to a solution of 80 mL acetonitrile containing pentafluorobenzyl acetoacetate (10 g, 35.44 mmol, 1.0 equiv.) and triethylamine (3.94 g, 39 mmol, 1.1 equiv.). The reaction mixture was stirred overnight at room temperature. Afterward, lithium hydroxide (2.54 g, 106 mmol, 3.0 equiv.) dissolved in 100 mL water was added into the above solution, and the mixture was stirred for an additional four hours at room temperature. Subsequently, the crude product was extracted three times with diethyl ether. All the organic phases were combined and then washed with water and dried through $MgSO_4$. For further purification, after removing the solvent, the residue was purified by column chromatography with dichloromethane or ethyl acetate/petrol ether (1:50 to 1:4) as eluent. Finally, the target product was obtained as a yellowish liquid. Yield: 7.4 g (78%).

^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 5.20 (2H, O*CH*$_2$), 4.73(1H, *CH*COO).

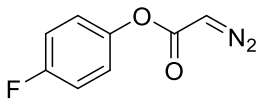
^{19}F NMR (377 MHz, $CDCl_3$):

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*).

^{13}C NMR (101 MHz, $CDCl_3$)**:**

δ (ppm) = 165.69 (*C=O*), 147.43 and 144.55 (dm, $^1J_{CF}$ = 255 Hz, 2 x *meta C*–F), 143.11 and 140.57 (dm, $^1J_{CF}$ = 255 Hz, 2 x *para C*–F), 138.78 and 136.26 (dm, $^1J_{C-F}$ = 255 Hz, 2 x *ortho C*–F), 109.30 (td, $^2J_{CF}$ = 17 Hz, $^3J_{CF}$ = 4 Hz, OCH_2C_{PFB}), 53.46 (OCH_2), 44.56 (N_2CH).

Synthesis of 4-fluorophenyl 2-diazoacetate



Step A: 4-fluorophenol (2.00 g, 1.64 mL, 17.84 mmol), pyridine (2.85 mL, 35.68 mmol), and acetonitrile (80 mL) were loaded in a round bottom flask. Then bromoacetyl bromide (2.6 mL, 31.22 mmol) was dropwise added to the suspension cooled at 0 ℃, and the mixed solution was stirred at 0 ℃ for 15 min. Afterward, the reaction mixture was quenched with 25 mL water, and the mixture was extracted three times with dichloromethane. The combined dichloromethane was washed with brine and dried over $NaSO_4$. After filtration and removal of the solvent under reduced pressure, the residual was utilized for the subsequent reaction without further purification.

Step B: 4-fluorophenyl 2-bromoacetate (4.16 g, 17.84 mmol, 1.0 equiv.), *N*,*N*'-ditosylhydrazine (12.15 g, 35.68 mmol, 2 equiv.) and 30 mL THF were placed in a round bottom flask and cooled to 0 ℃. After 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (13.19 mL, 13.43 g, 53.52 mmol, 3 equiv.) was dropwise added to the mixture, the concomitantly resulted mixture was stirred for additional 20 minutes while keeping at 0 ℃. Subsequently, a saturated $NaHCO_3$ solution was added, and the concomitant reaction mixture was extracted three times with diethyl ether. The combined organic

phases were washed with brine, and the crude product was obtained after drying over $MgSO_4$ and removing the solvent under reduced pressure. The residual was done by column chromatography utilizing dichloromethane or ethyl acetate/petrol ether eluent for further purification. The product was obtained as a yellowish liquid, yield: 1.1 g (34%).

^{1}H NMR (400 MHz, $CDCl_3$):

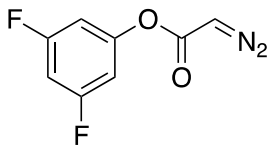
δ(ppm) = 7.2–7.0 (m, 4H, H_{ar}), 4.96 (br, 1H, N_2=*CH*–).

^{19}F NMR (377 MHz, $CDCl_3$):

δ(ppm) = -116.87 (s, 1F, *para*-F_{ar})

The analytical data is consistent with the referred literature.[20b]

Synthesis of 3,5-difluorophenyl 2-diazoacetate



3,5-difluorophenyl 2-diazoacetate was synthesized with a similar procedure for the synthesis of 4-fluorophenyl 2-diazoacetate except for the use of 3,5-difluorophenol instead of 4-fluorophenol. Obtained diazoacetate as yellowish liquid (31%).

^{1}H NMR (400 MHz, $CDCl_3$):

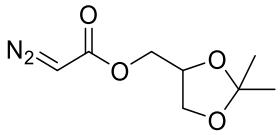
δ(ppm) = 6.7–6.8 (m, 3H, H_{ar}), 4.92 (br, 1H, N_2=*CH*–).

^{19}F NMR (377 MHz, $CDCl_3$):

δ(ppm) = -109 (s, 2F, *meta*-F_{ar})

The analytical data is consistent with the referred literature.[20b]

Synthesis of (±) (2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate



Step A: The synthesis of pentafluorobenzyl acetoacetate was done by loading (±) (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (5 g, 37.83 mmol, 1.0 equiv.) and 2,2,6-trimethyl-4H-1,3-dioxin-4-one (5.38 g, 37.83 mmol, 1.0 equiv.) in a round flask charging with 50 mL toluene. The reaction was heated and refluxed overnight. Subsequently, the solvent was evaporated, and the crude product was utilized for the synthesis of (±) (2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate without further purification and characterization.

Step B: **The synthesis of (±) (2,2-dimethyl-1,3-dioxolan-4-yl)methyl l 2-diazoacetate:** tosyl azide (11.26 g, 57.11 mmol, 1.3 equiv.) in 30 mL acetonitrile was dropwise added to a solution of 80 mL acetonitrile containing (±) (2,2-dimethyl-1,3-dioxolan-4-yl)methyl acetoacetate (9.50 g, 43.93 mmol, 1.0 equiv.) and triethylamine (4.89 g, 48.33 mmol, 1.1 equiv.). The reaction mixture was stirred overnight at room temperature. Afterward, lithium hydroxide (3.16 g, 131.80 mmol, 3.0 equiv.) dissolved in 80 mL water was added into the above solution, and the mixture was stirred for an additional four hours at room temperature. Subsequently, the crude product was extracted three times with diethyl ether. All the organic phases were combined and then washed with water and dried through $MgSO_4$. For further purification, after removing the solvent, the residue was purified by column chromatography with dichloromethane or ethyl acetate/petrol ether (1:50 to 1:4) as eluent. Finally, the target product was obtained as a yellowish liquid. Yield: 2.4 g (27%).

^{1}H NMR (400 MHz, $CDCl_3$):

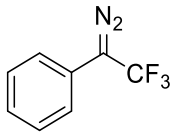
δ(ppm) = 4.75 (s, 1H, N_2–*CH*), 4.31– 4.21 (m, 1H, $CH_{5\text{-ring}}$), 4.19 (dd, J = 11.4, 4.5 Hz,

1H, COO–*CH*$_2$), 4.11 (dd, *J* = 11.4, 5.9 Hz, 1H, COO–*CH*$_2$), 4.01 (dd, *J* = 8.5, 6.5 Hz, 1H, *CH*$_{2,\ 5\text{-ring}}$), 3.68 (dd, *J* = 8.5, 6.0 Hz, 1H, *CH*$_{2,\ 5\text{-ring}}$), 1.36 (d, *J* = 0.8 Hz, 3H, *CH*$_3$), 1.30 (d, *J* = 0.7 Hz, 3H, *CH*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 166.64 (*C*=O), 108.54 (O–*C*$_{5\text{-ring}}$–O), 73.69 (*C*H$_{5\text{-ring}}$), 66.20 (*C*H$_{2,\ 5\text{-ring}}$), 64.94 (COO–*C*H$_2$), 46.35 (N$_2$–*C*H), 26.66 (*C*H$_3$), 25.36 (*C*H$_3$).

Synthesis of (1-diazo-2,2,2-trifluoroethyl)benzene.



Step A: synthesis of 4-methyl-*N*'-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide: To a round bottom flask was loaded tosyl hydrazide (1 equiv.) and minimum quantity of methanol needed to dissolve the hydrazide at reflux (approximately 1.5 M). Subsequently, the reaction was cooled to room temperature, and trifluoroacetophenone (1 equiv.) was added in one portion. The resulted reaction mixture was heated at 65 ℃ for 12 h (monitored by TLC). The product was precipitated out of the solution when it cooled to 0 ℃. The precipitate was collected by vacuum filtration and washed with pentane. As the hydrazone derivative usually is unstable on silica gel, the obtained crude product was utilized for the next step without further purification. When 2,2,2-trifluoroacetophenone (5.00 g, 28.72 mmol, 1 equiv.) and tosyl hydrazide (5.35 g, 28.72 mmol. 1 equiv.) was used in the reaction, the target product was obtained as a white solid in 81% yield (8.0 g).

Step B: synthesis of (1-diazo-2,2,2-trifluoroethyl)benzene: 4-methyl-N'-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (1 equiv.) and a solution of KOH (2 equiv.) in methanol were loaded in a round bottom flask. The reaction mixture

was refluxed for 1.5 hours. Subsequently, the reaction was cooled to room temperature and diluted with water. The crude product was extracted with pentane, washed with saturated $NaHCO_3$ and brine consecutively, and dried with magnesium sulfate. After removing the solvent under reduced pressure, the product was purified by silica gel chromatography with pentane as eluent. CAUTION: diazo compounds are presumed to be toxic and potentially and easily explosive; thus, they should be dealt with in the fume hood with care. 4-Methyl-*N*'-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (2 g, 5.9 mmol, 1 equiv.) and KOH (0.65 g, 11.7 mmol, 2 equiv.) were utilized for this reaction. The target product was obtained as a volatile red liquid in a 40% yield (0.42 g).

^{1}H NMR (400 MHz, $CDCl_3$):

δ (ppm) = 7.34–7.29 (m, 2H), 7.14–7.08 (m, 1H), 7.02 (ddt, J = 7.7, 2.0, 1.0 Hz, 2H).

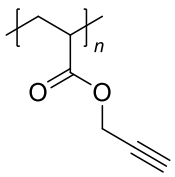
^{13}C NMR (101 MHz, $CDCl_3$):

δ (ppm) = 129.39, 126.99, 125.65(q, CF_3, $^{1}J_{CF}$ = 269 Hz), 123.53, 122.23.

^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) = -57.41.

The analytical data is consistent with the referred literature.[64]

5.3. Synthesis and Characterizations of polymers



Synthesis of poly(propargyl acrylate) (PPAc)

A dry 1,4-dioxane solution containing propargyl acrylate (4.9 g, 44.50 mmol, 100 equivalents) and AIBN (73.07 mg, 0.445 mmol, 1 equivalent) was degassed with air at

room temperature for 10 min. After degassing, the reaction mixture was stirred at 80 °C for 16 h. The reaction mixture was then cooled down and exposed to air to quench the reaction. The polymer was purified by re-precipitation three times in hexane to obtain a white solid. Yields: 3.3 g of white solid (0.29 mmol, 67%).

^{1}H NMR (400 MHz, $CDCl_3$):

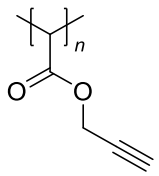
δ/ppm = 4.71 (s, 2H, O*CH*$_2$), 2.50 (s, 1H, C*CH*), 1.2–2.4 (br, 3H, *CHCH*$_2$, backbone peaks).

^{13}C NMR (101 MHz, $CDCl_3$):

δ/ppm = 168.31(*C*=O), 77.57 (CH_2*C*≡CH), 74.61 (CH_2C≡*C*H), 53.39 (*C*H_2*C*≡CH), 40.90 (CH_2*C*$H_{backbone}$), 34.95 (*C*$H_2CH_{backbone}$).

FT-IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3284, 2949, 2128, 1729, 1440, 1151, 989, 649

Synthesis of poly(propargyl 2-ylidene-acetate) (PPA)



Similar to other polymerizations,[21i] propargyl diazoacetate (2.2 g, 17.73 mmol, 50 equivalents) and [(*L*-prolinate) Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] (124.9 mg 0.35 mmol) were separately dissolved in 7.5 mL chloroform. Then, the monomer solution was rapidly added to the monomer solution, and the resulting solution was stirred for 22 h at room temperature; after filtering through Celite, the polymer was precipitated in hexane several times and yielded a light pale-yellow solid. Yield: 670 mg (40%).

^{1}H NMR (400 MHz, $CDCl_3$):

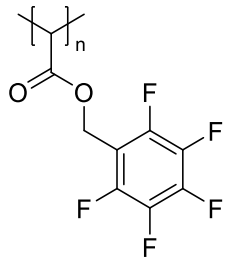
δ/ppm = 4.79 (m, 3H, *CH*, O*CH*$_2$), 2.5 (s, 1H C*CH*).

^{13}C NMR (101 MHz, $CDCl_3$):

δ/ppm = 171.47 (C=O), 77.23 ($CH_2C \equiv CH$), 75.56 ($CH_2C \equiv CH$), 53.61(CH_2, $CH_{backbone}$).

FT-IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3281, 2945, 2128, 1731, 1155, 990.

Synthesis of poly(pentafluorobenzyl 2-ylidene-acetate) (pPFBDA)



Similar to other polymerizations [65] , pentafluorobenzyl 2- diazoacetate (1.2 g, 4.5 mmol, 50 equiv.) and [(*L*-prolinate) Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] (34 mg, 0.09 mmol, 1 equiv.) 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 3 times and yielded a pale light solid. Yield: 160 mg (16%).

^{1}H NMR (400 MHz, *d*8-Toluene):

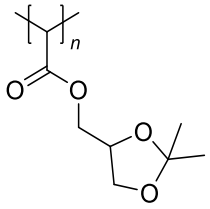
δ/ppm = 5.04 (br, 2H, O*CH*$_2$), 3.53 (br, 1H, *CH*COO).

^{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.

Synthesis of poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate] (pDDMDA)



Similar to other polymerizations [65], (±) (2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate (1 g, 5 mmol, 50 equiv.) and [(*L*-prolinate) Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] (36 mg, 0.1 mmol, 1 equiv.) 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 3 times and yielded a pale-yellow solid. Yield: 176 mg (21%).

^{1}H NMR (400 MHz, $CDCl_3$):

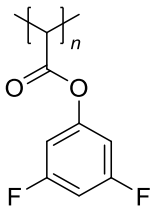
δ/ppm = 4.4–4.2, 4.1–3.9 and 3.7–3.6 (br, 5H, O–*C*H_2–*C*H–*C*H_2), 3.15 (br, 1H, C$H_{backbone}$), 1.40 (s, 3H, *C*H_3), 1.32 (s, 3H, *C*H_3).

^{13}C NMR (101 MHz, $CDCl_3$):

δ/ppm = 171.89 (*C*=O), 108.75 (O–C(CH_3)$_2$–$O_{5\text{-ring}}$), 71.97 (CH_2–*C*H–$CH_{2,\ 5\text{-ring}}$), 67.06(*C*$H_{2,5\text{-ring}}$), 66.33 (*C*H_2), 44.53 ($CH_{backbone}$), 27.03 (CH_3), 25.05 (CH_3).

FT-IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2989, 2943, 2885, 1730, 1369, 1153, 1053, 837.

Synthesis of poly(3,5-difluorophenyl 2-ylidene-acetate)



Similar to other polymerizations [65] , (±) (2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate (1 g, 3.76 mmol, 50 equiv.) and [(*L*-prolinate) Rh^{I}(1,5-dimethyl-1,5-cyclooctadiene)] (36 mg, 0.08 mmol, 1equiv.) 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 3 times and yielded a pale light solid. Yield: 90 mg (11 %).

^{1}H NMR (400 MHz, $CDCl_3$):

δ/ppm = 6.9–6.2 (br, 3H, C*H*$_{Ar}$), 4.1 (br, 1H, C*H*$_{backbone}$).

^{19}F NMR (377 MHz, $CDCl_3$):

δ(ppm) = -107(d, 2F, *meta*-*F*$_{ar}$).

The analytical data is consistent with the referred literature.[20b]

5.4. Post-modification of the obtained polymers

Post-modification of polymer: Copper-Catalyzed Azide-Alkyne click reaction (Cu-AAC Reaction):

(a) If the azido compound is liquid, I referred to procedure **A**. Standard polymer (40 mg, 0.29 mmol), CuBr (2.05 mg, 0.15 mmol, 0.05 equivalent) and *N*-pentamethyldiethylenetriamine (PMDETA) (3.46 mg, 0.020 mmol and 0.07 equivalent) were loaded in to a dry Schlenk tube or vial. The system was degassed by three freeze-pump-thaw cycles, and the flask was refilled with nitrogen. Afterward, THF (2 mL) and azido compound (0.35 mmol, 1.2 equivalent) were added sequentially. Then the combined solution was stirred at room temperature for 24h. After filtration through an aluminum oxide pad and repeated precipitation in the corresponding solvent, then obtained the product.

(b) Given that the azido compound is solid, I referred to procedure **B.** Standard polymer (40 mg, 0.29 mmol), CuBr (2.05 mg, 0.15 mmol, 0.05 equivalent) and PMDETA (3.46 mg, 0.020 mmol, 0.07 equivalent) and azido-compound (0.35 mmol, 1.2 equivalent) were loaded in to a dry Schlenk tube or vial. The system was degassed by three freeze-pump-thaw cycles, and the flask was refilled with nitrogen. Afterward, THF (2 mL) was added, and the combined solution was stirred at room temperature for 24h. After filtration through an aluminum oxide pad and repeated precipitation in the corresponding solvent, then obtained the product.

Note: As to the C2 polymer, I utilized 40 mg (0.29 mmol) standard polymer to run the reaction; As to the C1 polymer, I utilized 30 mg (0.24 mmol) into the standard reaction.

The general procedure of the cascade post-modification of PPA via CuAAC and PFTR

CuAAC is the same as the standard procedure narrated as mentioned above. Regarding the subsequent PFTR reaction, concerning one equivalent repeating unit of the polymer, five equivalents of dodecanethiol and six equivalents triethylamine were added and reacted at ambient temperature for 24 hrs. The reaction is monitored via ^{19}F NMR spectroscopy

The general procedure of the post-modification of pPFBDA via PFTR reaction.

Polymer pPFBDA (20 mg, 0.083 mmol) and 0.5 mL THF were loaded in a vial. Afterward, 1.1 equivalent thiols and 1.1 equivalent DBU were added. Then the solution was stirred at 45 °C for 2 hours. After precipitating into methanol or *n*-hexane, the product was obtained, and the conversion is confirmed by ^{19}F NMR spectroscopy.

Post-modification of polymer poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate] (pDDMDA) via hydrolysis

Acid hydrolysis of pDDMDA was carried out according to reported literature[66] . 0.5 mL 1 N HCl solution was added dropwise to THF solution of pDDMDA (0.05 g) under continuous stirring in a round-bottom flask at room temperature. After removing the volatile on rotavapor, the mixture was dried via lyophilization, and the ultimate product was obtained.

The copper-catalyzed reaction between PPA and ethyl 2-diazoacetate.

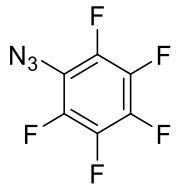
Ethyl 2-diazoacetate (114 mg, 1 mmol) was added to a solution of PPAc (110 mg, 1 mmol) and CuI (9.51 mg, 0.05 mmol) in anhydrous MeCN (2 mL). The resulted mixture was stirred at room temperature for 18 hours, after removing the volatiles, and dried under a high vacuum. The post-modified products were characterized via ^{1}H NMR spectroscopy.

5.5. Genera procedure for the preparation of various azides

Synthesis procedure General procedure A: Synthesis of aryl azides (Scheme 2) were prepared following literature[67] : Aniline was added to HCl (1 mL per 1 mmol of aniline; 12 M) in water (1 mL per mmol of aniline) at 0 °C. A solution of $NaNO_2$ (1.2 equiv.) in water (1 mL per 1 mmol of aniline) was added portion-wise, and the solution was stirred at 0 °C for 2 h. A solution of NaN_3 (1.5 equiv.) in water (0.5 mL per 1 mmol of aniline) was added dropwise at 0 °C (CAUTION: a vigorous release of N_2), and the reaction was stirred for 2 h and allowed to warm to room temperature. The aqueous layer was extracted twice with diethyl ether, and the combined organic layers were washed with water, sodium bicarbonate, brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield the corresponding pure aryl azide.

General procedure B: Synthesis of alkyl azides were synthesized in the following procedure[68] : To a stirred solution of NaN_3 (1.1 equiv.) in DMSO (0.6 M) was added corresponding bromide or chloride (1 equiv.). The reaction mixture was stirred at 80 °C overnight. Then the reaction mixture was cooled to room temperature and diluted with water (10 mL). The mixture was extracted with ether (3x5 mL) and washed by brine, dried over Na_2SO_4, and concentrated under vacuum to produce quantitative yields. It was used directly without further purification.

azido-2,3,4,5,6-pentafluorobenzene (2n).



General Procedure[69] : Aniline (20 mmol) was dissolved in TFA (25 mL) and cooled to -2 ℃. After about 15 min, $NaNO_2$ (12 mmol) was added in portions while stirring. After stirred at 0 ℃ for 1 h, sodium azide (30 mmol) was added, and the mixture was stirred at -2–0 ℃ for 1 h. The mixture was diluted with Et_2O (50 mL), washed with water, and then saturated $NaHCO_3$ and dried over $MgSO_4$. After removing the solvent, the residual was purified by a flash column using pentane as eluent to give the product.

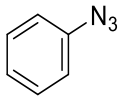
^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 142.22 (dt, *J* = 12.7, 4.0 Hz, *para–C*), 139.98–139.00 (m, 2C, *ortho–C*), 137.42–136.51 (m, 2C, *meta*–C), 115.89 (td, *J* = 12.6, 4.6 Hz, N_3–*C*).

^{19}F NMR (377 MHz, $CDCl_3$):

δ(ppm) = -152.17–-152.28 (m, 2F, *ortho-F*), -160.60 (tt, *J* = 21.1, 2.3 Hz, 1F, *para-F*), -162.33–-162.50 (m, 2F, *meta-F*).

1-azidobenzene (2a)



Following the general procedure A for preparation of 1-azidobenzene from aniline (1.6 g, 16.8 mmol), the title compound was obtained as a brown oil (1.5 g, 75%). Spectroscopic data for this compound is following the literature.[70]

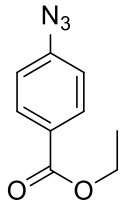
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 7.23–7.28 (m, 2H), 7.02–7.06 (m, 1H), 6.92–6.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 140.05, 129.78, 124.79, 119.05.

4-Ethyl azidobenzoate (2b)



Following the general procedure A for preparation of 4-ethyl aminobenzoate (2.78 g, 16.80 mmol), the title compound was obtained as a yellow oil (2.89 g, 90%) spectroscopic data of this compound was following the literature.[67a]

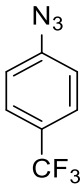
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 7.93 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J*= 8.8Hz, 2H), 4.28(q, *J* =7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 165.51, 144.47, 131.35, 126.97, 118.63, 60.60, 14.32

1-Azido-4-(trifluoromethyl)benzene (2c)



Following the general procedure, A for preparation of 1-azido-4-(trifluoromethyl)benzene from trifluoromethylaniline (16.80 mmol), the target compound was obtained as an orange oil (2.98 g, 95%). Spectroscopic data for this compound is following the literature.[71]

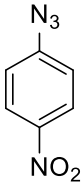
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 7.49(d, *J* = 8.4 Hz), 6.99(d, *J* = 8.4 Hz).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 142.9, 126.9(q, *J* = 33Hz), 126.7 (q, *J* = 3 Hz), 124.0 (q, *J* = 270 Hz), 118.7

1-Azido-4-nitrobenzene (2d)



Following the general procedure, A for the preparation of 1-azido-4-nitrobenzene from 4-nitroaniline (2.0 g, 14.3 mmol), the target compound was obtained as a yellow solid (2.11 g, 90%). Spectroscopic data for this compound is following the literature.[72]

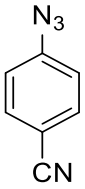
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 8.15 (d, *J* = 9.2 Hz, 2H), 7.06 (d, *J* = 9.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) =146.9, 144.7, 125.6, 119.4.

4-Azidobenzonitrile (2e)



Following the general procedure, A for preparation of 4-azidobenzonitrile from 4-bromobenzonitrile (1.98 g, 16.8 mmol), the title compound was obtained as an off-white solid (2.18 g, 90%). Spectroscopic data for this compound is following the literature.[67a]

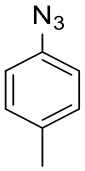
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 7.58 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 145.65, 134.14, 119.75, 116.45, 107.12.

1-Azido-4-methylbenzene (2f)



Following the general procedure, A for preparation of 1-azido-4-methylbenzene from *p*-toluidine (2.0 g, 18.7 mmol), the title compound was obtained as a brown solid (2.14 g, 86%). Spectroscopic data for this compound is following the literature.[73]

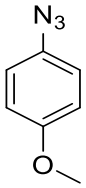
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 6.99 (d, *J* = 9.2 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 137.01, 134.42, 130.36, 118.88, 20.73.

1-Azido-4-methoxybenzene (2g)



Following the general procedure, A for preparation of 1-azido-4-methoxybenzene from *p*-anisidine (1.6 g, 13.4 mol), the title compound was obtained as a brown solid (1.69 g, 85%). Spectroscopic data for this compound is following the literature.[74]

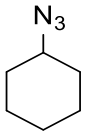
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 6.81 (d, *J* = 9.2 Hz, 2H), 6.75 (d, *J* = 9.2 Hz, 2H), 3.65 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 156.9, 132.3, 120.0, 115.1, 55.5.

Azidocyclohexane (2h)



Following the general procedure B for preparation of azidocyclohexane from bromocyclohexane (2.0 g, 12.27 mmol), the title compound was obtained as a colorless oil (1.23 g, 80%). Spectroscopic data for this compound is following the literature.[75]

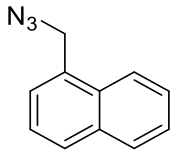
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 3.27 (m, 1H), 1.81 (m, 2H), 1.68 (m, 2H), 1.49 (m, 1H), 1.12-1.35 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 60.37, 40.40, 29.69, 25.27, 24.23.

1-(Azidomethyl)naphthalene (2i)



Following the general procedure B for preparation of 1-(azidomethyl) naphthalene from 1-(chloromethyl)naphthalene (2.00 g, 11.32 mmol), the title compound was obtained as a colorless oil (2.01 g, 97%). Spectroscopic data for this compound is consistent with the literature.[76]

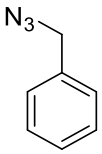
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 8.10–8.12 (m, 1H), 7.92–7.99 (m, 2H), 7.60–7.68 (m, 2H), 7.50–7.54 (m, 2H), 4.78 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 134.03, 131.48, 131.13, 129.53, 128.96, 127.37, 126.86, 126.30, 125.36, 123.63, 53.25.

(Azidomethyl)benzene (2j)



Following the general procedure B for preparation of (1-azidomethyl)benzene from (1-bromomethyl)benzene (2.0 g, 15.8 mmol), the title compound was obtained as a

colorless oil (2.0 g, 95%). Spectroscopic data for this compound is following the literature.[76]

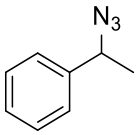
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 7.37(m, 5H), 4.35 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 146.63, 128.87, 128.33, 128.25, 54.80.

(1-Azidoethyl)benzene (2k)



Following the general procedure B for preparation of (1-azidoethyl)benzene from (1-bromoethyl)benzene (2.0 g, 10.81 mmol), the title compound was obtained as a pale-yellow oil (1.29 g, 84%). Spectroscopic data for this compound is following the literature.[67a]

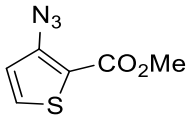
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 7.22–7.33 (m, 5H), 4.54 (q, *J* = 6.8 Hz. 1H), 1.45 (d, 6.8Hz).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 140.92, 128.82, 128.17, 126.43, 58.94, 23.30.

Methyl 3-azidothiophene-2-carboxylate (2l)



Following the general procedure A, for preparation of methyl 3-azidothiophene-2-

carboxylate from methyl 3-aminothiophene-2-carboxylate (2.64 g, 16.80 mmol), the title compound was obtained as a dark-yellow solid (2.84 g, 92%). Spectroscopic data for this compound is following the literature.[67a]

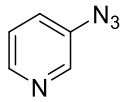
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 7.40 (d, 5.6 Hz, 1H), 6.84 (d, 5.6Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, CDCl3):

δ(ppm) = 160.70, 140.61, 131.73, 122.10, 116.68, 53.39.

3-Azidopyridine (2m)



Following the general procedure A for preparation of 3-azidopyridine from pyridin-3-amine (1.58 g, 16.80 mmol), the title compound was obtained as an orange oil (1.4 g, 70%), Spectroscopic data for this compound is following the literature.[67a]

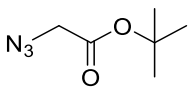
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 8.30–8.33 (m, 2H), 7.31–7.27 (m, 1H), 7.21–7.24 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 145.92, 140.20, 137.17, 126.44, 123.65.

tert-Butyl 2-azidoacetate (2n)



Following the general procedure B for preparation of *tert*-butyl 2-azidoacetate from tert-butyl 2-bromoacetate (2.00, 10.25 mmol), the title compound was obtained as a colorless oil. [75] Spectroscopic data for this compound:

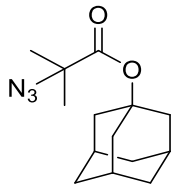
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 3.68 (s, 2H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 164.99, 83.06, 49.78, 27.59.

(3s,5s,7s)-adamantan-1-yl 2-azido-2-methylpropanoate(2o)

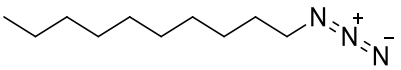


Following the general procedure B for preparation of (3s,5s,7s)-adamantan-1-yl 2-azido-2-methylpropanoate from (3s,5s,7s)-adamantan-1-yl 2-bromo-2-methylpropanoate, the title compound was obtained as a colorless oil (0.7 g).

^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 2.20 (m, 3H), 2.15 (m, 6H), 1.69 (m, 6H), 1.41(s, 6H).

1-Azidodecane (2p)



Following procedure B for preparation of 1-azidodecane from 1-bromodecane (2.00 g, 9.04 mmol), the title compound was obtained as pale yellow oil. Spectral data for this compound:

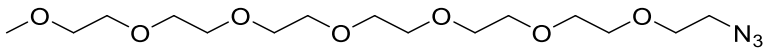
^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 3.18 (t, *J* = 7.0 Hz, 2H), 1.61–1.46 (m, 2H), 1.35–1.09 (m, 14H), 0.85–0.77 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$):

δ(ppm) = 50.90, 31.88, 29.51, 29.49, 29.29, 29.16, 28.85, 26.73, 23.60, 15.14.

PEG-Azide (2q)



Synthesis procedure: Mesylation of methyl PEG [77] : (A) MethylPEG (400). A solution of the methyl-PEG (400) (5.0 g, 12.5 mmol) was added to a 250 ml flask and azeotropically dried in toluene. After most of the toluene was distilled, anhydrous CH_2Cl_2 (50 mL) and triethylamine (5.20 mL, 37.5 mmol) were added to the flask. The flask was cooled to 0°C, then methanesulfonyl chloride (13.75 mmol) was then slowly added. After stirring at ambient temperature for another 24 h, 100 mL water was added, and the mixture was extracted with CH_2Cl_2 (40 × 5 ml). The combined organic layer was washed with HCl solution (1 M) and brine, respectively. The organic layer was dried over $MgSO_4$, concentrated, and dried under vacuum.

(B)Following general procedure B for preparation PEG-azide from mesylate methyl PEG (2.0 g, 4.32 mmol), the title compound was obtained as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):

δ(ppm) = 3.70–3.51 (m, 28H), 3.51–3.46 (m, 2H), 3.32 (dd, *J* = 4.7, 2.7 Hz, 2H), 3.31 (s, 3H).

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7. Appendix

7.1. List of Hazardous Chemicals

Chemicals (CAS number)	Hazard class	H-Phrases	P-Phrases
Bromoacetyl bromide (598-21-0)	 GHS05	H314	P280-P305 + P351+ P338-P310
Chloroform (67-66-3)	 GHS06 GHS08	H302-H315-H319-H331-H336-H351-H361d-H372	P201-P261-P304 +P340 + P312-P305+ P351 +P338-P308 +P313-P403 + P233
1,5-Cyclooctadiene (111-78-4)	 GHS02,GHS07, GHS08	H226 - H302 + H332 - H304 - H410	P280-P305 + P351 + P338
1,8-Diazabicyclo-[5.4.0]undec-7-ene (6674-22-2)	 GHS05, GHS06	H290 - H301 - H314 - H412	P273 - P280 - P301 + P310 + P330 - P301 + P330 + P331 - P303 + P361 + P353 - P305 + P351 + P338
Dichloromethane (75-09-2)	 GHS07, GHS08	H315 - H319 - H336 - H351	P201 - P202 - P261 - P302 + P352 - P305 + P351 + P338 - P308 + P313

Diethyl ether (60-29-7)	 GHS02, GHS07	H224 - H302 - H336	P210 - P301 + P312 + P330 - P403 + P233
Methanol (67-56-1)	 GHS02 GHS06 GHS08	H225 - H301 + H311 + H331 - H370	P210 - P233 - P280 - P301 + P310 - P303 + P361 + P353 - P304 + P340 + P311
Petrol ether (101316-46-5)	 GHS02 GHS07 GHS08  GHS09	H225 - H304 - H315 - H336 - H411	P210 - P273 - P301 + P310 + P331 - P302 + P352
L-Proline (147-85-3)	/	/	/
Propargyl alcohol (107-19-7)	 GHS02 GHS05 GHS06  GHS08 GHS09	H226 - H301 - H310 + H330 - H314 - H373 - H411	P210 - P273 - P280 - P303 + P361 + P353 - P304 + P340 + P310 - P305 + P351 + P338
Sodium bicarbonate (144-55-8)	/	/	/
Sodium azide (26628-22-8)	 GHS06 GHS08 GHS09	H300 + H310 + H330 - H373 - H410	P262 - P273 - P280 - P302 + P352 + P310 - P304 + P340 + P310 - P314

Tetrahydrofuran (109-99-9)	 GHS02 GHS07 GHS08	H225 - H302 - H319 - H335 - H336 - H351	P201 - P202 - P210 - P301 + P312 - P305 + P351 + P338 - P308 + P313
Toluene (108-88-3)	 GHS02 GHS07 GHS08	H225 - H304 - H315 - H336 - H361d - H373 - H412	P201 - P210 - P273 - P301 + P310 + P331 - P302 + P352 - P308 + P313
p-Toluenesulfonyl chloride (98-59-9)	 GHS05 GHS07	H290 - H315 - H317 - H318	P280 - P302 + P352 - P305 + P351 + P338 + P310
p-Toluenesulfonyl hydrazide (1576-35-8)	 GHS02 GHS06	H242 - H301	P210 - P234 - P235 - P301 + P310 - P370 + P378 - P403
Triethylamine (121-44-8)	 GHS02 GHS05 GHS06	H225 - H302 - H311 + H331 - H314 - H335	P210 - P280 - P301 + P330 + P331 - P303 + P361 + P353 - P304 + P340 + P311 - P305 + P351 + P338 + P310
2,2,6-Tri- methyl-4H-1,3-dioxin-4-one (5394-63-8)	 GHS02 GHS07	H225 - H319	P210 - P305 + P351 + P338
2,3,4,5,6-Pentafluoroaniline (771-60-8)	 GHS07	H315 - H319	P305 + P351 + P338
Aniline	 GHS05 GHS06 GHS08	H301 + H311 + H331 - H317 - H318 - H341 -	P201 - P273 - P280 - P301 + P310 + P330 - P302 +

(62-53-3)	 GHS09	H351 - H372 - H410	P352 + P312 - P305 + P351 + P338 + P310
ethyl 4-aminobenzoate (94-09-7)	 GHS07	H317	P261 - P272 - P280 - P333 + P313 - P362 + P364 - P501
4-(Trifluoromethyl) aniline (455-14-1)	 GHS06 GHS09	H301 - H319 - H410	P273 - P301 + P310 - P305 + P351 + P338 - P501
4-Nitroaniline (100-01-6)	 GHS06 GHS08	H301 + H311 + H331 - H373 - H412	P273 - P280 - P301 + P310 - P302 + P352 + P312 - P304 + P340 + P311 - P314
4-Aminobenzo nitrile (873-74-5)	 GHS06	H301 - H319	P301 + P310 + P330 - P305 + P351 + P338
p-Anisidine (104-94-9)	 GHS06 GHS08 GHS09	H300 + H310 + H330 - H350 - H373 - H400	P201 - P202 - P273 - P280 - P302 + P352 + P310 - P304 + P340 + P310
1-(Chloromethyl) Naphthalene (86-52-2)	 GHS05 GHS07	H302 - H312 - H314	P280 - P305 + P351 + P338 - P310
1-(Bromoethyl) Benzene (585-71-7)	 GHS07	H315 - H319 - H335	P302 + P352 - P305 + P351 + P338

Benzyl bromide (100-39-0)	 GHS07	H315 - H319 - H335	P261 - P264 - P271 - P280 - P302 + P352 - P305 + P351 + P338
Methyl 3-amino-2-thiophene Carboxylate (22288-78-4)	 GHS07	H315 - H319 - H335	P302 + P352 - P305 + P351 + P338
3-Aminopyridine (462-08-8)	 GHS06 GHS08	H301 + H311 + H331 - H315 - H319 - H335 - H373	P280 - P301 + P310 - P302 + P352 + P312 - P304 + P340 + P311 - P305 + P351 + P338 - P314
tert-Butyl bromoacetate (5292-43-3)	 GHS02 GHS07	H226 - H315 - H319 - H335	P210 - P302 + P352 - P305 + P351 + P338
1-Bromodecane (112-29-8)	 GHS07	H315 - H319	P302 + P352 - P305 + P351 + P338
1-Dodecanethiol (112-55-0)	 GHS05 GHS07 GHS09	H314 - H317 - H410	P273 - P280 - P301 + P330 + P331 - P303 + P361 + P353 - P305 + P351 + P338
11-Mercapto-1-undecanol (73768-94-2)	 GHS07	H315 - H319 - H335	P302 + P352 - P305 + P351 + P338

1-Butanethiol (109-79-5)	 GHS02 GHS07	H225 - H302 + H332 - H315 - H317 - H319 - H335	P210 - P280 - P301 + P312 + P330 - P302 + P352 - P304 + P340 + P312 - P305 + P351 + P338
Thiophenol (108-98-5)	 GHS02 GHS06 GHS08  GHS09	H226 - H300 + H310 + H330 - H315 - H319 - H335 - H361 - H372 - H410	P210 - P273 - P280 - P303 + P361 + P353 - P304 + P340 + P310 - P305 + P351 + P338
L-Cysteine (52-90-4)	/	/	/
Cysteamine (60-23-1)	 GHS07	H302 - H315 - H319 - H335	P301 + P312 + P330 - P302 + P352 - P305 + P351 + P338
(3-Mercaptopropyl) Trimethoxysilane (4420-74-0)	 GHS07 GHS09	H302 - H317 - H411	P273 - P280 - P301 + P312 + P330 - P302 + P352
(±)-2,2-Dimethyl-1,3-dioxolan-4-methanol (100-79-8)	 GHS07	H319	P264 - P280 - P305 + P351 + P338 - P337 + P313
Propargyl acrylate (10477-47-1)	 GHS02 GHS07	H226 - H315 - H319 - H335	P210 - P302 + P352 - P305 + P351 + P338

3,5-difluorophenol (2713-34-0)	 GHS07	H302 + H312 + H332 - H315 - H319 - H335	P280 - P301 + P312 + P330 - P302 + P352 + P312 - P304 + P340 + P312 - P305 + P351 + P338
4-fluorophenol (371-41-5)	 GHS07	H302 - H312 - H315 - H319 - H332 - H335	P261 - P280 - P305 + P351 + P338

7.2. List of Abbreviations

Abbreviation	Full name
AIBN	Azobisisobutyronitrile
ATR	Attenuated total reflectance
COD	1,5-cyclooctadiene
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DSC	Ethyl 2-diazoacetate
FRP	Free-radical polymerization
FT-IR	Fourier transform infrared spectroscopy
MMA	Methyl methacrylate
M_n	Number average molecular weight
M_W	Average molecular weight
NHC	N-heterocyclic carbenes
NMR	Nuclear magnetic resonance
RDRP	Reversible-deactivation radical polymerization
DFT	Density-functional theory
equiv.	Equivalent
CuAAC	Copper-catalyzed azide-alkyne cycloaddition
PFTR	Para-Fluoro-Thiol reaction
S_N2	Second-order Nucleophilic Substitution
PTSA	p-Toluenesulfonic acid
HCl	Hydrochloric acid
MSA	Methyl salicylate acrylate
NHS	N-hydroxysuccinimide
PPA	Poly(propargyl 2-ylidene-acetate)
OLED	Organic light-emitting diodes
PPAc	Poly(propargyl acrylate)
GPC	Gel permeation chromatography
DMAC	N, N-Dimethyl acetamide
HSQC	H–C Heteronuclear single quantum correlation
PEG	Polyethylene glycol

PMDETA	Pentamethyldiethylenetriamine
CuBr	Copper Bromide(I)
$CDCl_3$	Chloroform
THF	Tetrahydrofuran
PFB	Pentafluorobenzyl
pPFBDA	Poly(pentafluorobenzyl 2-ylidene-acetate)
pPFBMA	Poly(pentafluorobenzyl methacrylate)
TGA	Thermogravimetric Analysis
Đ or PDI	Polydispersity
DSC	Differential scanning calorimetry
DMSO	Dimethyl sulfoxide
DMF	*N*,*N*-dimethylformamide
pDDMDA	Poly[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-diazoacetate]
COSY	H–H Correlated Spectroscopy
RI	Differential Refractive Index
SEC	Size Exclusion Chromatography
Rh	Rhodium
$MgSO_4$	Magnesium sulfate
$NaHCO_3$	Sodium bicarbonate
KOH	Potassium hydroxide
TLC	Thin-layer chromatography
$NaNO_2$	Sodium nitrite
NaN_3	Sodium azide
CuI	Copper(I) iodide
Na_2SO_4	Sodium sulfate
TFA	Trifluoroacetic acid
Et_2O	Diethyl ether
nq	Naphthoquinones
EDA	Ethyl diazoacetate

7.3. Supplementary Information (selected spectra)

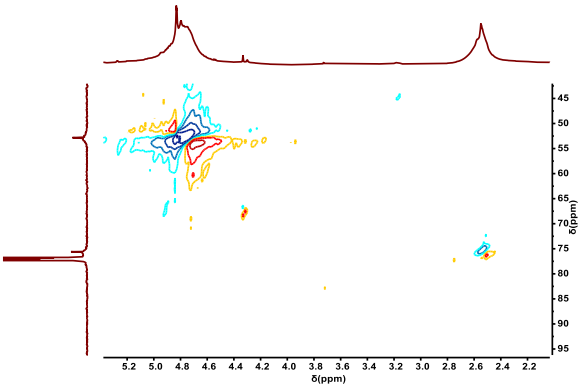


Figure S1. HSQC (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz) spectra of C1 polymer PPA.

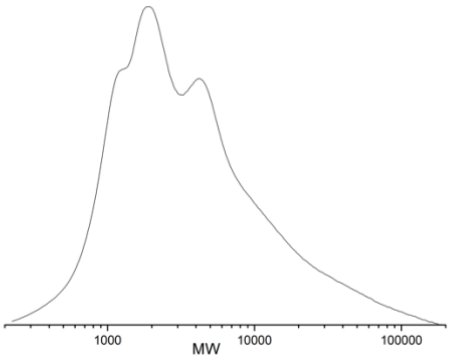


Figure S2. GPC graph of PPA with DMAC as eluent.

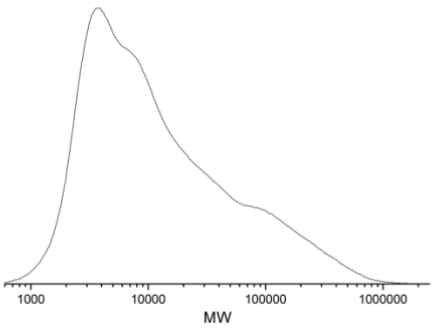


Figure S3. GPC graph of PPAc with DMAC as eluent.

Representative graphs of the post-modified products of PPA and PPAc.

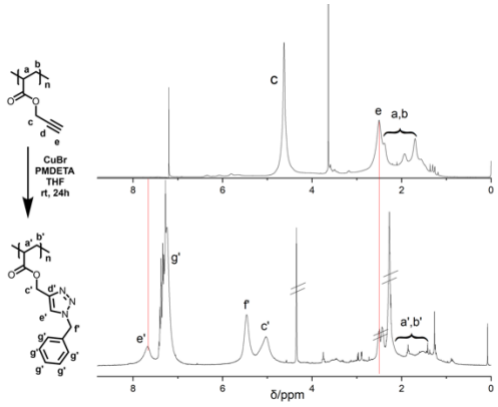


Figure S4. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of C2 polymer PPAc before and after post-modification by CuAAC reaction with benzyl azide.

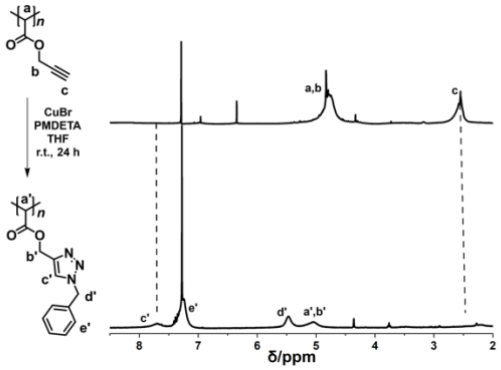


Figure S5. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of C1 polymer PPA before and after post-modification by CuAAC reaction with benzyl azide.

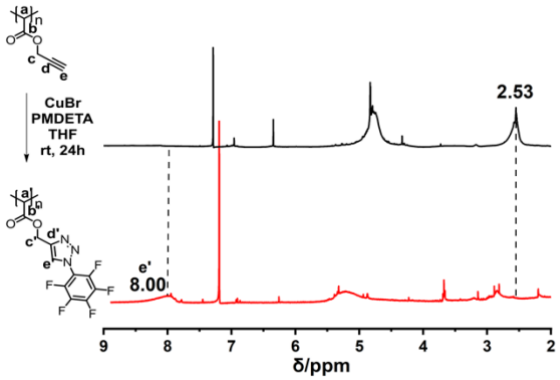


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of PPA before and after reacting with 1-azido-2,3,4,5,6-pentafluorobenzene.

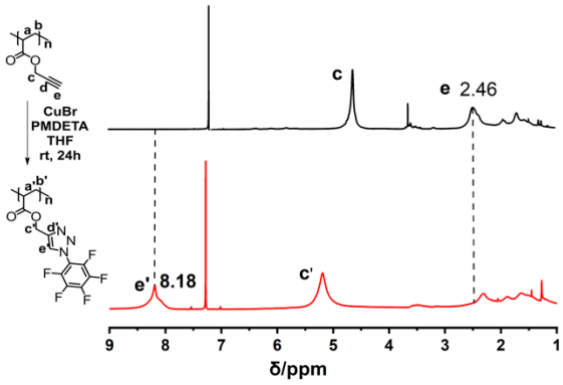


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of PPAc before and after reacting with 1-azido-2,3,4,5,6-pentafluorobenzene.

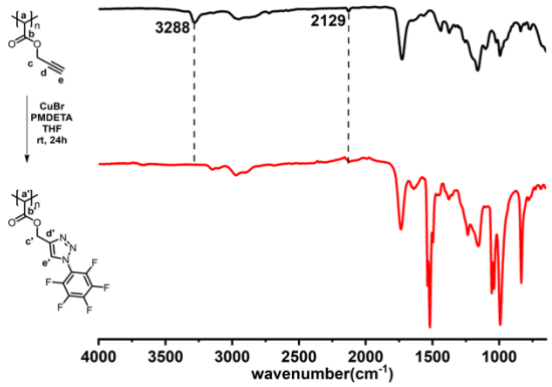


Figure S8. FT-IR spectra of PPA before and after reacting with 1-azido-2,3,4,5,6-pentafluorobenzene.

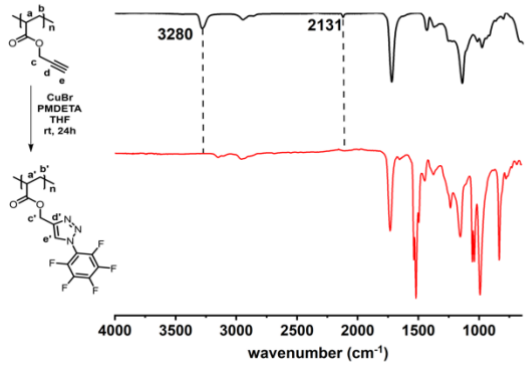


Figure S9. IR spectra of PPAc before and after reacting with 1-azido-2,3,4,5,6-pentafluorobenzene.

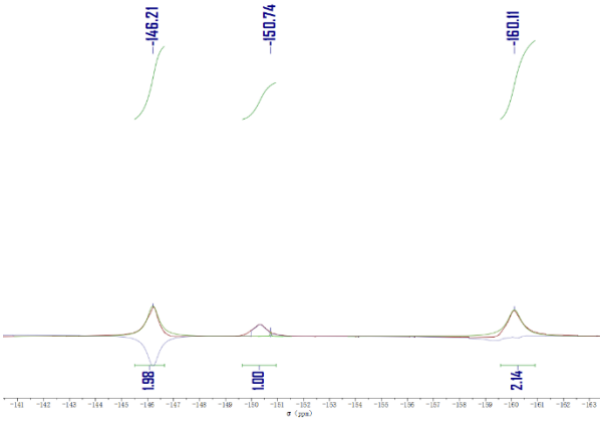


Figure S10. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of PPAc after reacting with 1-azido-2,3,4,5,6-pentafluorobenzene.

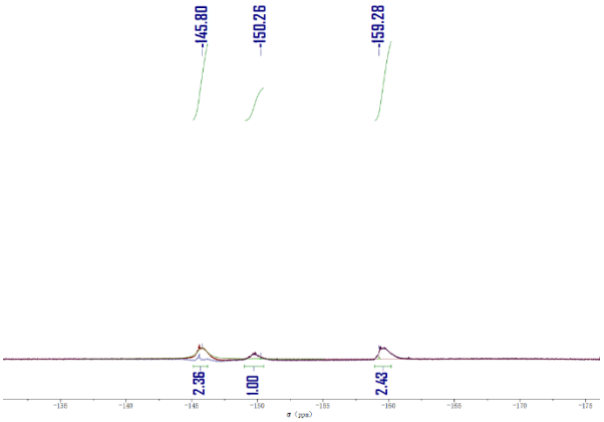


Figure S11. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of PPA before and after reacting with 1-azido-2,3,4,5,6-pentafluorobenzene.

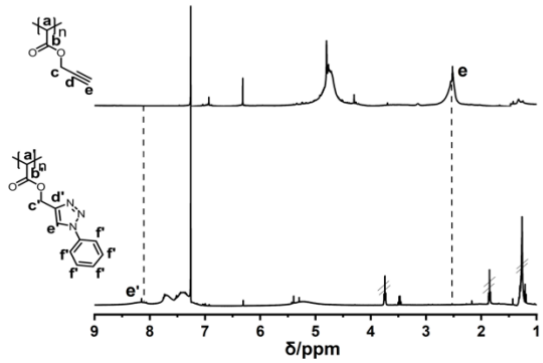


Figure S12. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra before and after the post-modification of PPA with azidobenzene.

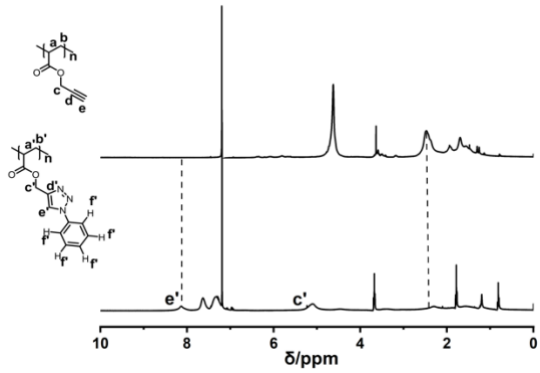


Figure S13. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra before and after the post-modification of PPAc with azidobenzene.

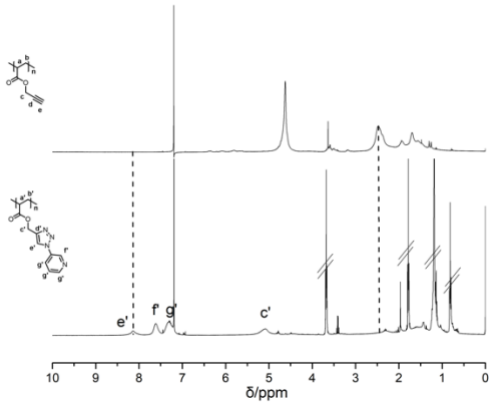


Figure S14. Post-modification of PPAc with 3-azidopyridine—^{1}H NMR spectra ($CDCl_3$, 400 MHz).

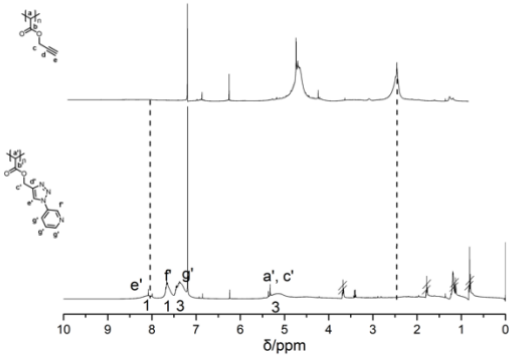


Figure S15. Post-modification of PPA with 3-azidopyridine—^{1}H NMR spectra ($CDCl_3$, 400 MHz).

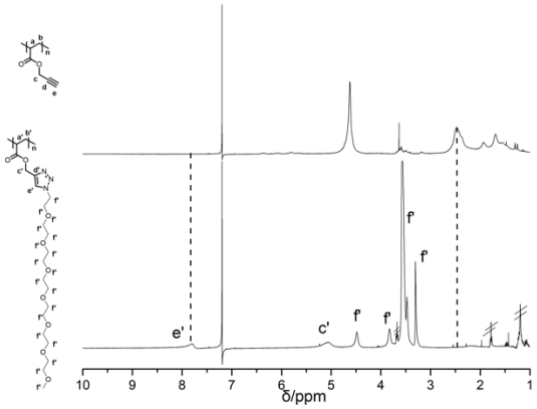


Figure S16. Post-modification of PPAc with PEG–azide—^{1}H NMR spectra ($CDCl_3$, 400 MHz).

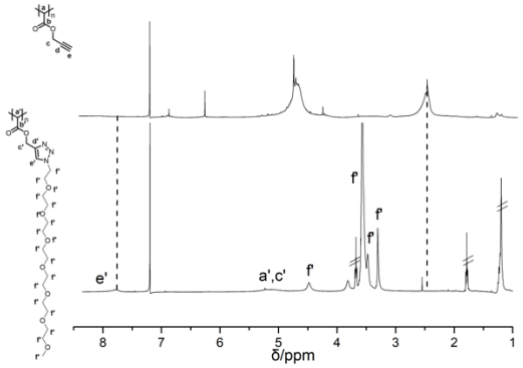


Figure S17. Post-modification of PPA with PEG-azide—^{1}H NMR spectra ($CDCl_3$, 400 MHz).

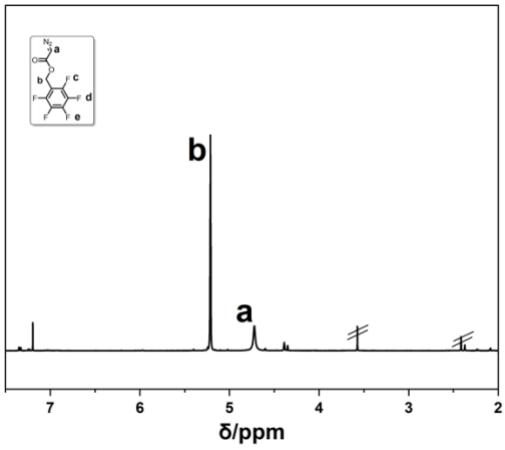


Figure S18. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of 2,3,4,5,6-pentafluorobenzyl 2-diazoacetate.

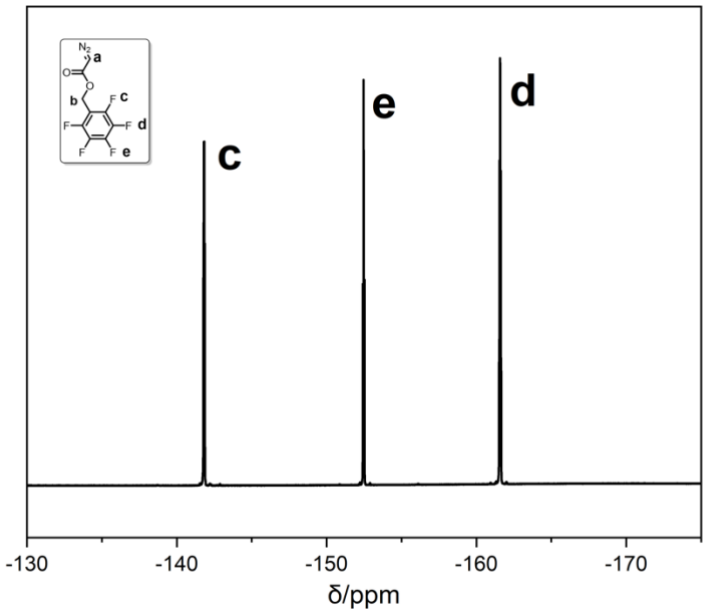
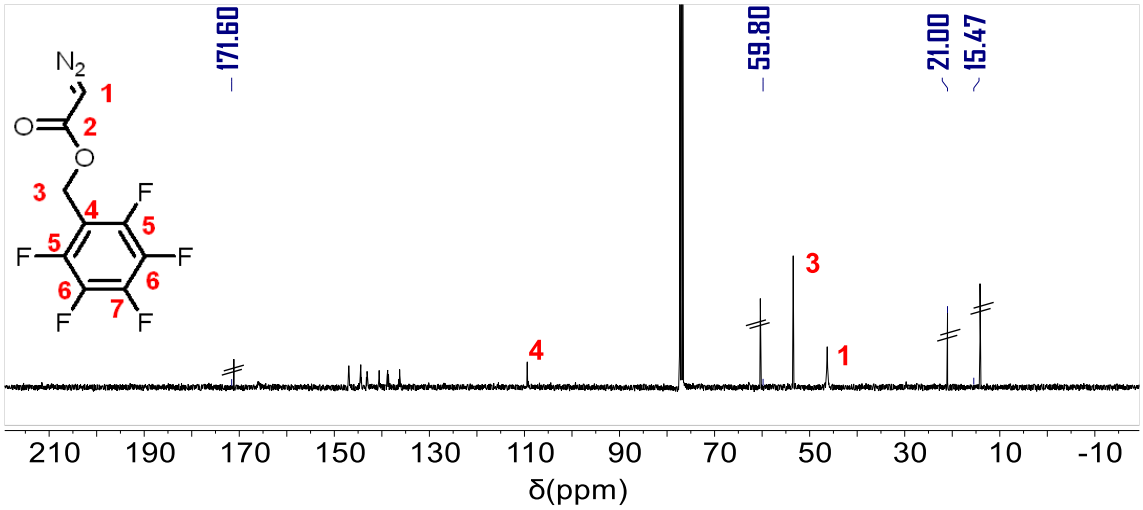
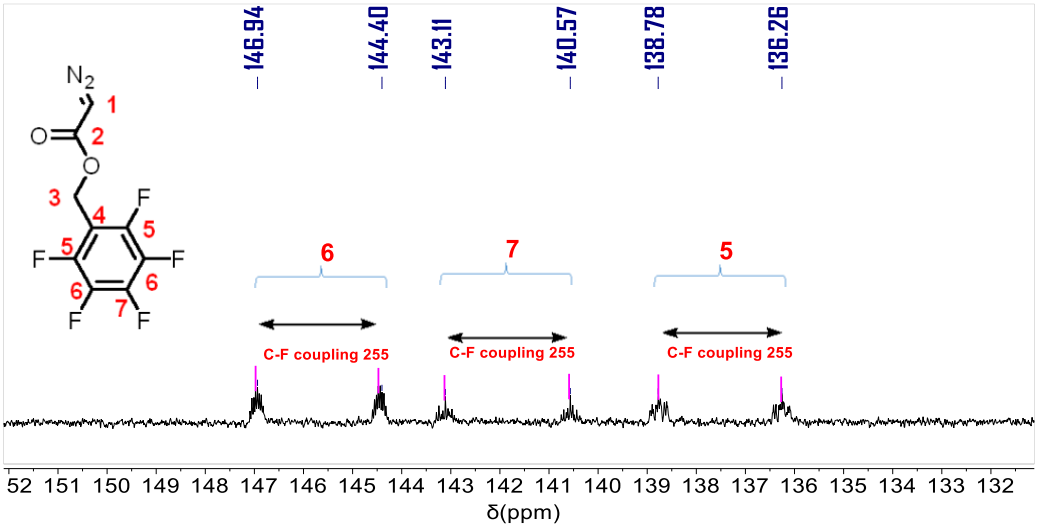


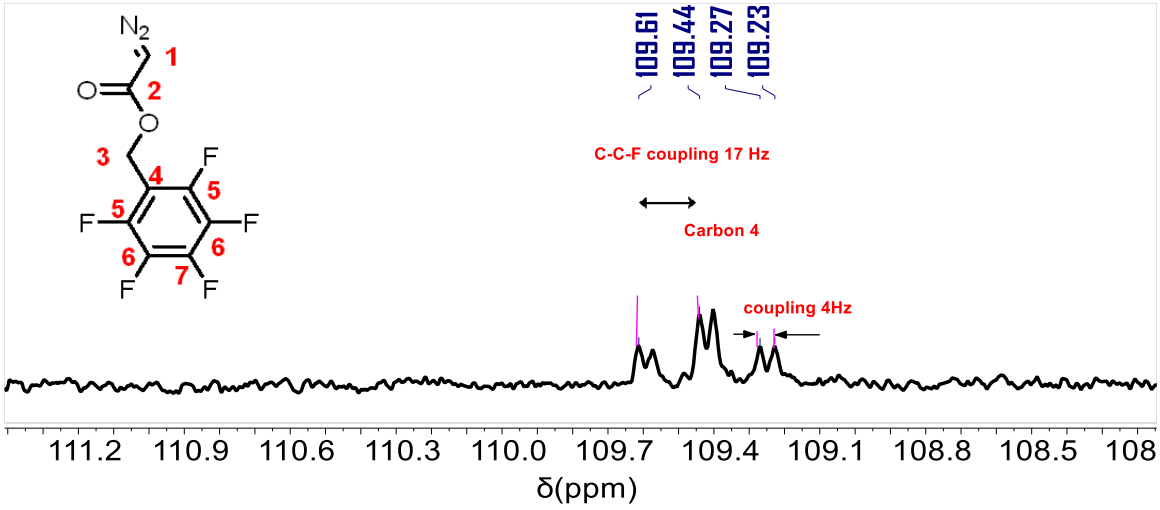
Figure S19. ^{19}F NMR ($CDCl_3$, 400 MHz) spectrum of 2,3,4,5,6-pentafluorobenzyl 2-diazoacetate.



(A)



(B)



(C)

Figure S20. (A) ^{13}C NMR ($CDCl_3$, 101 MHz) spectrum of 2,3,4,5,6-pentafluorobenzyl 2-diazoacetate; (B) The magnified spectrum between 132 ppm to 152 ppm; (C) The magnified spectrum of peak 4 at the chemical shift between 108 ppm to 110 ppm.

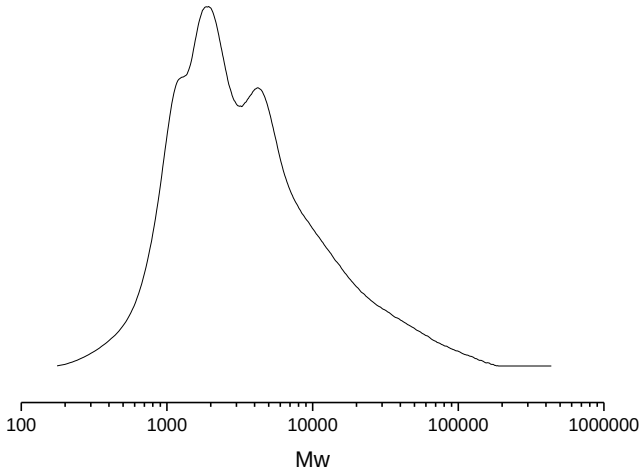


Figure S21. SEC graph of pPFBDA. Dimethylacetamide (DMAC) was utilized as an eluent.

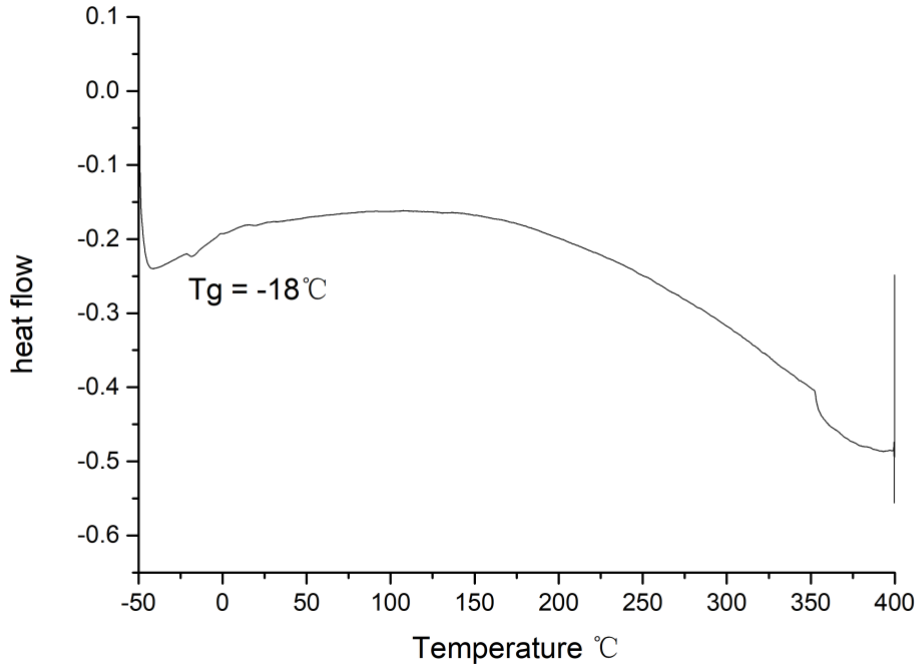


Figure S22. DSC curve of the second heating process.

Spectral data after post-modification of pPFBDA with thiols

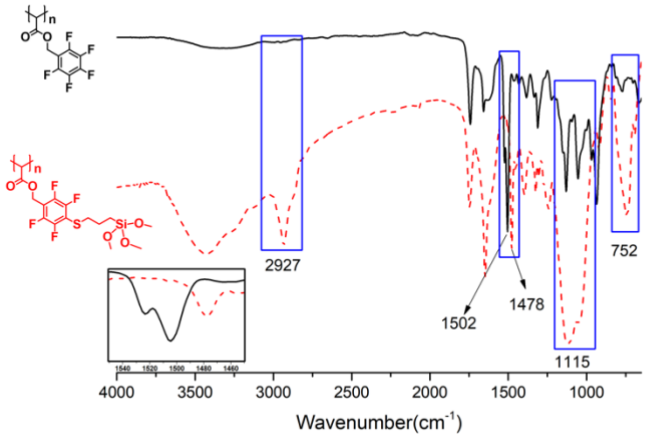


Figure S23. FT-IR spectra of pPFBDA (black) and after modification with (3-mercaptopropyl)trimethoxysilane 7 (red dashed).

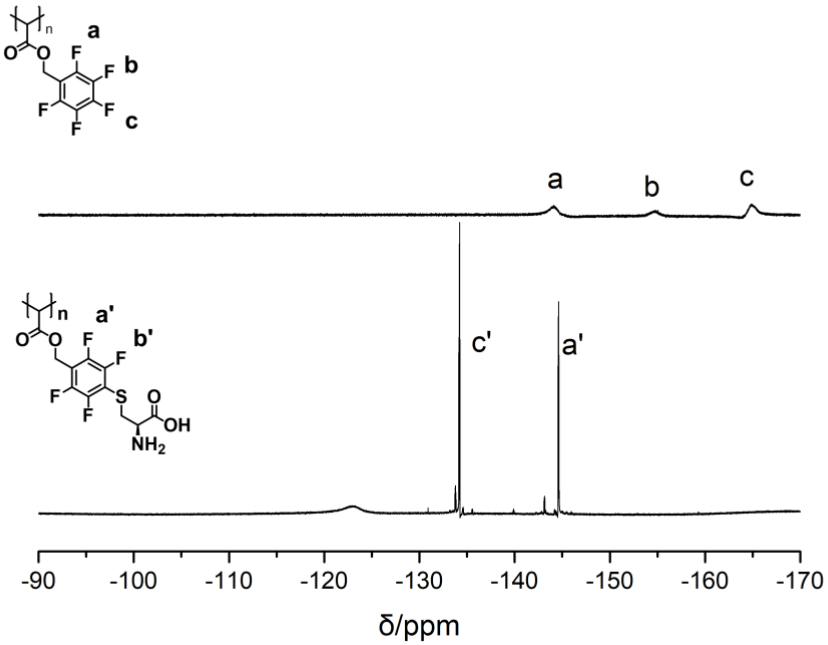


Figure S24. ^{19}F NMR ($CDCl_3$, 377 MHz) spectrum of post-modification of pPFBDA with *L*-cysteine; pPFBDA was measured in d8-toluene (377 MHz).

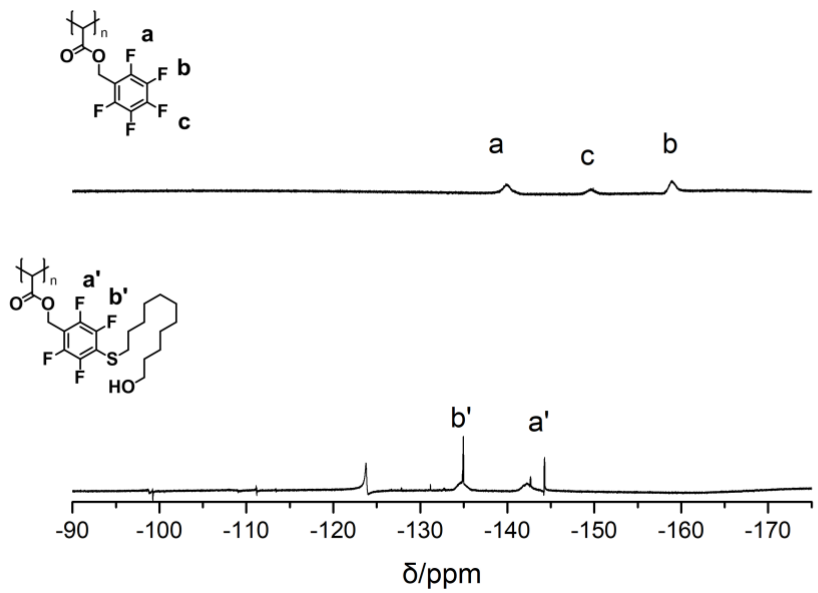


Figure S25. ^{19}F NMR ($CDCl_3$, 377 MHz) spectrum of post-modification of pPFBDA with 11-mercaptoundecan-1-ol; pPFBDA was measured in d8-toluene (377 MHz).

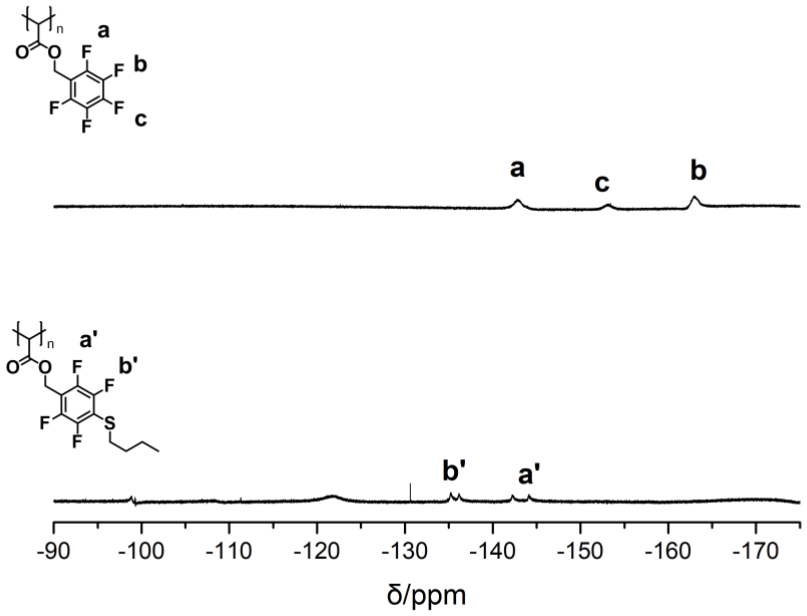


Figure S26. ^{19}F NMR ($CDCl_3$, 377 MHz) spectrum of post-modification of pPFBDA with butanethiol; pPFBDA was measured in d8-toluene (377 MHz).

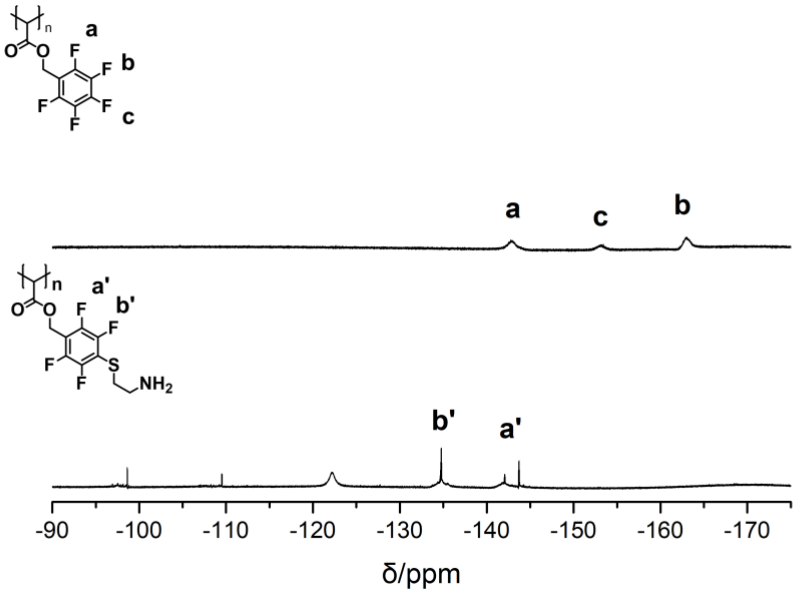


Figure S27. ^{19}F NMR ($CDCl_3$, 377 MHz) spectrum of post-modification of pPFBDA with cysteamine; pPFBDA was measured in d8-toluene (377 MHz).

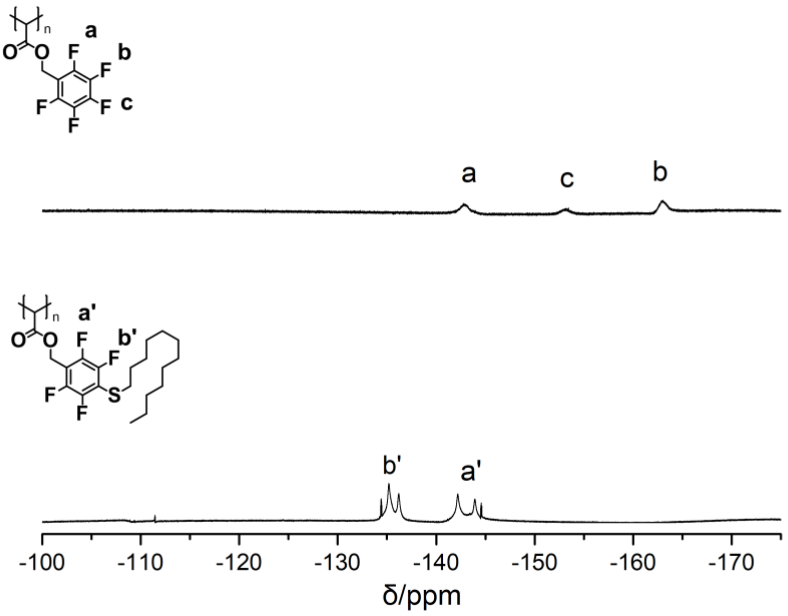


Figure S28. ^{19}F NMR ($CDCl_3$, 377 MHz) spectrum of post-modification of pPFBDA with dodecanethiol; pPFBDA was measured in d8-toluene (377 MHz).

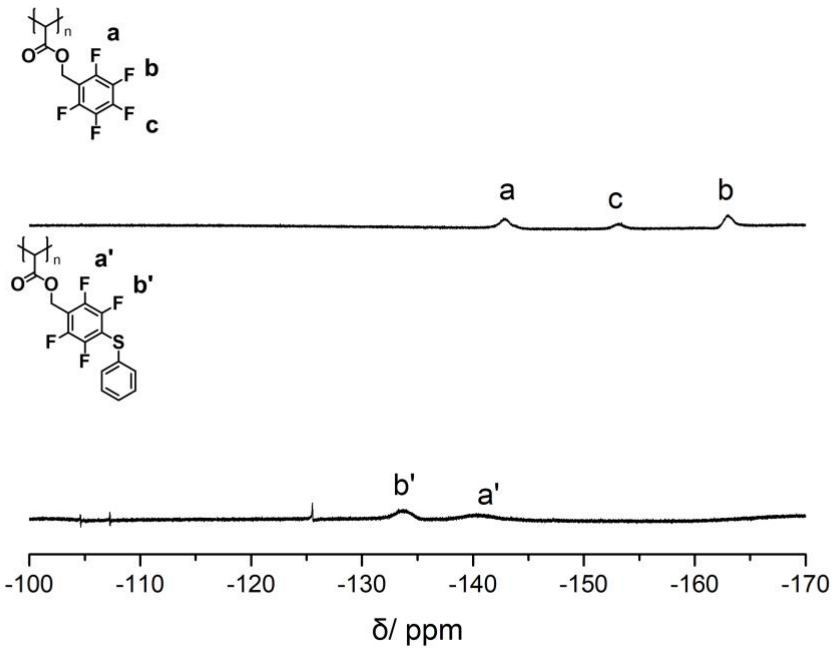


Figure S29. ^{19}F NMR ($CDCl_3$, 377 MHz) spectrum of post-modification of pPFBDA with benzenethiol; ^{19}F NMR spectrum of pPFBDA was measured in d8-toluene (377 MHz).

8. List of Publications

[1] **Zengwen Li,** Hatice Mutlu, Patrick Theato*, and Stefan Bräsec*. Synthesis and Post-Polymerization Modification of Poly(propargyl 2-ylidene-acetate). *Eur. Polym. J.* accepted.

[2] **Zengwen Li,** Hongxin Zhang, Patrick Theato*, and Stefan Bräse*. Poly(pentafluorobenzyl 2-ylidene-acetate): Polymerization and Post-Polymerization Modification. *Macromolecular. Rapid. Communications.* Preparation for Submission.

[3] Xiaoxiao Zhang, **Zengwen Li,** Shaojian Lin, and Patrick Theato*. Fibrous Materials Based on Polymeric Salicyl Active Esters as Efficient Adsorbents for Selective Removal of Anionic Dye. *ACS Appl. Mater. Interfaces.2020,18,21100-21113.*

[4] **Zengwen Li,** Patrick Theato*, and Stefan Bräse*. First Synthesis of Air-stable Disubstituted Allenes Post-modified Poly(propargyl acrylate) via Copper(I)-Catalyzed Cross-Coupling reaction with Diazo Compounds and Poly(propargyl acrylate) at ambient temperature. In preparation.

9. Acknowledgment

So far, my Ph.D. life is almost approaching the end when my thesis writing is nearly done. As I recollect over the past four and a half years, without the help and support of the people I met I could not go into my current step. Hence, I would like to use this opportunity to express my sincere gratitude towards all the people who support me to keep moving forward and help me be confident and optimistic in front of difficulties.

First and foremost, I would like to express my sincere gratitude to my Ph.D. supervisor Professor Dr. Stefan Bräse. Thank you sincerely for accepting me at my hardest time and for the support of applying for the funding at my final Ph.D. phase. Thank you for your tireless and efficient review of my drafts and thesis and also of my publishing. I appreciate your careful instructions on my projects and the upcoming examination of my Ph.D. defense.

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I would also thank Dr. Xia Huang and Xiaohui give me so much help on the characterization of the materials, thank you for your company from Hamburg to Karlsruhe.

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Special thanks Yunji Xie, thank you for your so kind and selfless help, even when I was done and met some tricky issues.

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