Title “Nitroxide-mediated Polymerization of Styrenic Triarylamines and Chain End Functionalization with a Ruthenium Complex: Towards Tailored Photoredox-active Architectures”

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General Information

Figure 1. Reaction vessel used in kinetic analysis of P6 and P7.

Instrumentations

NMR spectra were recorded on a 250, 300, 400 or 600 MHz NMR spectrometer (Bruker AVANCE) in deuterated solvents at 25 °C. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual solvent signal.[1]

MALDI-ToF MS spectra have been measured on an Ultraflex III TOF/TOF (Bruker Daltonics GmbH) equipped with a Nd:YAG laser and a collision cell. All spectra were measured in the positive reflector mode using dithranol as a matrix.

ESI-Q-TOF-MS measurements were performed with micrOTOF (Bruker Daltonics) mass spectrometer equipped with an automatic syringe pump which is supplied from KD Scientific for sample injection. The mass spectrometer was operating in the positive ion mode. The standard electrospray ion (ESI) source was used to generate the ions. The concentration the polymer sample was 10 µg/mL and it was injected using a constant flow (3 µL/min) of sample solution. The solvent was a dichloromethane/acetonitrile mixture. The ESI-Q-TOF-MS instrument was calibrated in the m/z range 50-3000 using a calibration standard (Tunemix solution) which is supplied from Agilent. All data were processed via Bruker Data Analysis software version 4.0. ESI mass spectra were deconvoluted to obtain singly charged species and this deconvoluted spectrum was utilized to calculate $M_n$ value of the polymer.

Elemental analyses were carried out on a λ EuroVector EuroEA3000 elemental analyzer.

Electrochemical measurements were performed on a Metrohm Autolab PGSTAT30 potentiostat with a standard three-electrode configuration using a graphite-disk working electrode, a platinum-rod auxiliary electrode and an Ag/AgCl reference electrode; scan
rates from 20 to 1,000 mV/s were applied. The experiments were carried out in
degassed solvent (spectroscopy grade) containing tetra-n-butylammonium
hexafluorophosphate salt (0.1 M). Ferrocene (Fc) was added at the end of each
experiment as an internal standard. The potentials are quoted vs. the Fc/Fc⁺ couple.

GC-MS measurements were performed on the Shimadzu GCMS-2010 (carrier gas:
he; detector: mass spectrometer; column: Ultra Alloy Capillary Column UAC-5
(30 m length, 0.25 mm inner diameter, 0.25 µm film thickness, (5% phenyl)
methylpolysiloxane)). GC spectra were measured on the Shimadzu GC-2010 (carrier
gas: helium; detector: flame ionization with hydrogen and air as detector gases; column:
Restek Rtx-5 (30 m length, 0.25 mm inner diameter, 0.25 µm film thickness, 5%
diphenyl polysiloxane 95% dimethyl polysiloxane)).

Size-exclusion chromatography results were obtained by two different systems:
1.) Waters system (degasser: DG-980-50, pump: HPLC 1515, oven: Column Heater
1500, UV/Vis-detector: PDA detector 2996, RI-detector: RID 2414, eluent: DMAc +
0.08% NH₄PF₆, flow rate: 1 mL/min, temperature: 50 °C, column: Waters pre/Phenomenex Phenogel 103 Å/105 Å, separation range: 1,000 to 1,000,000 g/mol).
2.) Shimadzu system (controller: SCL-10A VP, degasser: DGU-14A, pump: LC-10AD
VP, auto sampler: SIL-10AD VP, oven: Techlab, UV-detector: SPD-10AD VP, RI-
detector: RID-10A, eluent: chloroform/iso-propanol/TEA [94:2:4], flow rate: 1 mL/min,
temperature: 40 °C, column: PSS SDV pre/lin S, separation range: 100 to
150,000 g/mol).
3.) Agilent 1200 series (degasser: PSS, pump: G1310A, autosampler: G1329A, oven:
Techlab, DAD detector: G1315D, RI-detector: G1362A, eluent DMAc + 0.21 % LiCl,
flow-rate 1 mL/min, 40°C PSS GRAM guard/1000/30 Å, 10 µm particle size).

Flash column chromatography was conducted on a Biotage Isolera One System using
Biotage SNAP Cartridges KP-Sil and a UV/Vis detector. Microwave reactions were
performed in the Biotage Initiator Sixty Microwave synthesizer.
NMR spectra

Figure 2. $^1$H NMR (300 MHz CDCl$_3$) of 1.

Figure 3. $^{13}$C NMR (75 MHz CDCl$_3$) of 1.
Figure 4. COSY of 1.

Figure 5. HSQC of 1.
Figure 6. $^1$H NMR (400 MHz, CDCl$_3$) of 2.

Figure 7. $^{13}$C NMR (100 MHz, CDCl$_3$) of 2.
Figure 8. COSY of 2.

Figure 9. HSQC of 2.
Figure 10. $^1$H NMR (300 MHz, CDCl$_3$) of 3.

Figure 11. $^{13}$C NMR (75 MHz, CDCl$_3$) of 3.
Figure 12. COSY of 3.

Figure 13. HSQC of 3.
Figure 14. $^1$H NMR (300 MHz, CDCl$_3$) after UV-exposure of 3.

Figure 15. $^1$H (400 MHz, CDCl$_3$) of MAA-SG1.
Figure 16. $^1\text{H}$ NMR of MAA-SG1 without P-decoupling (top), and with P-decoupling (bottom).

Figure 17. $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$) of MAA-SG1.
Figure 18. COSY of MAA-SG1.

Figure 19. P-H HMBC of MAA-SG1.
Figure 20. HSQC of MAA-SG1.

Figure 21. $^1$H NMR (300 MHz, CDCl$_3$) of CMSt-TIPNO.
Figure 22. $^{13}$C NMR (75 MHz, CDCl$_3$) of CMSt-TIPNO.

Figure 23. COSY of CMSt-TIPNO.
Figure 24. HSQC of CMSt-TIPNO.

Figure 25. HSQC of CMSt-TIPNO (aliphatic region).
Figure 26. $^1$H NMR (250 MHz, CD$_3$CN) of 4.

Figure 27. $^{13}$C NMR (63 MHz, CD$_3$CN) of 4.
Figure 28. COSY of 4.

Figure 29. HSQC of 4.
Figure 30. $^1$H NMR (CDCl$_3$, 400 MHz) of P5 (top) and aliphatic region (bottom).

Figure 31. Complete $^1$H NMR spectra of P6.
Figure 32. $^1$H NMR (CDCl$_3$, 300 MHz) of initiator (top) and purified P6 (bottom). Selected protons of the two diastereoisomers (white and grey box) are depicted, vertical dashed lines indicate the corresponding signals in the polymers.
Mass spectra

Figure 33. Proposed structure of photo-dimer of 3.

Figure 34. EI-MS of photodimer of 3.
Figure 35 MALDI-ToF data of P6: (top, matrix: dithranol) MS with cut off at 1200, selected MS-MS traces with the molar mass of the precursor ions.

Figure 36. Inset of the MS-MS of P6.
Figure 37. MALDI-ToF data of Ru-PF6: (top, matrix: dithranol) MS spectrum, and (bottom) MS/MS spectrum of a selected specimen (vertical arrow).

Figure 38. ESI-ToF data of Ru-P6: (top) MS spectrum, and (bottom traces) MS/MS spectra of selected species with given parent ion masses.

m/z

Ru-P6

1348
1497
1647
1797
1947
2097

m/z
Figure 39. Inset of ESI MS/MS of Ru-P6.

Figure 40. Expansion of representative species from ESI-ToF MS/MS data of Ru-P6: (left) experimental (a) and simulated isotope pattern (b) of the allyl-fragment, (right) experimental (a) and simulated isotope pattern (b) of the complex fragment (4-H⁺).
Figure 41. Normalized SEC traces (UV-detection at 342 nm; CHCl₃, iso-propanol, triethylamine 94/2/4) of P6 applying PS-calibration.

Figure 42. Inset of normalized SEC traces (UV-detection at 342 nm; CHCl₃, iso-propanol, triethylamine 94/2/4) of P6 applying PS-calibration.
Figure 43. Linear plot of $\ln(M_0/M_t)$ vs. time of P5-P7.

Figure 44. 3D SEC data (wavelength vs. elution time) DMAc + 0.8% NH$_4$PF$_6$ of crude P6 prior modification.
Figure 45. 3D SEC data (wavelength vs. elution time, DMAc + 0.8% NH₄PF₆) plot of complex 4.