SUPPORTING INFORMATION FOR

End Functional ROMP Polymers via Degradation of a Ruthenium Fischer Type Carbene

Amit A. Nagarkar, Andreas F. M. Kilbinger*

Department of Chemistry, University of Fribourg, Chemin du musée 9, CH-1700 Fribourg, Switzerland

Table of Contents

Experimental Section
- Materials .................................................................................................................. 2
- Instrumentation ....................................................................................................... 2
- Typical polymerization procedure in an NMR Tube .............................................. 2
- Typical procedure for Ring-Opening Metathesis Polymerization ...................... 2
- Quenching with MDHP and H2SO4 ................................................................... 3
- Typical procedure for post polymerization modification of the end group ....... 3
- Synthesis of Fe3O4 nanoparticles (SPIONs) .......................................................... 3
- Typical procedure for polymer-SPION conjugate synthesis .............................. 3
- Typical procedure for MALDI-TOF sample preparation .................................... 3

Analytical Section
- Figure S1 ESI-MS studies for degradation of the Fischer carbene .................... 4
- Figure S2 Ruthenium containing peaks in the ESI-MS study .............................. 4
- Figure S3 1H-NMR of the aldehyde end functionalized polymer polymers ...... 5
- Figure S4 13C-NMR of the aldehyde end functionalized polymer polymers ...... 5
- Figure S5 MALDI-ToF spectrum of polymer quenched without degassing ...... 6
- Figure S6 MALDI-ToF spectrum of the all-proto acetal polymer ....................... 7
- Figure S7 MALDI-TOF spectrum of the catechol end functionalized polymer .... 8
- Figure S8 GPC Traces of aldehyde end functional polymers synthesized with G1 ......................................................................................................................... 9
- Table S1 GPC analysis of aldehyde end functional polymers synthesized with G1 ................................................................. 9
- Figure S9 GPC Traces of aldehyde end functional polymers synthesized with G3 ......................................................................................................... 10
- Table S2 GPC analysis of aldehyde end functional polymers synthesized with G3 ......................................................................................................... 10
- Figure S10 Superimposed 1H-NMR spectra for kinetics of G3 catalyst .......... 11
- Figure S11 GPC Trace of dopamine functionalized polymer ............................ 12
- Table S3 GPC analysis of dopamine end functionalized polymer ................. 12
- Figure S12 1H-NMR of reductive amination with p-nitroaniline .................... 13
- Figure S13 MALDI-ToF spectrum of reductive amination with p-nitroaniline .... 13
EXPERIMENTAL SECTION

Materials:
Analytical grade solvents were purchased from Honeywell or Sigma-Aldrich and were used without further purification. Dry pyridine over molecular sieves was purchased from Sigma-Aldrich with the highest possible purity and used without further purification. Grubbs initiators G1 and G3, ethyl vinyl ether, sodium cyanoborohydride, dopamine hydrochloride, Fe(CO)5, oleic acid and dry (CH3)2NO were purchased from Sigma-Aldrich and used without further purification. 2-methoxy-3,4-dihydro-2H-pyran (MDHP) was purchased from Acros Chemicals and used without further purification. Exo-N-methylnorbornene imide (MNI) was synthesized as reported previously3. Molecular sieves were purchased from Sigma-Aldrich and activated at 100°C under vacuum for 24 hours before use. Deuterated solvents (CD2Cl2, CDCl3) were purchased from Cambridge Isotope Laboratories, Inc. Deuterated dichloromethane was degassed by 3 successive freeze-vacuum-thaw cycles immediately before use.

Instrumentation:
ESI-MS analysis was carried out on a Bruker Daltonics Esquire HCT Mass Spectrometer with acetonitrile as the solvent. Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-ToF)-MS analyses of the polymers were carried out on a Bruker ultrafleXtreme™ using 2-(2E)-3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix and silver trifluoroacetate as the ionizing salt. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) equipped with a Viscotek GPCmax VE2001 GPC Solvent/Sample Module, a Viscotek UV-Detector 2600, a Viscotek VE3580 RI-Detector, and two ViscotekT6000 M columns (7.8×300 mm, 103–107Da) connected in series. All measurements were carried out at room temperature using THF as the eluent with a flow rate of 1 mL/min. The system was calibrated with polystyrene standards in a range from 10^3 to 3×10^6 Da. NMR spectra were recorded on a Bruker Avance III 300 MHz NMR spectrometer (1H-NMR 300 MHz; 13C-NMR 75MHz). NMR signals were referenced internally to residual solvent signals. Ultra performance liquid chromatography / Mass spectrometry (UPLC-MS) analysis (LC-MS) was performed on a Waters UPLC® (H-Class Acquity) System equipped with a photodiode array detector (PDA), a SQ-detector (ESI & APCI ionisation mode) and an ACQUITY UPLC® BEH C18 column (1.7 µm, 2.1×50 mm).

Typical polymerization procedure in an NMR Tube:
The ruthenium initiator (either G1 or G3) was taken in an NMR tube and purged by continuous flow of argon for 15 min. Degassed dichloromethane-d2 was added and the NMR tube was shaken until all the initiator was dissolved. The monomer MNI was purged with argon in a separate vial. Degassed dichloromethane-d2 was added to the monomer under a flow of argon via a syringe. This solution was immediately transferred to the NMR tube containing the initiator. The NMR tube was capped and inverted once to ensure efficient mixing. The tube was kept standing for some time (typically 45 min) to ensure complete monomer consumption. MDHP was purged with argon for 30 min, dissolved in degassed dichloromethane-d2, and added to the NMR tube for end-functionalization. The NMR tube was inverted to ensure complete mixing and immediately transferred into the NMR spectrometer for subsequent recording of NMR spectra.

For the degradation kinetics, 1H-NMR was recorded every 5 minutes till two hours and then every 15 minutes till two more hours and finally every 30 minutes till no appreciable change in the integration of the carbene peak was observed.

Typical procedure for Ring-Opening Metathesis Polymerization:
The catalyst (G1 or G3), monomer (MNI), and MDHP were taken in separate Schlenk flasks and purged free of oxygen by three cycles of alternating vacuum and argon atmosphere. Dry dichloromethane was taken in a separate Schlenk flask and degassed by three consecutive freeze–vacuum–thaw cycles. This degassed dichloromethane was added to each Schlenk flask. The catalyst solution was added quickly to the MNI solution using a syringe, and the resulting solution...
was kept stirring at r.t. for 45 min. An aliquot of this solution was quenched with ethyl vinyl ether and analyzed as a reference sample. MDHP (30 equivalents with respect to the metathesis catalyst) was quickly added to the remaining solution via a syringe, and the solution was kept stirring for 12 hours. The polymer was precipitated in a 1:1 mixture of cold diethyl ether/hexane. The polymer was redissolved in DCM and reprecipitated once more, filtered, and dried under high vacuum.

**Quenching with MDHP and H₂SO₄:**

In case of quenching with H₂SO₄, one drop of 50% H₂SO₄ in degassed distilled water was added to the polymerizing mixture 30 minutes after the addition of MDHP. The mixture was stirred further for 30 minutes and then precipitated in cold diethyl ether/hexane, redissolved and reprecipitated, filtered and dried in vacuum.

**Typical procedure for post polymerization modification of the end group:**

The aldehyde end functionalized polymer was dissolved in dichloromethane and excess dopamine hydrochloride salt (30eq.) in pyridine was added. Activated 4 Å Molecular sieves were added to the mixture as a water scavenger. This mixture was stirred on a shaker for 1 hour and excess sodium cyanoborohydride (30 eq.) was added. The mixture was shaken on the shaker for 24 hours and then quenched with methanol and precipitated in cold methanol, filtered and dried in vacuum. Care must be taken in handling the polymer to exclude oxygen as the dopamine end group undergoes oxidation very easily.

**Synthesis of Fe₂O₃ nanoparticles:**

12 nm sized γ-Fe₂O₃ were prepared exactly according to the reported procedure.² 0.2 mL of Fe(CO)₅ (1.52 mmol) was added to a mixture of 10 mL of octyl ether and 1.28 g of oleic acid (4.56 mmol) at 100 °C. This mixture was then refluxed for 1 h. The orange solution slowly turned black. This black solution was cooled to r.t. and 0.34 g of dry (CH₃)₃NO (4.56 mmol) was added. The mixture was then heated to 130 °C under an argon atmosphere for 2 h. The solution color changed to brown. The mixture was further refluxed for 1 h and the color gradually turned black. The solution was then cooled to r.t., and ethanol was added. The black precipitate was separated by centrifuging. The resulting black powder was redispersed in hexane to have a final concentration of 5mg/mL.

**Typical procedure for polymer-SPION conjugate synthesis:**

0.05 mL of the 5 mg/mL solution of γ-Fe₂O₃ in hexane was added to a biphasic mixture of 1mL hexane and 1mL DMF and shaken vigorously. The nanoparticles remained in the hexane layer. Then, 0.25mL of a 60mg/mL solution of the end functional polymer in DMF was added and the mixture was stirred in a vortex shaker for 5 minutes. The biphasic mixture was allowed to settle down and it was clearly seen that the nanoparticles are pulled from the hexane layer into the DMF layer.

**Typical procedure for MALDI-TOF sample preparation:**

2 mg of the polymer was dissolved in 1mL of dichloromethane. 2µL of this solution was added to a 20 µL solution of 2mg/L DCTB in THF. 1 µL of 1M AgTFA in MeOH was added as the ionizing salt. This solution was stirred for 1 minute and then spotted on the MALDI target plate and left to crystallize for 30 minutes. Each MALDI-ToF measurement was calibrated against CsI₃ before recording the spectrum.
Analytical Section

ESI MS studies for degradation of the Fischer carbene:

G1 was reacted with 18 eq. of MNI at r.t. in degassed dichloromethane for 1 hour and then 30 equivalents of MDHP were added. The solution was stirred for 8 hours to ensure complete degradation of the carbene. One drop of this solution was diluted with 1mL acetonitrile and injected inside the ESI-MS.

Figure S1. ESI-MS spectrum of the solution after letting the acetal Fischer carbene decompose for 9 hours.

Figure S2. Zoomed in regions of the ESI-MS spectrum showing the peaks with isotopic distribution corresponding to ruthenium metal. The theoretically calculated isotopic distribution for each ruthenium complex is provided on the right.
**Figure S3.** $^1$H-NMR of the aldehyde end functionalized polymer (Mw = 3644, Mn = 3150, PDI = 1.26).

**Figure S4.** $^{13}$C-NMR of the aldehyde end functionalized polymer.
Figure S5. MALDI-ToF mass spectrum of the aldehyde end functionalized polymer when the quenching agent MDHP was not degassed. The peak at 3046.19 corresponds to the polymer resulting from the direct metathesis of the living ruthenium alkylidene with oxygen which has already been reported in literature.³
Figure S6. (top) MALDI-ToF mass spectrum of the degradation product of the polymer-Fischer carbene with one drop of proto-methanol added to confirm that the all-proto acetal is detected in MALDI-ToF spectrometry. (bottom) Enlarged section of the MALDI-ToF spectrum clearly showing the all-proto acetal. The peak at 3114 cannot be assigned to any deductable polymeric species as yet and is an unknown impurity.
However, the catechol is prone to oxidation and degradation is observed within minutes of purification of the polymer.

Figure S7. (top) Structure and (bottom) MALDI-TOF spectrum of the catechol end functionalized polymer. However, the catechol is prone to oxidation and degradation is observed within minutes of purification of the polymer.
**Figure S8** GPC Traces of aldehyde end functional polymers synthesized with G1

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<th>GPC trace color</th>
<th>Calculated Mol wt</th>
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**Table S1** GPC analysis of aldehyde end functional polymers synthesized with G1
Figure S9 GPC Traces of aldehyde end functional polymers synthesized with G3

Table S2 GPC analysis of aldehyde end functional polymers synthesized with G3
Figure S10 Time resolved $^1$H-NMR spectra of the degradation of the Fischer carbene with G3 catalyst. G3 was reacted with MNI for 10min and then 30eq. MDHP was added. The degradation continues for c.a. 7 hours. In this case, the rate constant was $4.012 \times 10^{-1} \text{s}^{-1}$ which is similar to the degradation rate constant with G1.
Figure S11 GPC trace of dopamine functionalized polymer

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Table S3 GPC analysis of dopamine end functionalized polymer
Reductive Amination with p-nitroaniline:

Figure S12. $^1$H-NMR of the polymer after reductive amination with p-nitroaniline.

Figure S13. MALDI-ToF spectrum of the polymer after reductive amination with p-nitroaniline.