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SUPPORTING INFORMATION FOR

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

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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 $(CH_3)_3NO$ 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 previously[1]. 3A Molecular sieves were purchased from Sigma-Aldrich and activated at 100^oC under vacuum for 24 hours before use. Deuterated solvents (CD_2Cl_2, $CDCl_3$) 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^{TM} using 2-[(2E)-3-(4-*tert*butylphenyl)-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 3×10^6Da. NMR spectra were recorded on a Bruker Avance III 300 MHz NMR spectrometer (^{1}H-NMR 300 MHz; ^{13}C-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 x50 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, ^{1}H-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 H_2SO_4:

In case of quenching with H_2SO_4, one drop of 50% H_2SO_4 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 Fe_2O_3 nanoparticles:

12 nm sized γ-Fe_2O_3 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 $(CH_3)_3NO$ (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-Fe_2O_3 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 CsI_3 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.

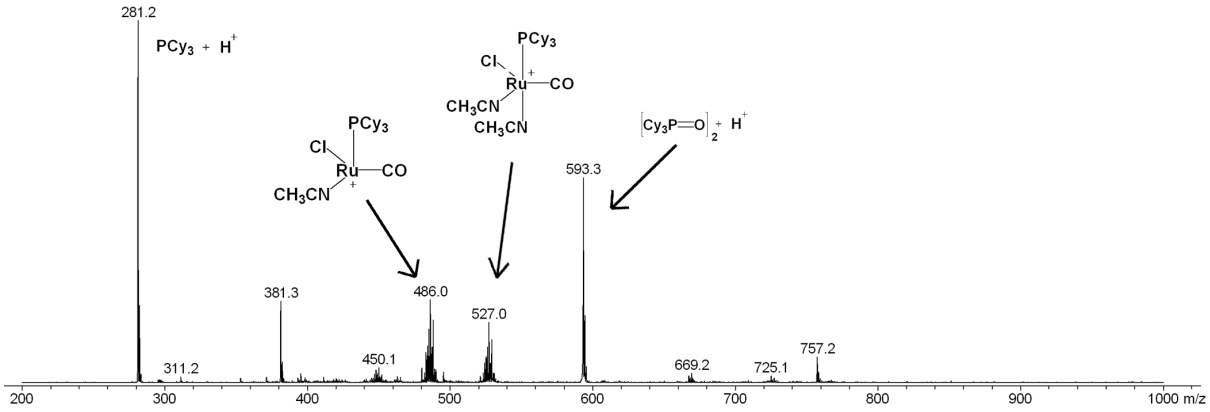

Figure S1. ESI-MS spectrum of the solution after letting the acetal Fischer carbene decompose for 9 hours.

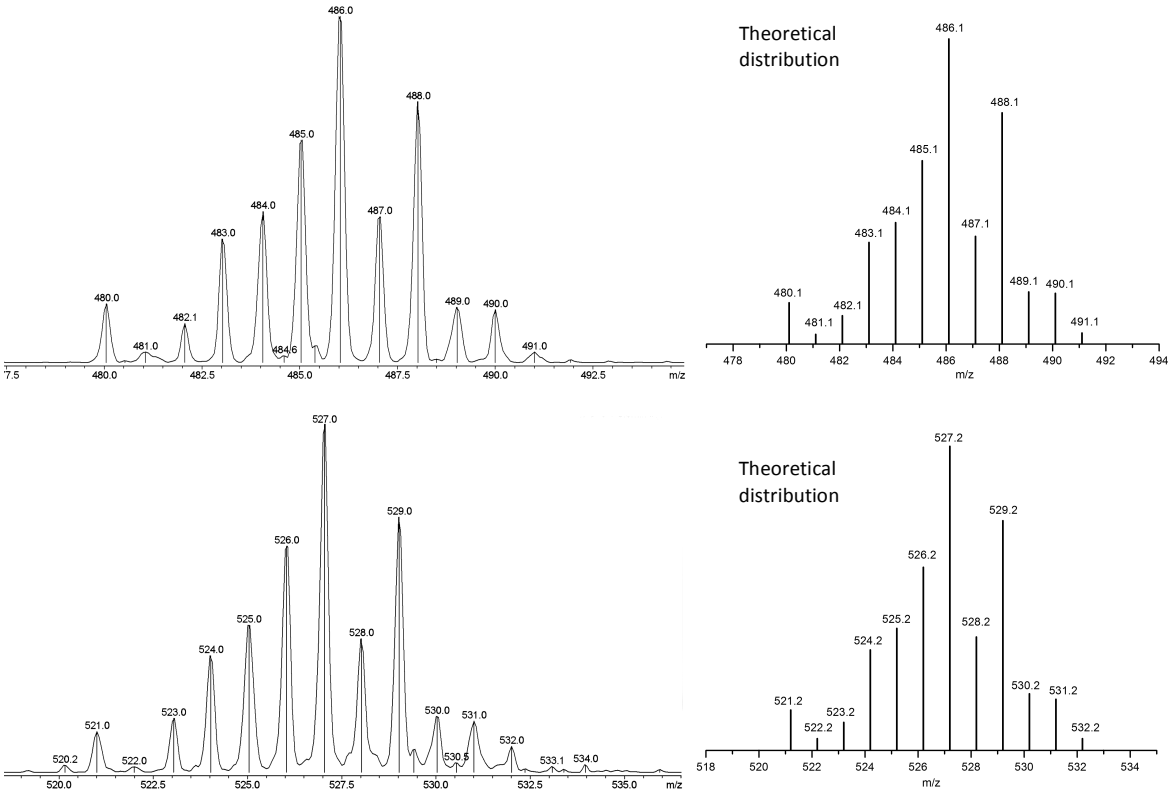

Figure S2. Zoomed in regions of the ESI-MS spectrum showing the peaks with isotopic distribution corresponding to ruthenium metal. The theoretically calculated isotopic distribution for each ruthenium complex is provided on the right.

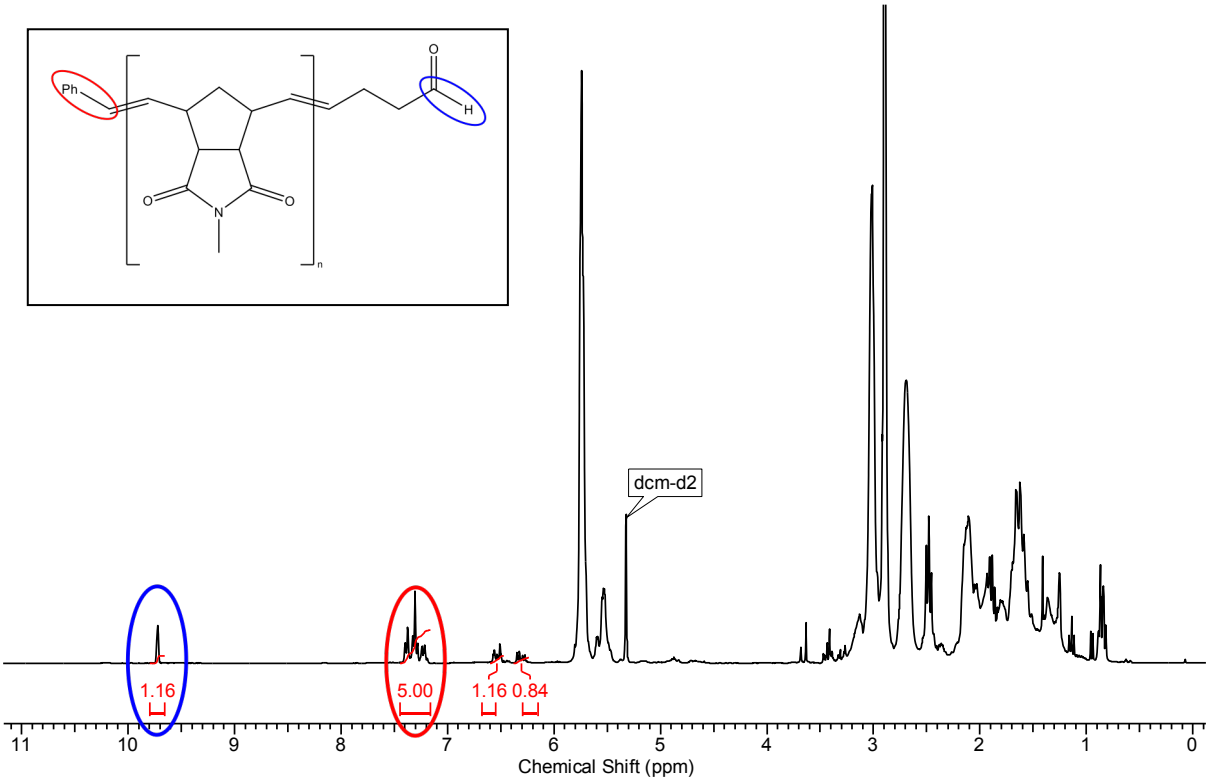

Figure S3. ^{1}H-NMR of the aldehyde end functionalized polymer (Mw = 3644, Mn = 3150, PDI = 1.26) .

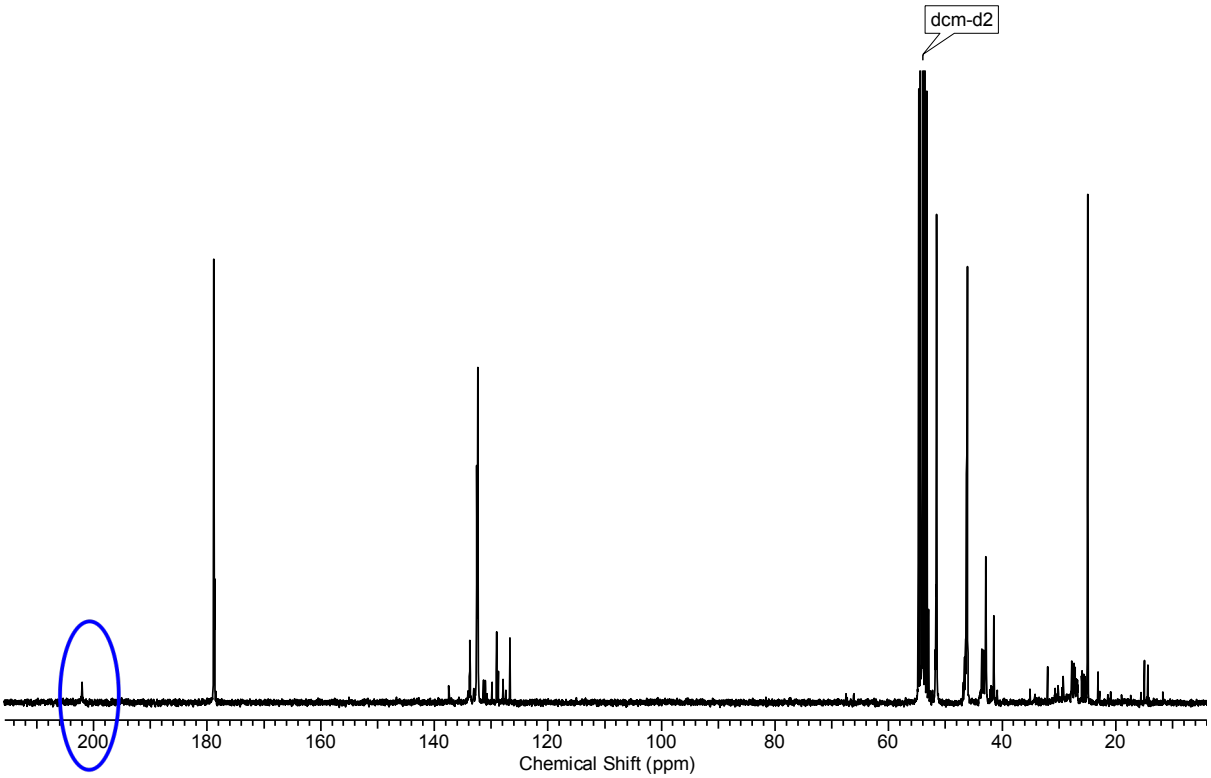

Figure S4. ^{13}C-NMR of the aldehyde end functionalized polymer.

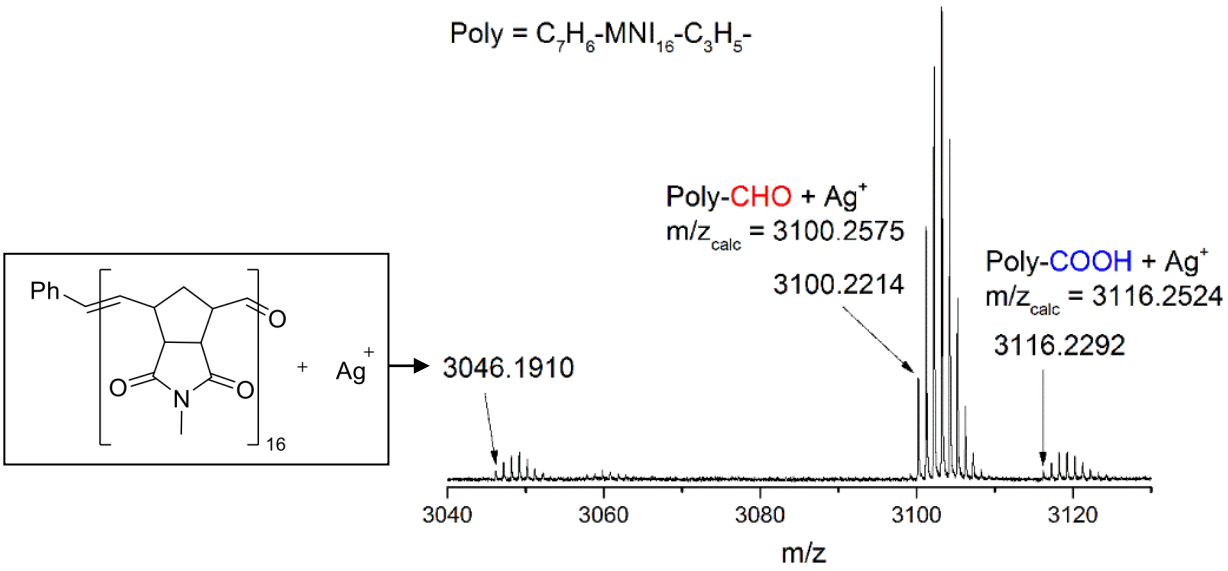

Figure S5. MALDI-ToF mass spectrum of the aldehyde end functionalized polymer when the quenching agent **MDHP** was not degassed. The peak at 3046.19 corresponds to the polymer resulting from the direct metathesis of the living ruthenium alkylidene with oxygen which has already been reported in literature.[3]

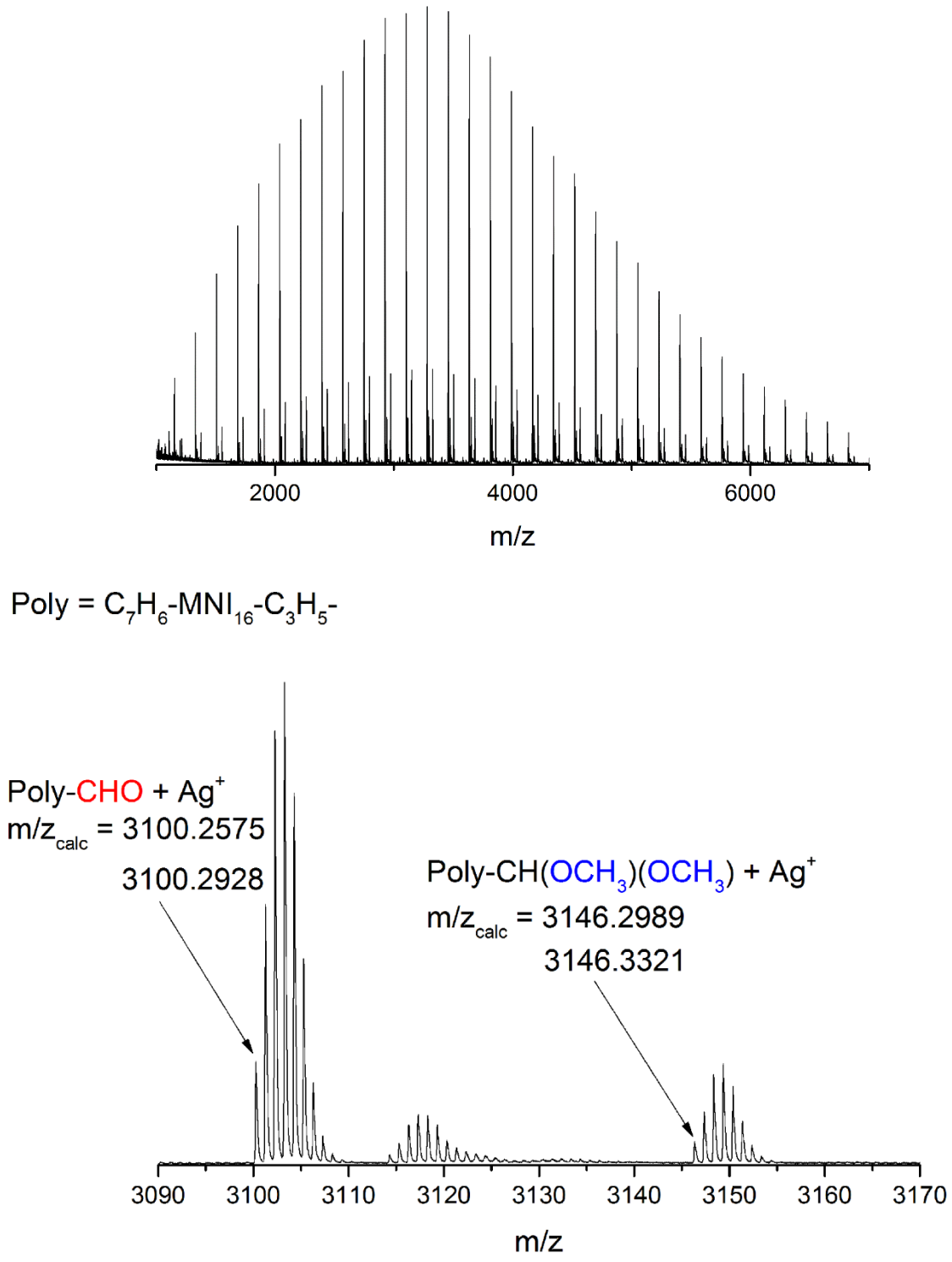

Figure S6. (top) MALDI-ToF mass spectrum of the degradation product of the polymer-Fischer carbene with one drop of proto-methanol added to confirm that the all-proto acetal is detected in MALDI-ToF spectrometry. (bottom) Enlarged section of the MALDI-ToF spectrum clearly showing the all-proto acetal. The peak at 3114 cannot be assigned to any deductable polymeric species as yet and is an unknown impurity.

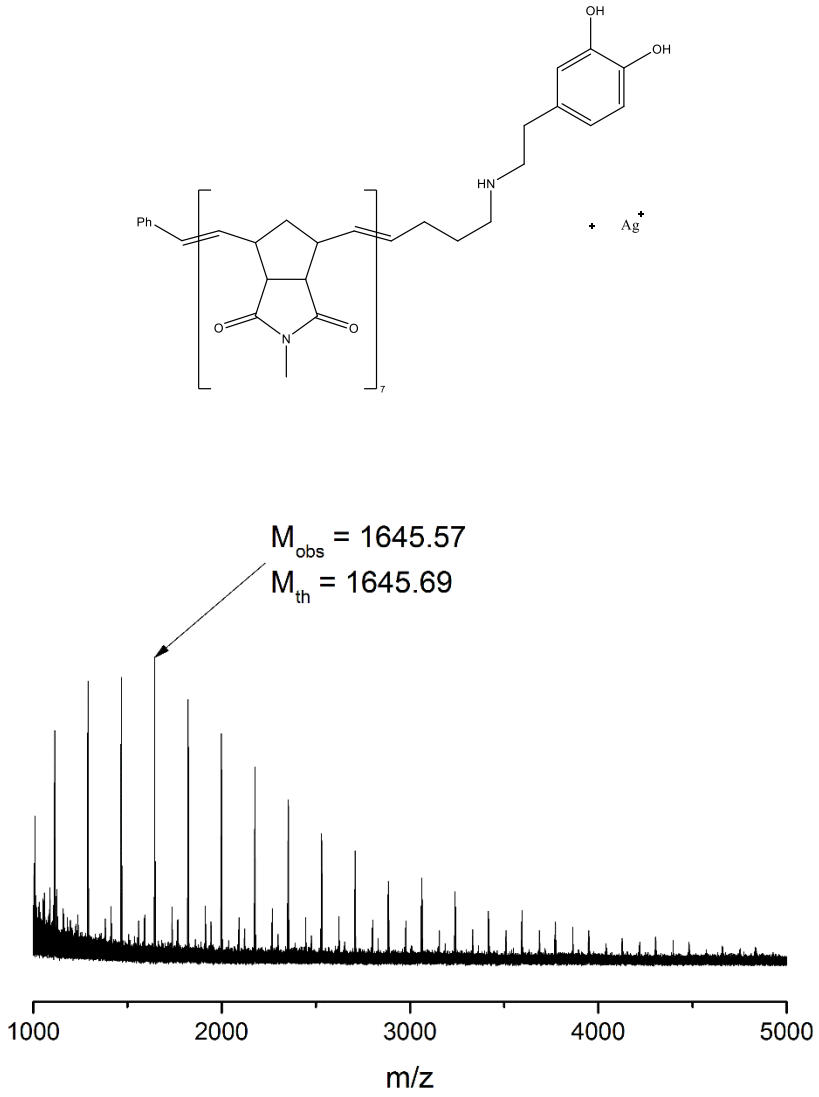

Figure S7. (*top*) Sturcture and (*bottom*) MALDI-TOF spectrum of the catechol end functionalized polymer. However, the catechol is prone to oxidation and degradation is observed within minutes of purification of the polymer.

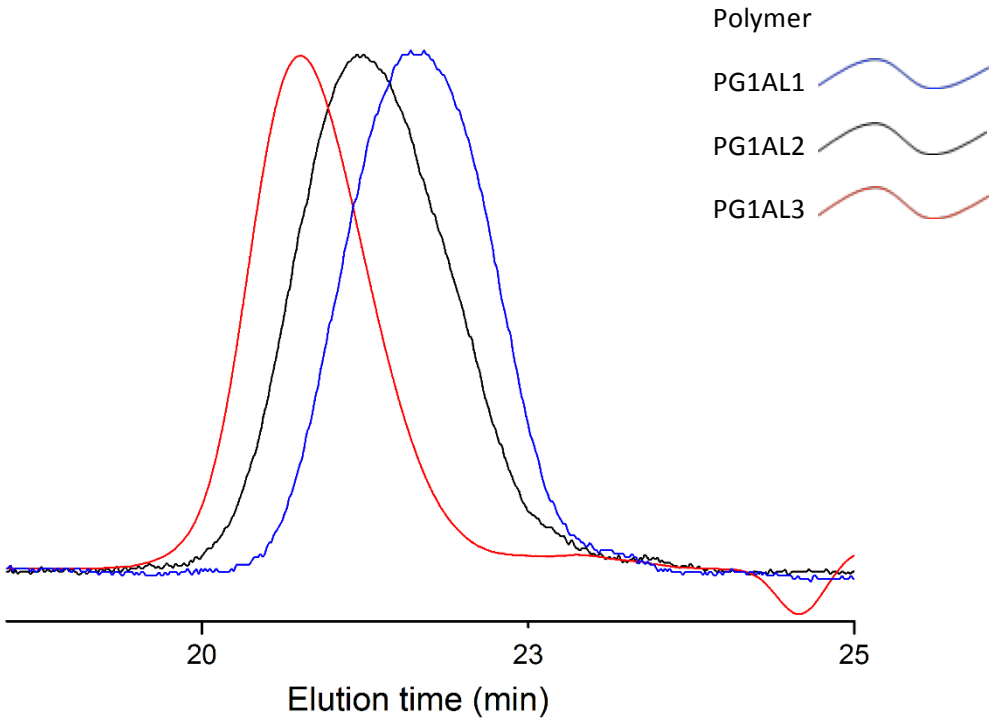

Figure S8 GPC Traces of aldehyde end functional polymers synthesized with **G1**

Polymer code	GPC trace color	Calculated Mol wt	GPC M_w	GPC M_n	PDI
PG1AL1		3500	3644	3012	1.26
PG1AL2		7000	7480	6448	1.20
PG1AL3		15000	16128	14273	1.12

Table S1 GPC analysis of aldehyde end functional polymers synthesized with **G1**

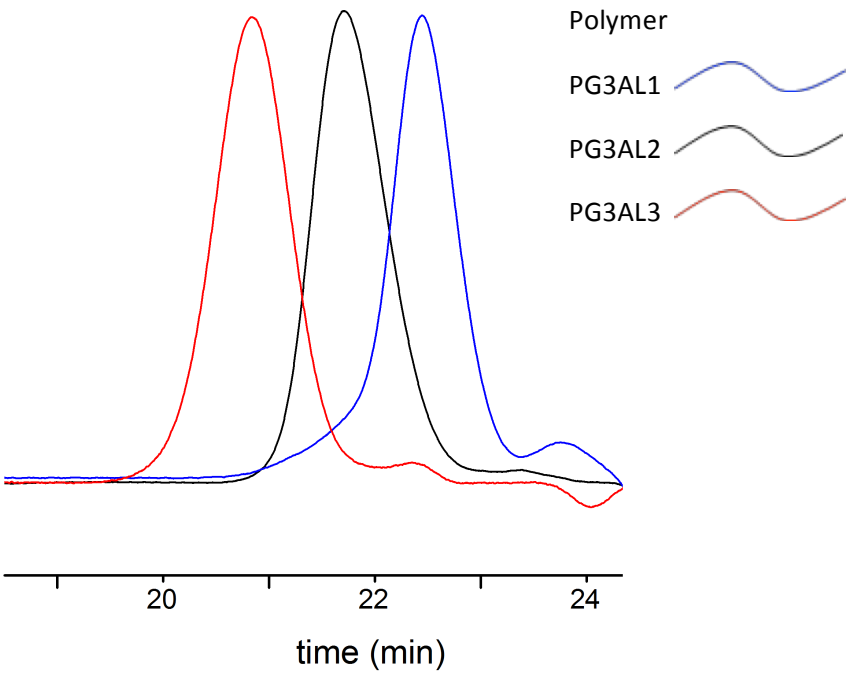

Figure S9 GPC Traces of aldehyde end functional polymers synthesized with **G3**

Polymer code	GPC trace color	Calculated Mol wt	GPC M_w	GPC M_n	PDI
PG3AL1		3500	3602	3188	1.13
PG3AL2		7000	7220	6446	1.12
PG3AL3		15000	15988	14668	1.09

Table S2 GPC analysis of aldehyde end functional polymers synthesized with **G3**

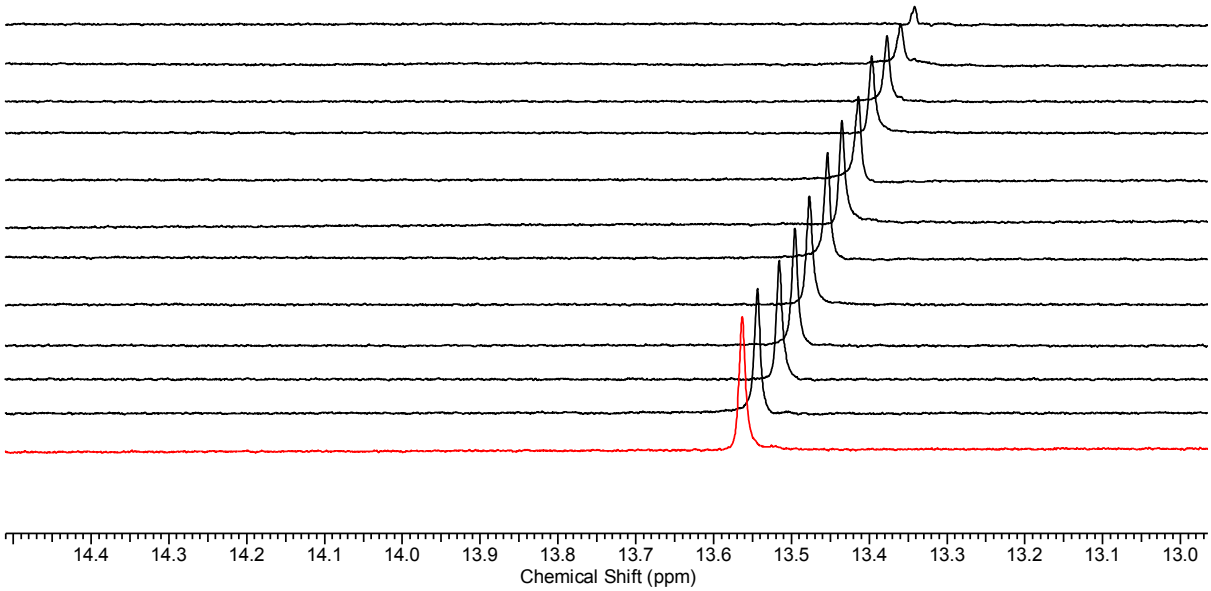

Figure S10 Time resolved ^{1}H-NMR spectra of the degradation of the Fischer carbene with **G3** catalyst. **G3** was reacted with **MNI** for 10min and then 30eq. MDHP was added. The degradation continues for c.a. 7 hours. In this case, the rate constant was 4.012 x 10^{-1} s^{-1} which is similar to the degradation rate constant with **G1**.

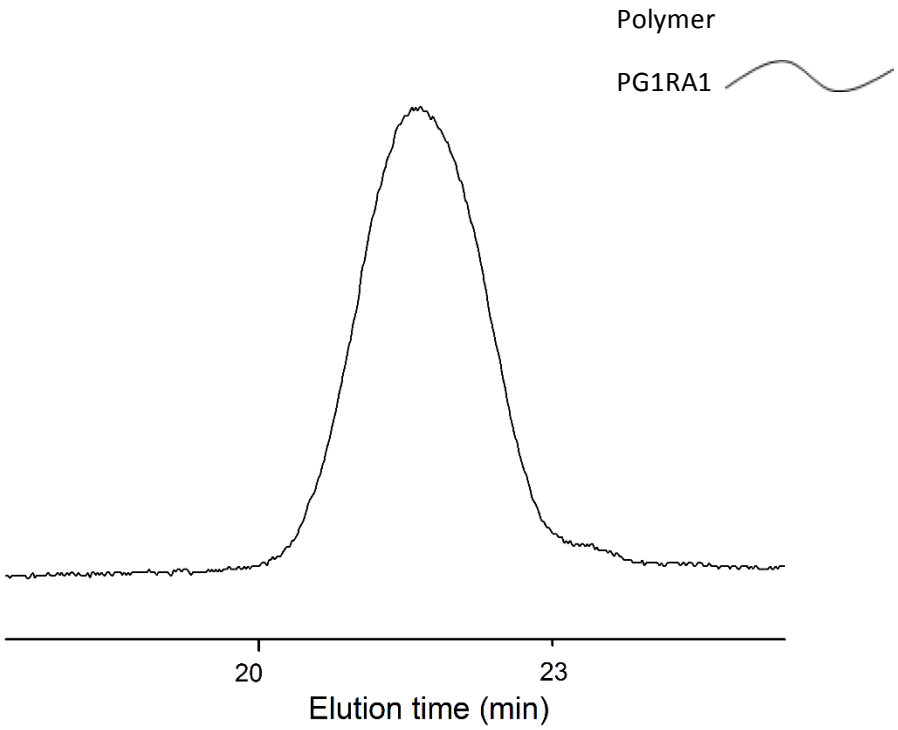

Figure S11 GPC trace of dopamine functionalized polymer

Polymer code	GPC trace color	Calculated Mol wt	GPC M_w	GPC M_n	PDI
PG1RA1		3650	3966	3098	1.28

Table S3 GPC analysis of dopamine end functionalized polymer

Reductive Amination with p-nitroaniline:

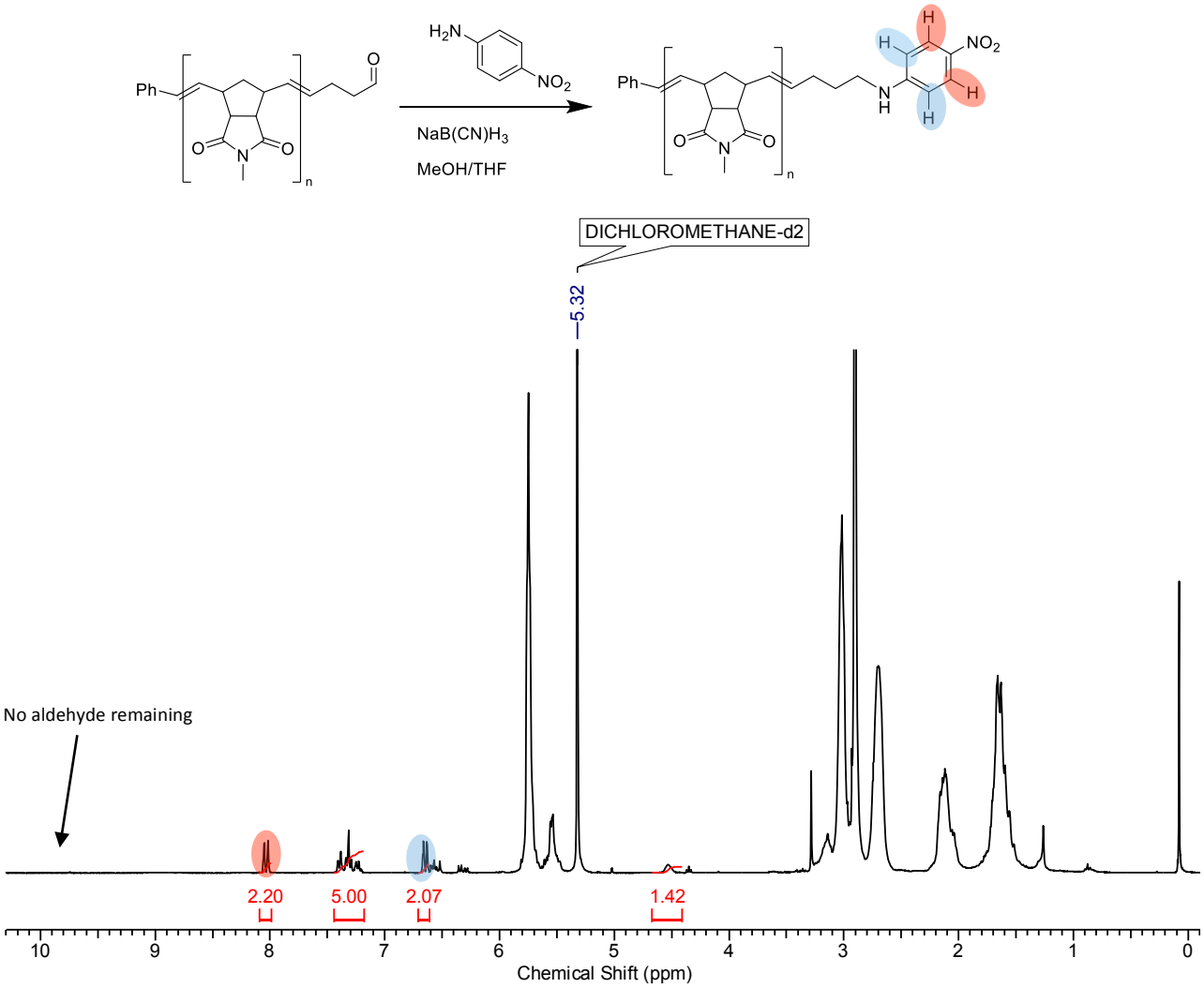

Figure S12. [1]H-NMR of the polymer after reductive amination with p-nitroaniline.

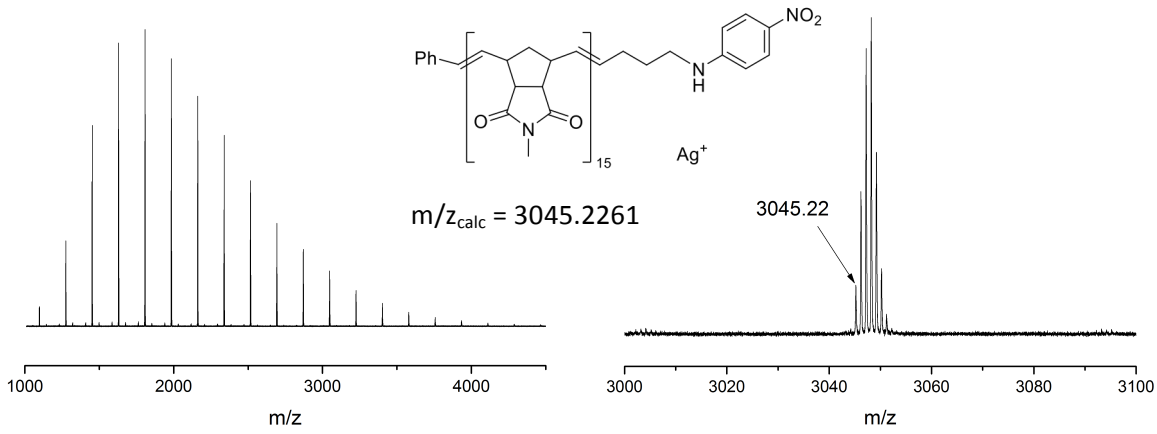

Figure S13. MALDI-ToF spectrum of the polymer after reductive amination with p-nitroaniline.

[1] Nagarkar A. A.; Crochet A.; Fromm K. M.; Kilbinger A. F. M. *Macromolecules*, **2012**, *45*, 4447–4453.
[2] Hyeon T.; Lee S. S.; Park J.; Chung Y.; Na H. B. *J. Am. Chem. Soc.* **2001,** *123,* 12798-12801
[3] Biagini S. C. G.; Davies R. G.; Gibson V. C.; Giles M. R.; Marshall E. L.; North M. *Polymer* **2001**, *42(15)*, 6669-6671