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POLYSTYRENE WITH CONTROLLED MOLECULAR WEIGHT VIA PHOTOINDUCED REVERSIBLE-DEACTIVATION RADICAL POLYMERIZATIONS

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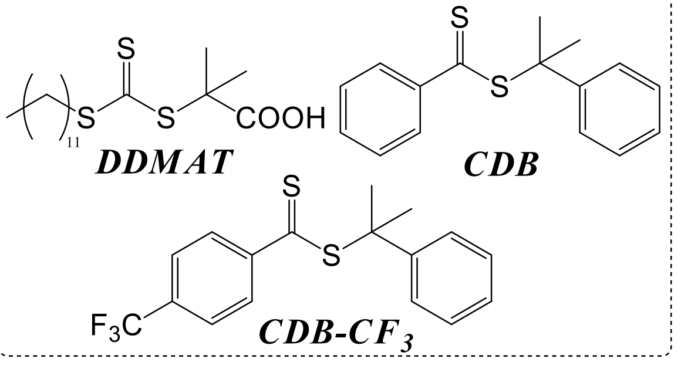
Introduction

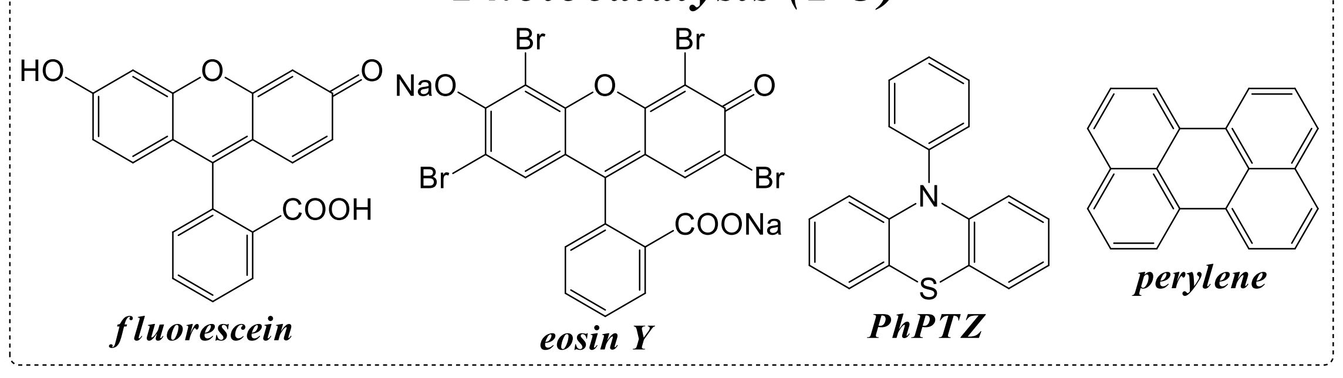
Photoinduced electron/energy transfer (PET) reversible addition-fragmentation chain transfer (RAFT) technique, which employs photoredox catalysis in conjunction with controlled radical polymerization process, offers a range of advantages over conventional polymerization. It provides enhanced control over the polymerization process by varying light wavelength and intensity, allows to easily "switch on" and "switch off" polymerization, while also being environmentally friendly. PET-RAFT process has been thoroughly investigated for the polymerization of acrylates, methacrylates and acrylamides, while comparatively less attention has been devoted to polymerization of styrene. This method can provide powerful tools for the synthesis of well-defined polymers and copolymers of styrene with desired molecular weight, composition, architectures and properties.

Reagents Used

Chain transfer agents (CTA)

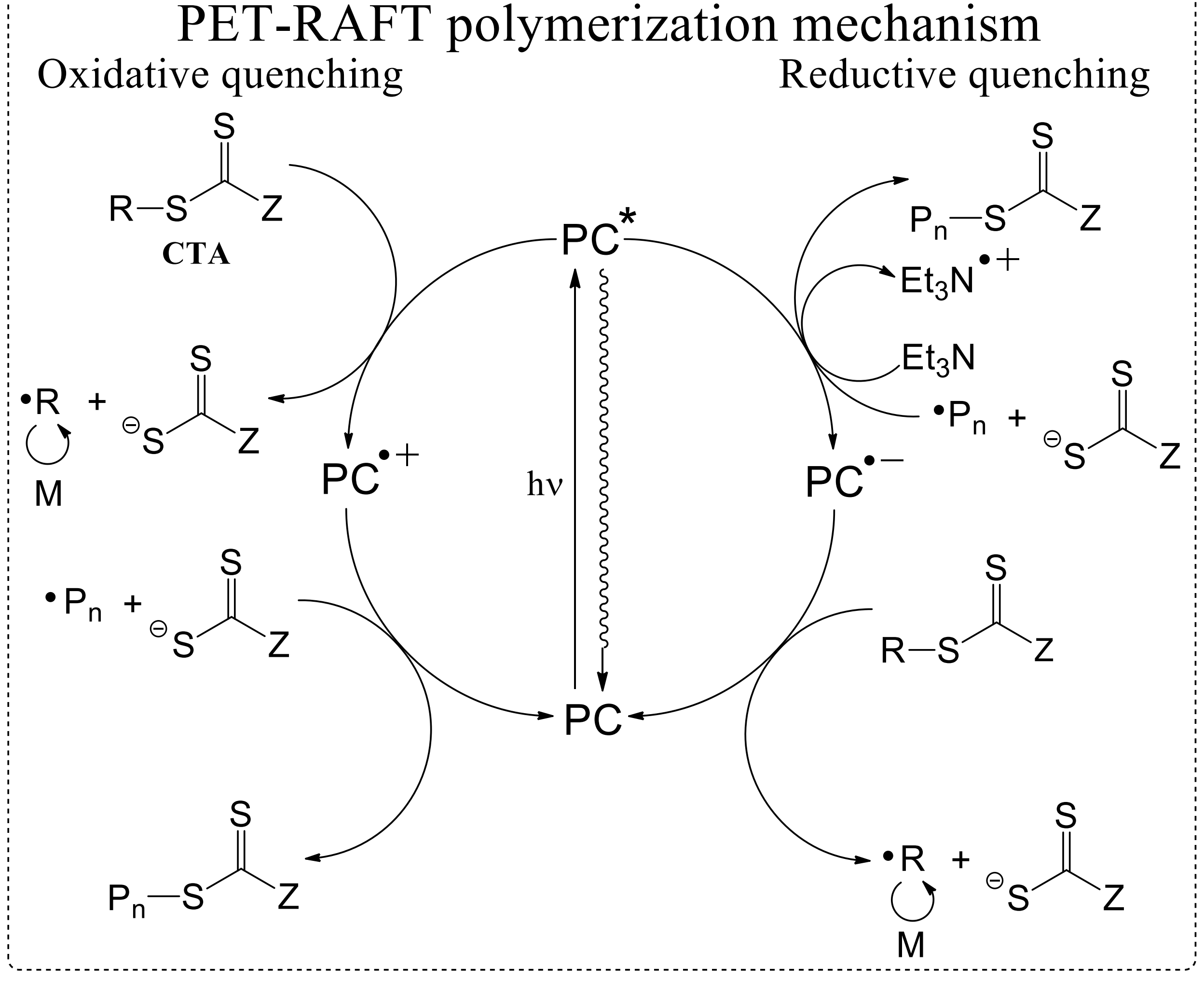


Photocatalysts (PC)

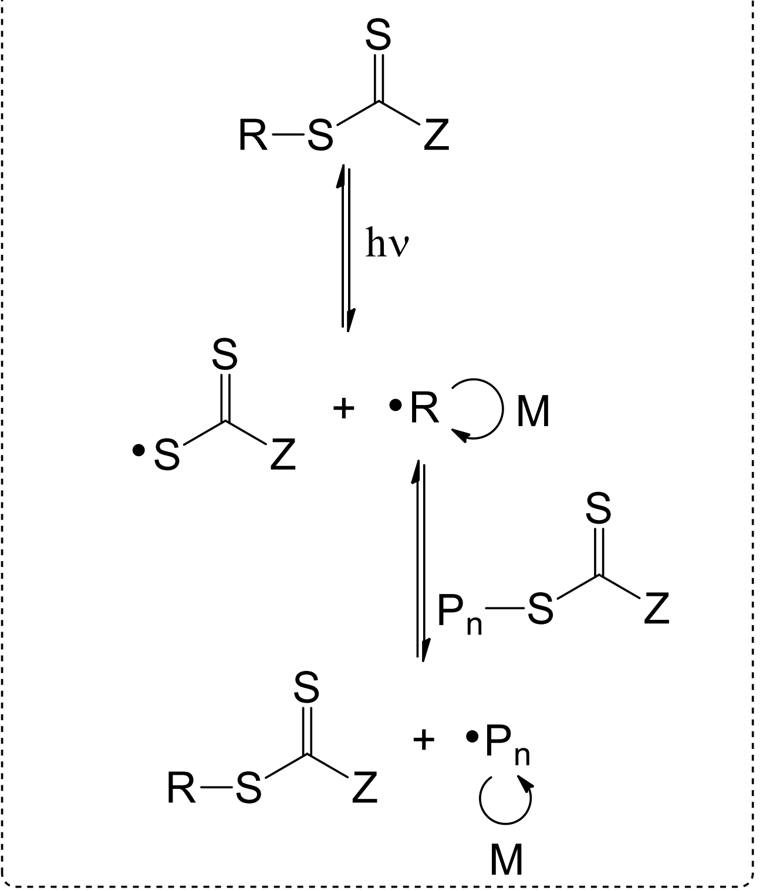


Mechanism

PET-RAFT polymerization mechanism



Photoiniferter/RAFT



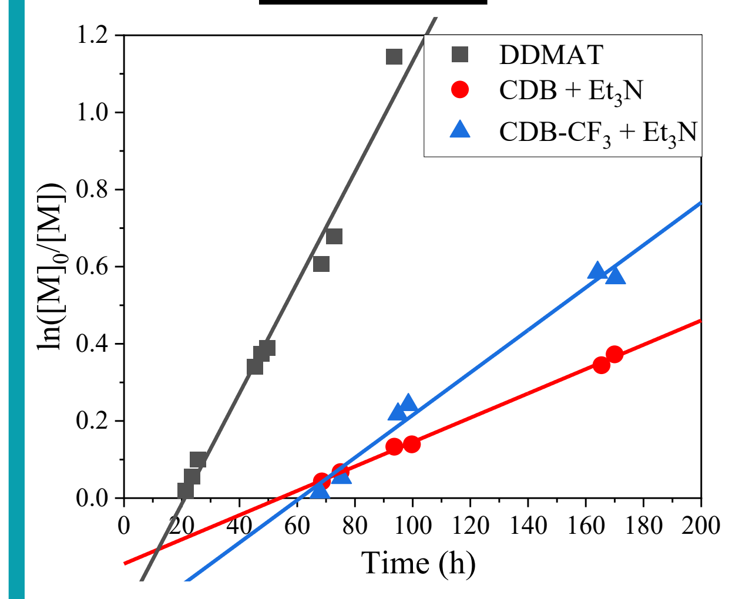
CTA - reversible chain transfer agent
PC - photocatalyst
M - monomer (styrene)
P_n - propagating chains

Selection of Efficient Photoinitiating System

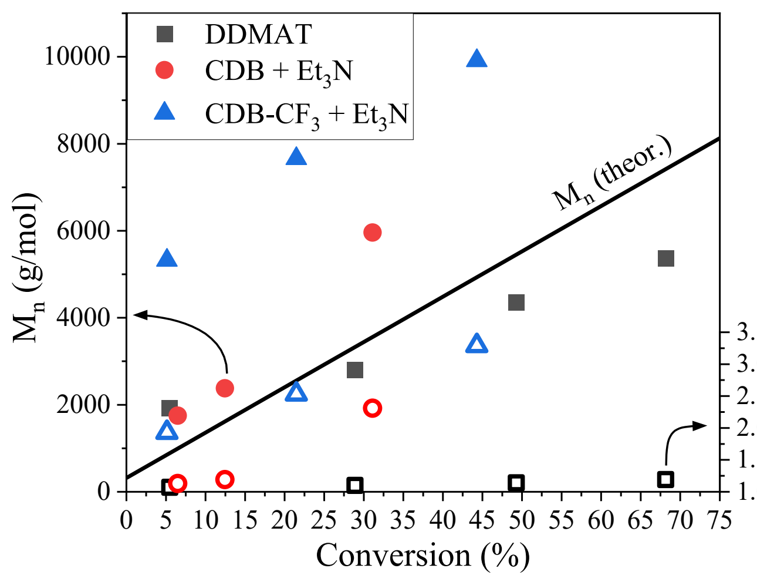
Polymerization conditions: [M]:[CTA]:[PC] = 1000:10:1 (in presence of Et_3N, [PC]:[Et_3N] = 1:20), [M] = 4.7 M, blue light irradiation (λ_{max} = 435 nm, 3.9 mW/cm^2), r.t.

1) Selection of reversible chain transfer agent (with fluorescein as PC)

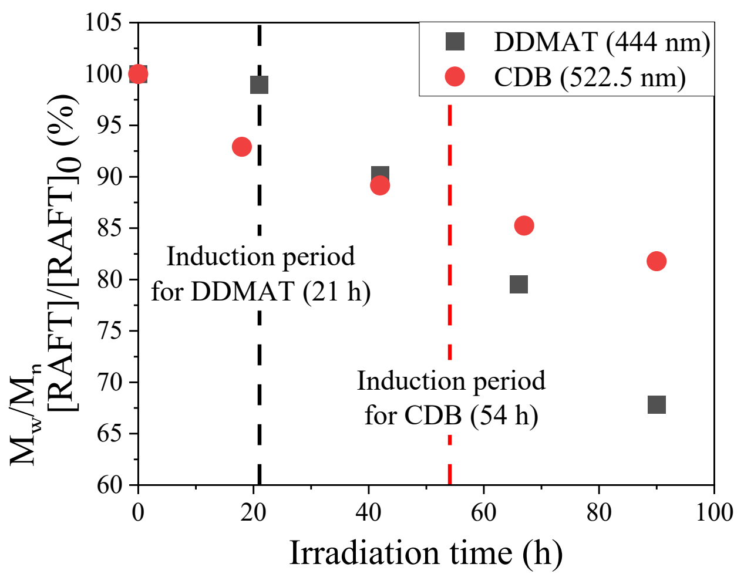
Kinetics



M_n vs Conversion



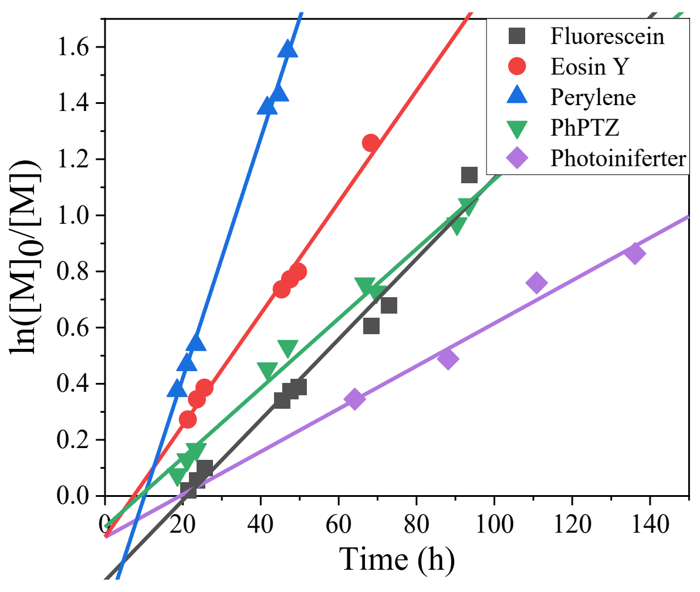
Photodegradation



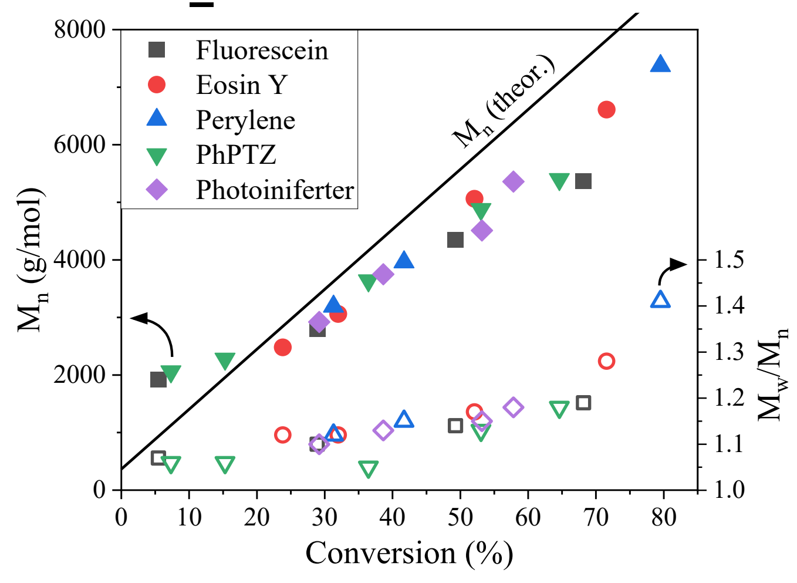
- PET-RAFT polymerization with ***DDMAT*** occurs through oxidative quenching cycle; with ***CDB*** and ***CDB-CF$_3$*** – only in presence of Et_3N through reductive quenching cycle
- Photodegradation of ***CDB*** before polymerization start (due to long induction period) can lead to low efficiency of corresponding photoinitiating system
- Low efficiency of photoinitiating systems with ***CDB*** and ***CDB-CF$_3$*** results in M_n(GPC) >> M_n(theor.)

2) Selection of photocatalyst (with DDMAT as CTA)

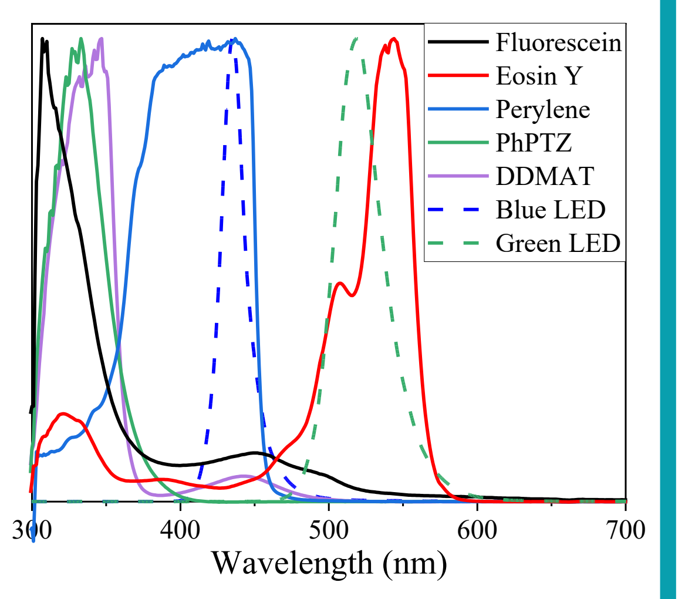
Kinetics



M_n vs Conversion



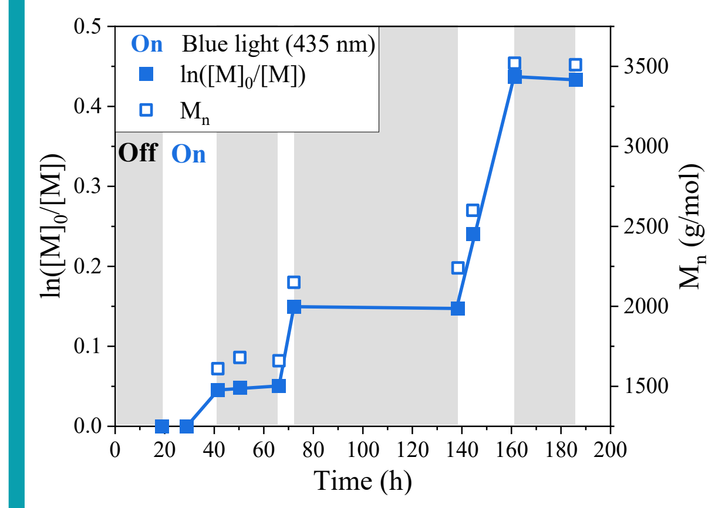
Absorbance



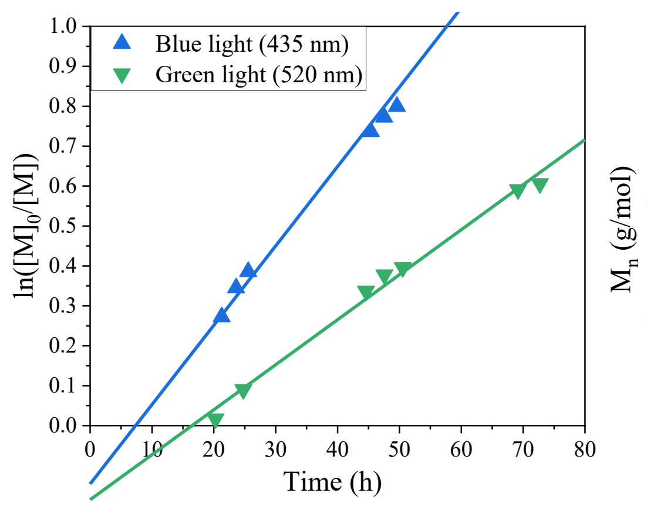
- The most effective photocatalysts – ***perylene*** and ***eosin Y***
- ***Perylene*** is effective due to intensive absorption of blue LED emission; ***eosin Y*** – due to low quantum yield of fluorescence and long lifetime of the excited state
- Photocatalyst nature has almost no effect on the conversion dependence of the molecular weight characteristics
- ***Eosin Y*** absorbs green light, enabling the polymerization under green light irradiation

DDMAT/Eosin Y Photoinitiating System

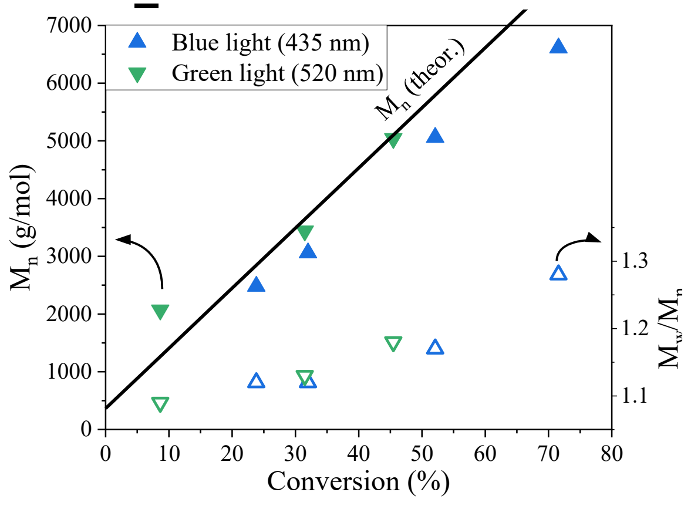
On/Off Experiment



Kinetics

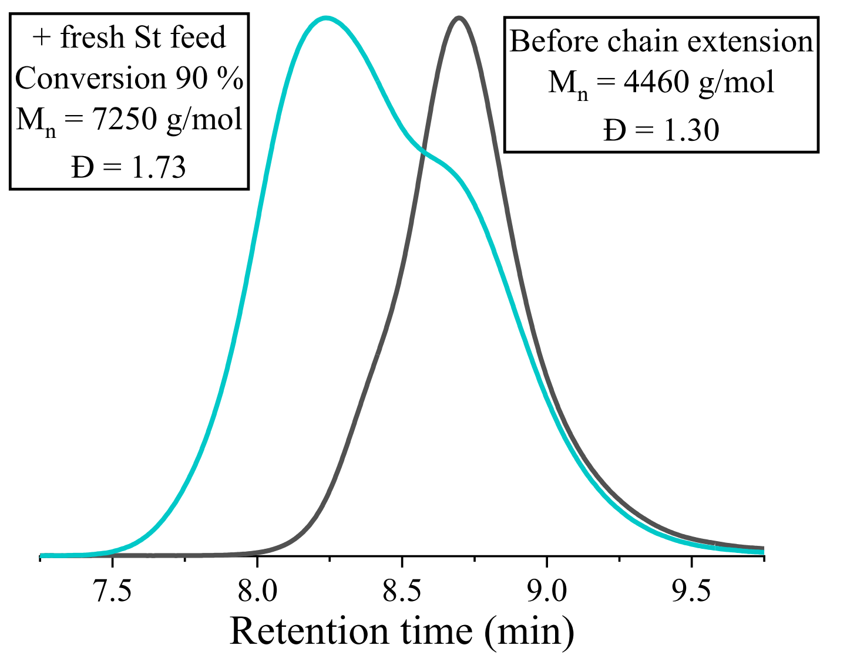


M_n vs Conversion



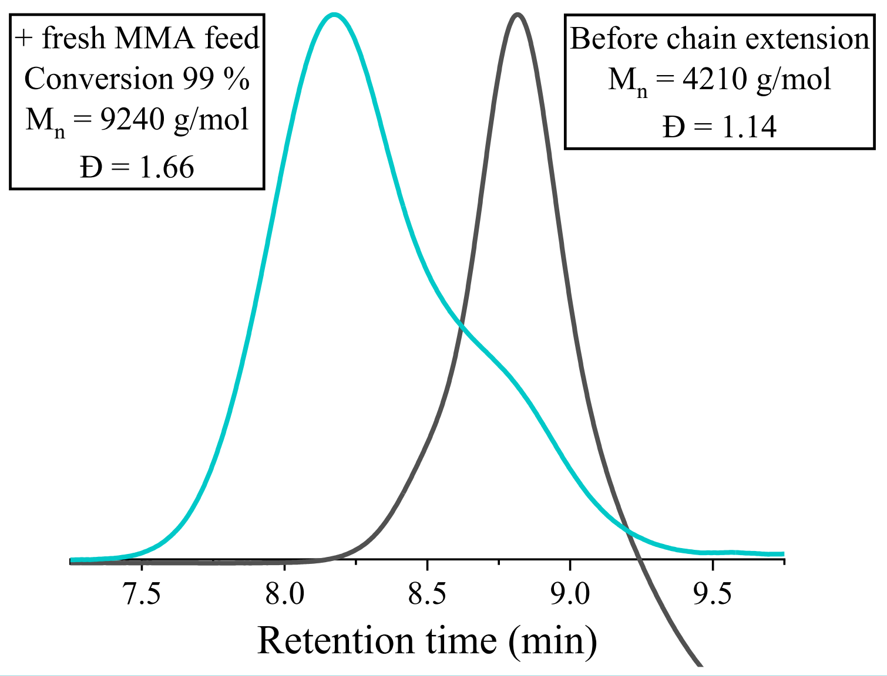
- It is possible to "switch on" and "switch off" the polymerization
- Polymerization under green light irradiation is slower due to absence of photoiniferter/RAFT process
- Absence of photoiniferter process results in a better control of molecular weights

GPC Traces of Chain Extension Experiment



+ fresh St feed
Conversion 90 %
M_n = 7250 g/mol
Đ = 1.73

Before chain extension
M_n = 4460 g/mol
Đ = 1.30

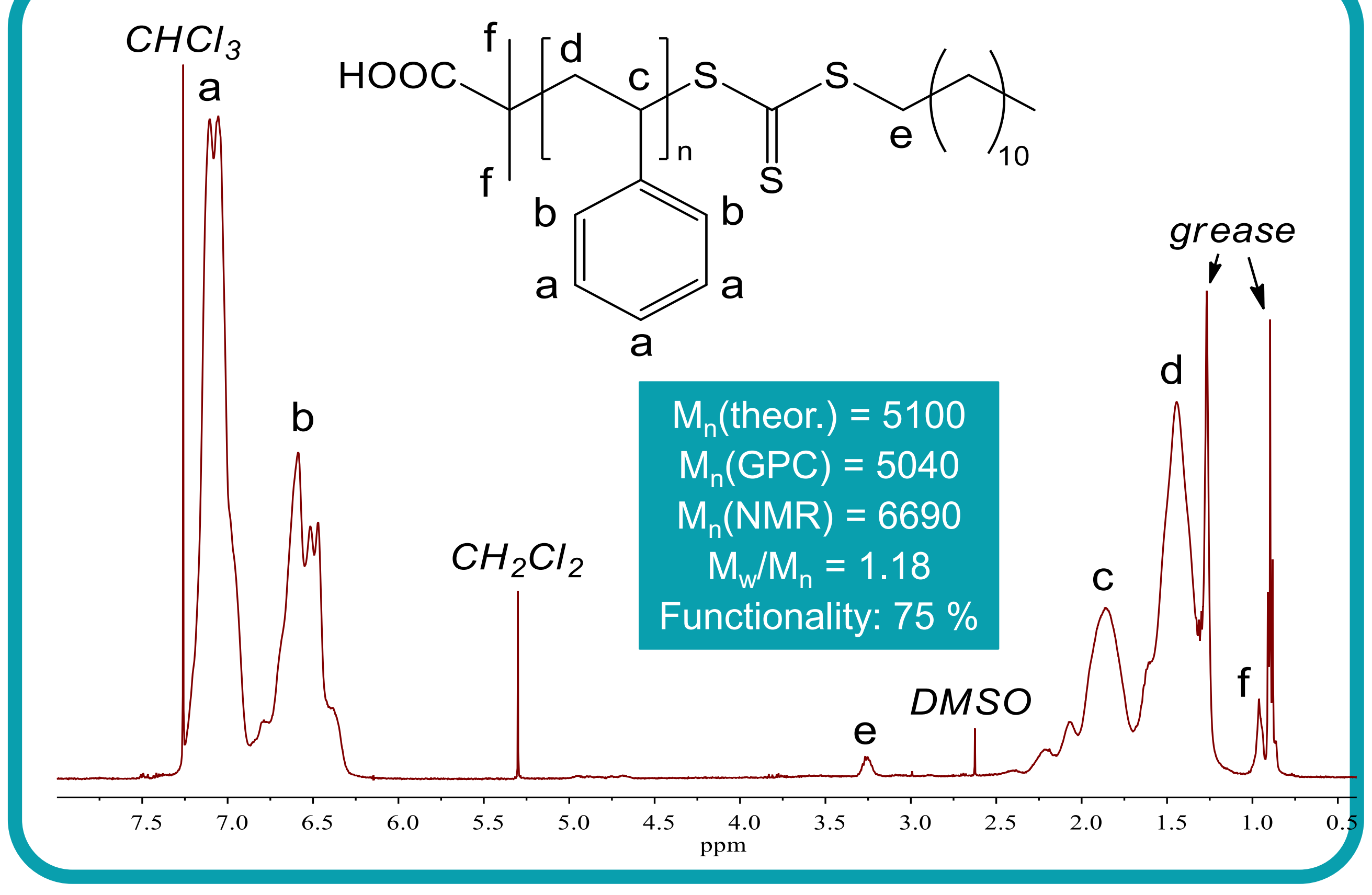


+ fresh MMA feed
Conversion 99 %
M_n = 9240 g/mol
Đ = 1.66

Before chain extension
M_n = 4210 g/mol
Đ = 1.14

- Terminal trithiocarbonate groups allows to continue the polymerization with new monomer portions
- Chain extension enables a substantial increase in molecular weights
- An increase in polydispersity may be associated with a gradual loss of terminal functionality due to its photodegradation and chain transfer processes

^{1}H NMR of PSt Obtained



M_n(theor.) = 5100
M_n(GPC) = 5040
M_n(NMR) = 6690
M_w/M_n = 1.18
Functionality: 75 %

Acknowledgments

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