Synthesis and Post-Polymerization Modification of Defined Functional Poly(vinyl ether)s

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Living cationic polymerization is known for a good control over chain growth yielding polymers with well-defined molar mass distributions and low dispersities. However, the practical challenges involved in the synthesis of poly(vinyl ether)s limited suitable post-polymerization modifications (PPM) via chemoselective click reactions. Herein the successful controlled cationic polymerization of vinyl ethers bearing pendant C=C double and C≡C triple bonds using a single-component initiation under ambient conditions is reported. Furthermore, the PPM *via thiol*-ene/*-yne* and copper*(I)-catalyzed alkyne*-azide *cycloaddition* reaction of the obtained polymers is successfully realized laying the foundation for the synthesis of unprecedented functional poly(vinyl ether)s.

1. Introduction

The modification of polymers is known since the early days of modern polymer science. The vulcanization of natural rubber using elemental sulfur in 1840[1] or the nitration of cellulose for the production of nitrocellulose in 1847[2] are two commonly known examples. While post-polymerization modifications (PPMs) had been around ever since, they received particular attention when being combined with rev*ersible*-deactivation radical polymerization (RDRP) techniques such as atom transfer radical polymerization (ATRP),[3] reversible additi*on-frag*mentation chain transfer (RAFT) polymerization[4] or nitroxide-*m*ediated polymerization (NMP).[5] In comparison to conventional free radical polymerization techniques these controlled polymerizations allowed
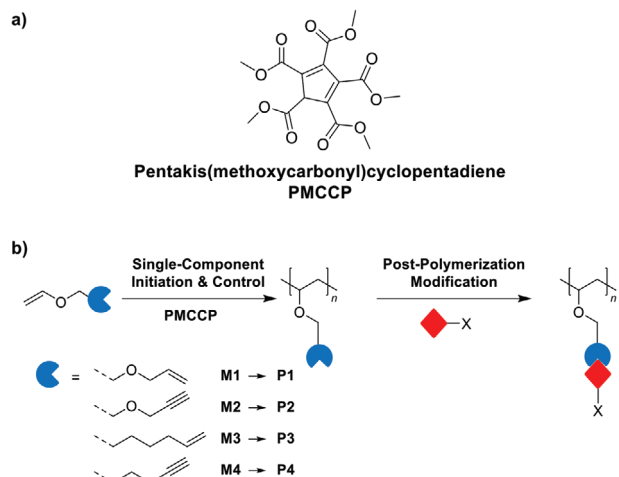
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for the synthesis of well-defined polymers while tolerating numerous functional groups.[6,7] However, the preparation of polymers bearing functional groups that enable further functionalization, that is, PPM, is not of a great value if the chemistry utilized for the PPM does not proceed in a quantitative fashion. Therefore, the development and application of so-called click reactions[8–10] such as thi*ol-en*e reactions[11] or copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC)[12] as *chemo-selective* and highly efficient reactions were essential for their utilization in PPM methods. However, both thiol-ene and CuAAC click reactions suffer from the same issue regarding their combination with RDRP techniques in the sense that the required functional group for PPM (i.e., C=C double and C≡C triple bond) is not inert toward a radical polymerization, leading to cross-linked polymers.[13] The synthesis of low molar masses polymers and the use of RDRP techniques can help to suppress these side reactions, but are not able to eliminate this issue completely.[14]

In contrast to this, vinyl ethers as electron rich monomers are typically polymerized by cationic polymerization and do not suffer from these radical side reactions.[15] Hence, pendant side groups featuring isolated C=C double or C≡C triple bonds do not interfere with the cationic polymerization itself. Yet it is surprising to note that until now not many studies of PPM of poly(vinyl ether)s bearing functional groups consisting of C=C double or C≡C triple bonds have been reported. Studies generally describing the PPM of poly(vinyl ether)s, for example, by C–H oxidation resulting in vinyl esters or by employing protected alcohol groups, which are deprotected after the polymerization and thus available for further modification, have been published but in comparison to other monomer classes reports on PPM of poly(vinyl ether)s are rare.[16,17] This might be due to the general requirements of controlled cationic polymerizations such as highly purified and dried reactants and solvents, the demand for a perfect inert atmosphere and usually low reaction temperatures.[18–20] Additionally, the limited scope of commercially available vinyl ethers is possibly also a consequence of their rare use in PPMs and vice versa.

In 2019, Kottisch et al.[21] reported on a remarkable advancement in the controlled cationic polymerization of vinyl ethers. They showed that pentakis(methoxycarbonyl)cyclopentadiene (PMCCP) (**Scheme 1**a) as a strong organic acid[22] enables the single-component initiation as well as the control over the cationic polymerization of a series of alkyl vinyl ethers in bulk under ambient atmosphere (mechanism shown in

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a)

**Pentakis(methoxycarbonyl)cyclopentadiene
PMCCP**

b)

Scheme 1. a) Structure of pentakis(methoxycarbonyl)cyclopentadiene (PMCCP). b) Strategy for the synthesis of functional poly(vinyl ether)s **P1**–**P4** bearing C=C double- or C≡C triple-bonds and their subsequent post-polymerization modification via click chemistry.

Scheme 2. Synthesis of functional vinyl ether monomers **M1**–**M4** bearing either C=C double- or C≡C triple-bonds starting from ethylene glycol vinyl ether (x = 1) or tetramethylene (x = 3) glycol vinyl ether.

Scheme S1, Supporting Information). The conducted polymerizations resulted in polymers with narrow dispersities (Đ) ranging from 1.06 to 1.33 with predictable experimental molar masses. Furthermore, they recently expanded their studies, showing that an added hydrogen bond donor molecule stabilizes the formed complex during polymerization and thus enables the synthesis of high molar mass alkyl-based poly(vinyl ether)s.[23] However, they did not investigate the polymerizations of vinyl ethers bearing any functional group.
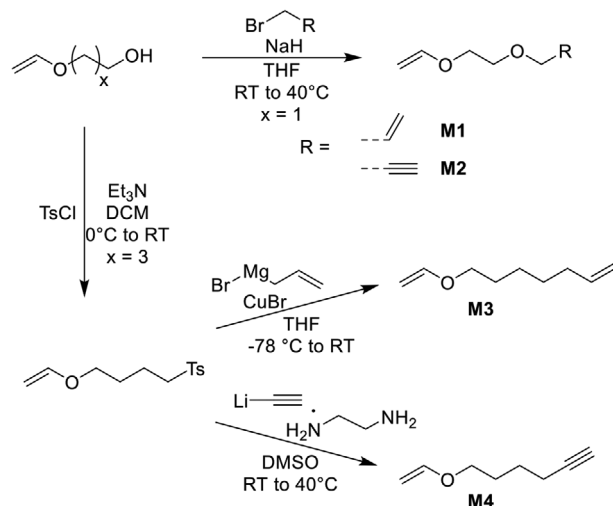
As a research group with a strong interest in PPMs,[24–27] we were intrigued by the straightforward cationic polymerization using PMCCP as it would open up the possibility for unprecedented PPMs of poly(vinyl ether)s. Thus, a series of different functionalized vinyl ethers are to be synthesized and their polymerization and subsequent modification to be investigated in order to provide a fundamental insight into the synthesis of functional poly(vinyl ether)s to broaden potential application areas of this polymer class.

2. Results and Discussion

2.1. Monomer Synthesis

In order to combine the novel described single-component initiation system by Kottisch et al.[21] with the prominent and highly efficient thiol-ene/-yne and CuAAC reactions for PPMs, two types of monomer classes bearing pendant C=C double- or C≡C triple-bonds, respectively, were investigated (Scheme 1b). Both functional groups were linked either via an alkyl spacer or an ethyleneglycol spacer to the vinyl ether monomer to investigate the potential influence of the spacer on the polymerization and subsequent PPM.

Monomers **M1** and **M2** were synthesized by nucleophilic substitution employing deprotonated ethylene glycol vinyl ether and allyl bromide or propargyl bromide, respectively (**Scheme 2**). Monomers **M3** and **M4** were synthesized from tosylated tetramethylene glycol vinyl ether using either an in situ gener-

ated organocuprate (monomer **M3**) derived from allyl magnesium bromide and copper(I) bromide or with lithium acetylide (monomer **M4**) (see Supporting Information for synthesis details).
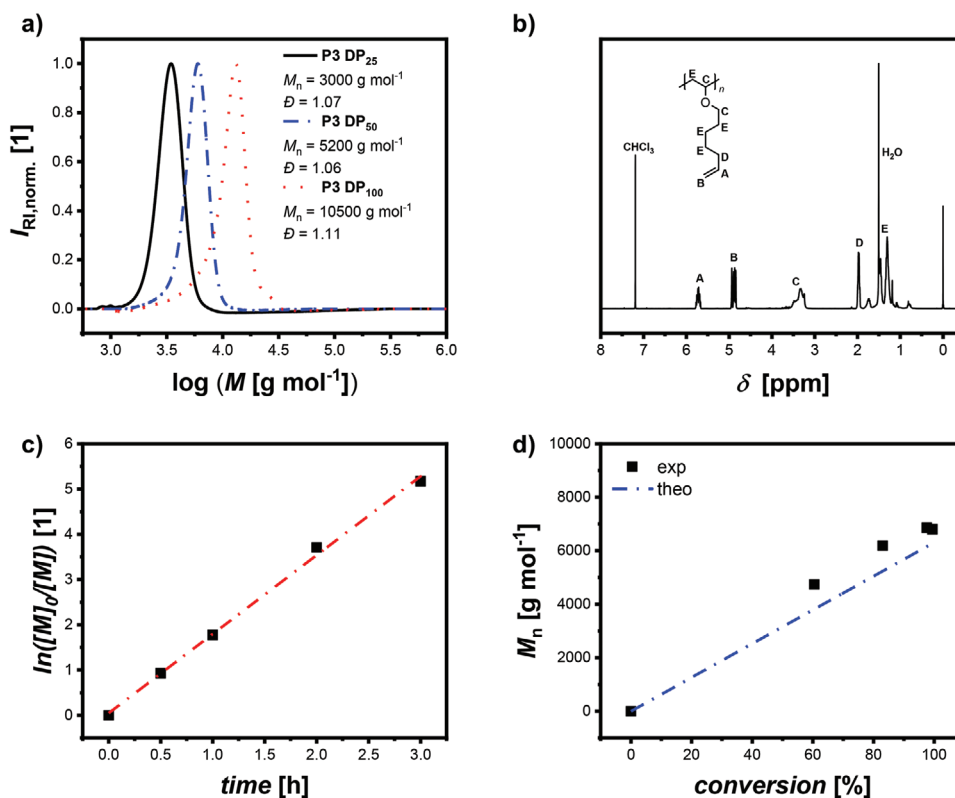
2.2. Controlled Cationic Polymerization

After the successful synthesis of the functional monomers, their cationic polymerization using PMCCP as single-component initiator and control agent was studied. Herein, for each monomer three polymerizations yielding polymers with a targeted degree of polymerization (DP) of 25, 50, and 100 were conducted in order to show the controlled character of the polymerization. In general, the targeted molar masses were reached in most cases within the tolerance of the molar mass determination by SEC while maintaining low dispersities (**Table 1**, exemplary **Figure 1**a,b). However, several trends were observed. Within each polymer series, polymers with the largest DP = 100 exhibited the highest dispersity. This is most probable due to the prolonged reaction time and less PMCCP present, which increased the chance for side reactions. Despite that, it appeared that the monomers featuring no additional oxygen atom in the spacer (i.e., monomers **M3** and **M4**) showed a better control over the polymerization in comparison to the ones with an additional oxygen atom in the spacer (i.e., monomers **M1** and **M2**). This becomes obvious when comparing the dispersities of the respective polymers **P3** and **P4** (Đ = 1.05 – 1.11) with polymers **P1** and **P2** (Đ = 1.14 – 1.36) and is further supported by the fact that it was not possible to synthesize polymers **P1** and **P2** with a DP of 100 in a controlled manner without changing the atmosphere to nitrogen (Table 1 **entry 3/4 and 7/8;** Figure S26, Supporting Information), while the polymerization of monomers **M3** and **M4** did not suffer from this issue under ambient conditions. Furthermore, we noticed that polymerizations conducted under air atmosphere resulted in polymers with broader distributions when the atmosphere was frequently changed, for example by removing the lid of the reaction vessel

Table 1. Overview of the polymerizations of the different monomers **M 1–4** using PMCCP.

Entry	Monomer	Equiv.	Atmosphere	Time [h]	$M_{n,theo}$ [a] [g mol^{-1}]	$M_{n,exp}$ [b] [g mol^{-1}]	$Đ$ [b] [1]
1	M1	25	Air	2	3200	3400	1.25
2	M1	50	Air	2	6400	5700	1.14
3	M1	100	Air	3	12 800	3700	1.56
4	M1	100	N$_2$	3	12 800	7500[c]	1.33
5	M2	25	Air	1	3150	4000	1.16
6	M2	50	Air	2	6300	7100	1.19
7	M2	100	Air	3	12 600	5100	1.45
8	M2	100	N$_2$	3	12 600	11 000	1.36
9	M3	25	Air	3	3500	3000	1.07
10	M3	50	Air	3	7000	5200	1.06
11	M3	100	Air	6	14 000	10 500	1.11
12	M4	25	Air	3	3100	3000	1.07
13	M4	50	Air	4	6200	6000	1.05
14	M4	100	Air	8	12 400	9800	1.10

[a] $M_{n,theo} = M(monomer) \times equiv$; [b] Determined by SEC with PMMA standards; [c] $M_p = 11\ 700$ g mol^{-1} (Showing that in principle the targeted molar mass is reached, but the broad dispersity results in a comparably low M_n).

Figure 1. a) SEC traces of the polymerization of monomer **M3** targeting DPs of 25, 50, and 100 using PMCCP. b) ^{1}H NMR of polymer **P3 DP$_{50}$** proving the untouched vinyl group after polymerization. c) Kinetic study of monomer **M2** (DP = 50) proving the controlled character of the reaction by the linear development of ln([M]$_0$/[M]) versus time as well as d) the linear development of the molar mass M_n with conversion, which is in good agreement with the theoretically calculated development.

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Table 2. Overview of the post-polymerization modification (PPM) reactions of polymers **P1**–**P4**.

Entry	Polymer	PPM	Reactant	Conversion[a]	$M_{n,before}$[b] [g mol^{-1}]	$Đ_{before}$[b] [1]	$M_{n,after}$[b] [g mol^{-1}]	$Đ_{after}$[b] [1]
1	P1	Thiol-ene	DDT	Quant.	5700	1.14	14 600	1.13
2	P1	Thiol-ene	TBBT	Quant.	5700	1.14	10100	1.14
3	P1	Thiol-ene	ME	Quant.	5700	1.14	7400	1.12
4	P2	Thiol-yne	DDT	Quant.	7100	1.19	19 200	1.22
5	P2	Thiol-yne	TBBT	Quant.	7100	1.19	15 500	1.33
6	P2	CuAAC	BzN$_3$	Quant.	7100	1.19	9900	1.11
7	P3	Thiol-ene	DDT	Quant.	5200	1.06	10 500	1.07
8	P3	Thiol-ene	TBBT	Quant.	5200	1.06	8700	1.07
9	P3	Thiol-ene	ME	Quant.	5200	1.06	6500	1.08
10	P4	Thiol-yne	DDT	Quant.	6000	1.05	15 000	1.06
11	P4	Thiol-yne	TBBT	Quant.	6000	1.05	12 200	1.10
12	P4	CuAAC	BzN$_3$	Quant.	6000	1.05	7400	1.05

[a] Quantitative conversion of the respective functional group as determined by ^{1}H NMR spectroscopy. DDT: 1-dodecanethiol; TBBT: 4-*tert*-butylbenzylthiol; ME: mercaptoethanol; BzN$_3$: benzyl azide. [b] Determined by SEC with PMMA standards.

during polymerization (Figure S27, Supporting Information). It therefore seems on the one hand that the PMCCP system can handle a certain amount of air, but not an unlimited exposure to ambient air. On the other hand, it seems that the polymerization is suffering if additional oxygen atoms are present in the monomer structure, probably due to an interaction of the second oxygen with the transition state complex,[21] and thus weakening the interaction with the vinyl ether oxygen, or an overall higher polarity of the monomer, both resulting in more possibilities for side reactions to take place and therefore eventually increasing the dispersity. Nonetheless, a straightforward polymerization of functional vinyl ethers was successful under air atmosphere in most cases.

In addition, an exemplarily kinetic study of the polymerization was conducted using monomer **M2** in order to further investigate its controlled character. For a controlled or "living" polymerization a linear increase of $\ln([M]_0/[M])$ with time as well as a linear correlation of the molar mass M_n and the conversion is necessary.[28–30] As shown in Figure 1c,d both characteristics were fulfilled proving the first order kinetic of the polymerization as wells as the linear increase of M_n with time, in accordance with the theoretically expected values of M_n. Therefore, it can be stated that side reactions are well suppressed and that a living character of the polymerization can be assumed for those functional vinyl ethers **M1**–**M4** in analogy to the alkyl vinyl ethers described by Kottisch et al.[21]
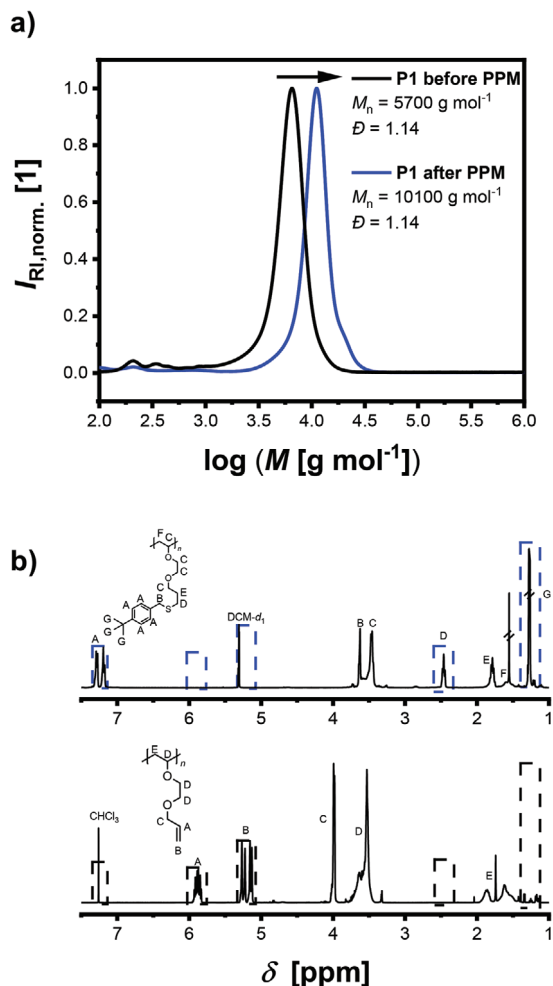
2.3. Post-Polymerization Modification

Next, the synthesized polymers **P1**–**P4** with a DP of 50 were used for a subsequent PPM via thiol-ene reaction of **P1** and **P3**, or thiol-yne and CuAAC reaction of **P2** and **P4**. Herein, thiol-ene reactions of the vinyl groups in **P1** and **P3** were conducted using three different substrates, that are, 1-dodecanethiol (DDT), 4-*tert*-butylbenzylthiol (TBBT) and mercaptoethanol (ME). The alkyne group containing polymers **P2** and **P4** were functionalized using DDT and TBBT for thiol-yne reactions as well as benzyl azide

for the CuAAC reaction (**Table 2**). Generally, all PPM reactions proceeded quantitatively in both the consumption of their functional group as well as the attachment of the substrate (Table 2), with the disappearance and appearance of the corresponding signals in the ^{1}H NMR spectra of the successfully formed products (see Supporting Information). Moreover, FT-IR as well as ESI-MS measurements were conducted to further prove the successful, quantitative conversion of the functional groups (Figures S29–S39, Supporting Information). Additionally, a shift of the polymers' molar masses M_n as indicated by SEC confirmed the efficient PPM using the employed click reactions (shown exemplarily in **Figure 2** for the thiol-ene reaction of polymer **P1** with 4-*tert*-butylbenzylthiol). Also the dispersity of the post-modified poly(vinyl ether)s remained more or less constant with some minor exceptions showing a slight increase in dispersity after functionalization(e.g., Table 2 entry 5). Probably, this is a result of a too high radical concentration causing minor radical coupling reactions of carbons next to the formed thioether moieties. Surely this broadening can be minimized by adjusting the reaction parameters, therefore we exemplarily studied the PPM of **P2** with TBBT, eventually successfully optimizing the conditions (Figure S28, Supporting Information).

3. Conclusion

In summary, a series of four different vinyl ether monomers **M1**–**M4** bearing pendant C=C double- or C≡C triple-bonds as functional group were successfully employed in the controlled cationic polymerization via the PMCCP single-component initiation system under air atmosphere. It was found that the system only tolerates certain disturbing factors, such as variations in the chemical monomer structure and targeted molar mass. Yet, a nitrogen atmosphere is beneficial to overcome this issue. Subsequently, we demonstrated the successful and quantitative PPM of the poly(vinyl ether)s **P1**–**P4** via thiol-ene/yne or CuAAC reaction using different substrates. Overall, we advanced the synthesis of diversely functionalized poly(vinyl ether)s by successfully combining the PMCCP controlled cationic polymerization

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a)

b)

Figure 2. PPM of polymer **P1** using 4-*tert*-butylbenzylthiol as shown by a) the clear shift of the SEC elugram while maintaining a low dispersity and a symmetrical signal and b) by the conversion of the double bond as well as the appearance of the corresponding signal of the *tert*-butylbenzylthio ether as determined by ^{1}H NMR spectroscopy (bottom: before, top: after).

of poly(vinyl ether)s with the efficient PPM via different click reactions, hence, minimizing the synthetic complexity.

Supporting Information

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

Conflict of Interest

The authors declare no conflict of interest.

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