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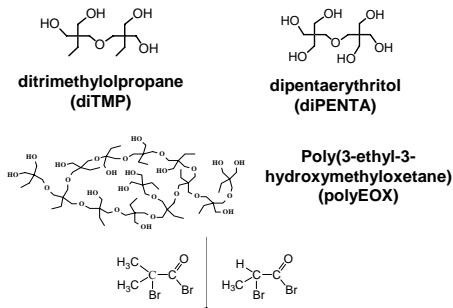
## Introduction

During the last several years Atom Transfer Radical Polymerization (ATRP) was successfully used by Polymer Chemistry Group of the Polymer Centre DTU to the synthesis of new functional homo and block copolymers. Recently this method has been extended further to include multifunctional initiators that would provide principally spherical growth to form star-shaped polymers.

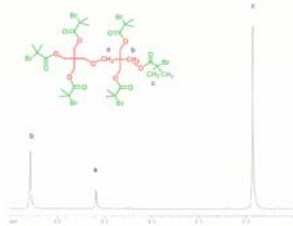
## Results

### Synthesis of multifunctional initiators (MI)

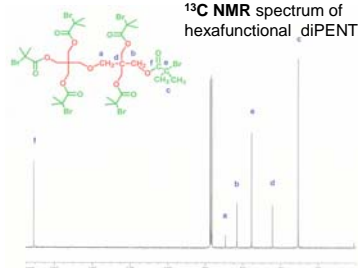
Multifunctional initiators were synthesized from polyols and bromoisobutryl or 2-bromopropionyl bromide.



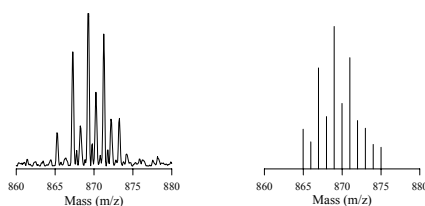
<sup>1</sup>H NMR spectrum of hexafunctional diPENTA-Br



<sup>13</sup>C NMR spectrum of hexafunctional diPENTA-Br

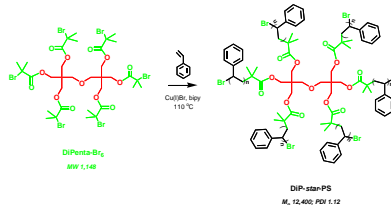


**MALDI TOF** analysis of tetrafunctional diTMP-Br (recorded and simulated spectra of fully functionalized MI)

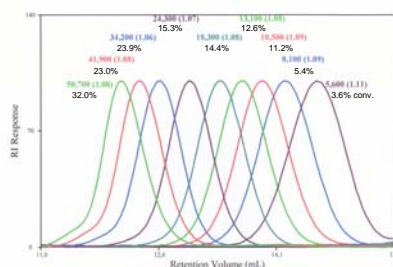


### ATRP of styrene and acrylates

Polymerization of styrene and acrylates (methyl, butyl and hexyl) resulted in star polymers with expected molecular weights and relatively narrow polydispersities.



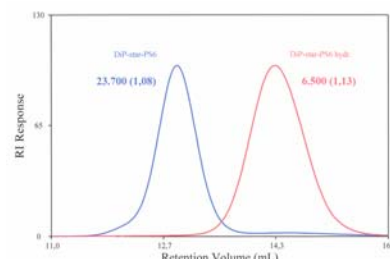
**KINETIC (SEC)** of ATRP of styrene with diPENTA-Br (MI)  
(bulk; [M]<sub>0</sub>/[MI]<sub>0</sub> = 2180)



Initiator	Conditions	Conv. %	M <sub>n</sub> SEC	PDI	M <sub>n</sub> calcd
Styrene					
diTMP-Br	Bulk, 110°, 5h	6.05	16 000	1.08	13 760
	Bulk, 110°, 5h	9.6	21 000	1.07	21 840
diTMP-Br	xylene, 110°, 1h	traces	2 690	1.09	
diPENTA-Br	Bulk, 110°, 5h	7.5	19 300	1.08	17 060
pEOX-Br(90)	Bulk, 110°, 5h	14.9	34 700	1.17	35 680
pEOX-Br(50)	xylene, 110°, 21h	47.4	35 000	1.23	25 370

Initiator	Conditions	Conv. %	M <sub>n</sub> SEC	PDI	M <sub>n</sub> calcd
Methyl acrylate					
diPENTA-Br	Xylene, 80°, 20h	50	51 400 (28 100)	1.22 (1.84)	56 900 (33 400)
pEOX-Br(90)	Xylene, 60°, 26h	27	8 570	1.41	15 250
pEOX-Br(90)	Bulk, 80°, 3h		5 170	1.21	
pEOX-Br(50)	xylene, 80°, 5.5h	82	25 900	1.19	30 900
Butyl acrylate					
pEOX-Br(90)	xylene, 80°, 20h	38	21 000	1.19	20 900
Hexyl acrylate					
pEOX-Br(90)	xylene, 80°, 19h	30	14 200	1.18	15 210

**HYDROLYSIS** of diPENTA-star-PS polymer (KOH, THF/acetone, reflux 20h)



## Conclusions

- Multifunctional initiators for ATRP were prepared by esterification of polyols with bromoisobutryl or 2-bromopropionyl bromide and were well characterized by spectroscopic methods.
- Four, six and 12 - arm star polymers with expected molecular weights and low polydispersities were obtained by ATRP of styrene and acrylates (methyl, butyl and hexyl).
- ATRP of styrene underwent fast in a controlled manner.
- Expected star shape (and the efficiency of the initiating MI) was confirmed by the hydrolysis of hexaarm-star-polystyrene.
- Not fully functionalized polymeric macroinitiator (polyEOX-Br) may be used for preparation of miktoarm stars by combination of radical (ATRP) and ionic polymerization started from the remaining -OH groups.

## References

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