Reversibly Crosslinked Block Copolyether Micelles by Bisborane Catalyzed Anionic Ring Opening Polymerization of Glycidyl Ethers

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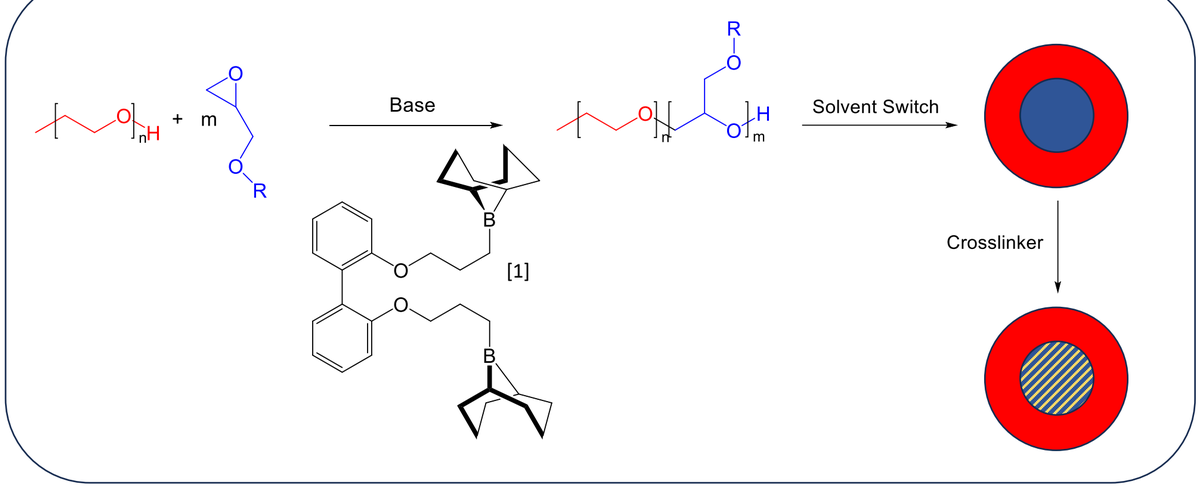
Motivation

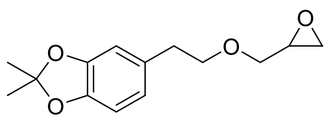
Functionalized block copolymers are a highly useful class of macromolecules due to their ability to form separated nanostructures in bulk and in solution. These make them suitable for application in surface coating, as nanoporous membranes, micellar nanocarriers or templates for mesoporous materials. Using commercially available **PEG**s as a macroinitiator for **AROP** with functionalized glycidyl ethers (GE) is a simple method of producing amphiphilic block copolymers with varying functional groups. However, if the steric or solubility characteristics of the monomer lead to reduced accessibility of the active chain end, sufficient degrees of polymerization can become difficult to achieve.

Organometallic monomer activating agents such as triethyl borane (**TEB**) can be used as a simple additive to increase the reactivity of GEs in AROP by withdrawing electron density from the epoxide ring by interaction with the lone electron pairs on the oxygen. However, with increasing chain lengths, the portion of TEB which interacts with the backbone instead of the monomer increases. By anchoring an additional borane moiety to the active chain end due to its negative charge, a bisborane catalyst can avoid this drawback and enable significantly higher degrees of polymerization for problematic monomers.

Core-crosslinked micelles

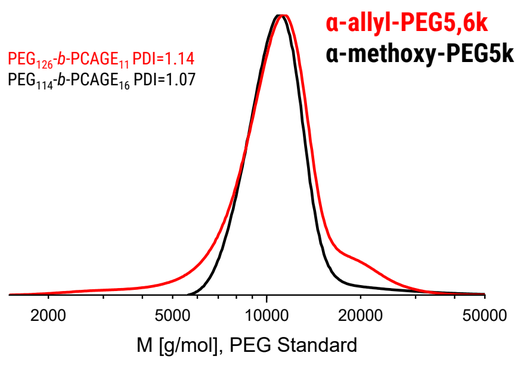


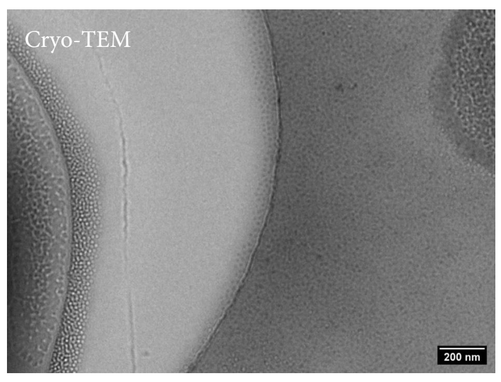
pH-sensitive reversible core-crosslinking



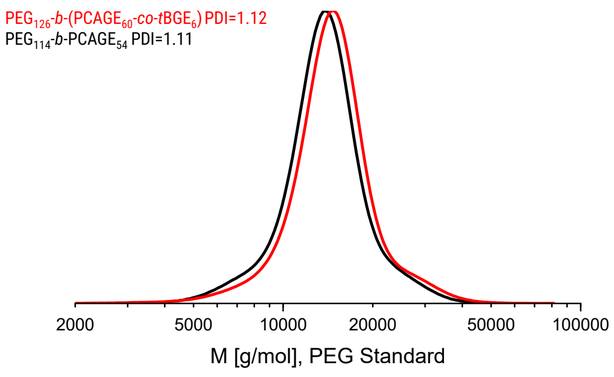
Catechol Acetonide Glycidyl Ether (**CAGE**)
- pH-dependent reversible **crosslinking**
- **Surface coating** *via* catechol adhesion

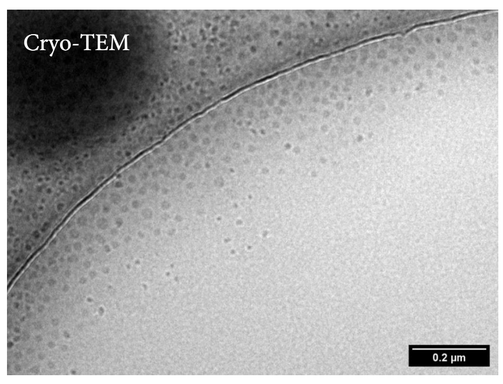
Polymerization with **TEB** -> DP limited to ≈20



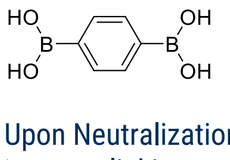


Polymerization with **Bisborane** -> DP exceeding 50

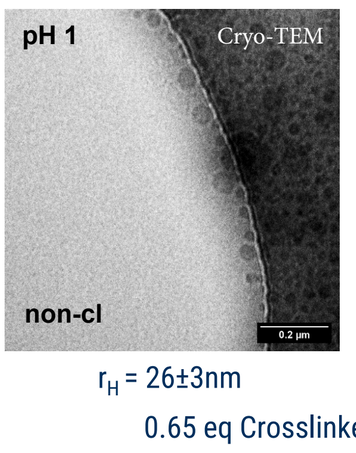


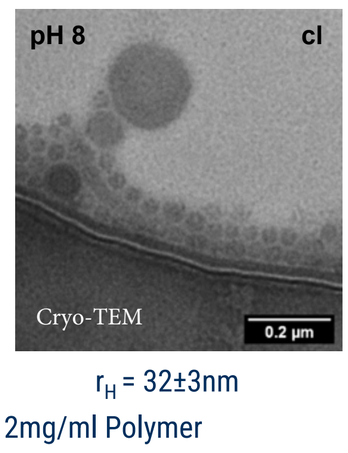


Crosslinker



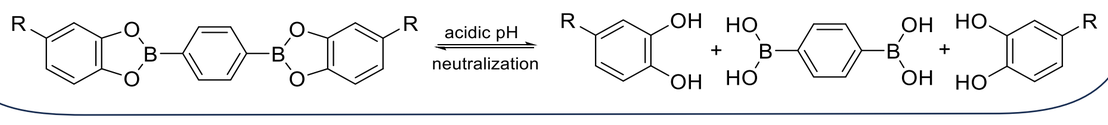
Upon Neutralization
- crosslinking
- swelling



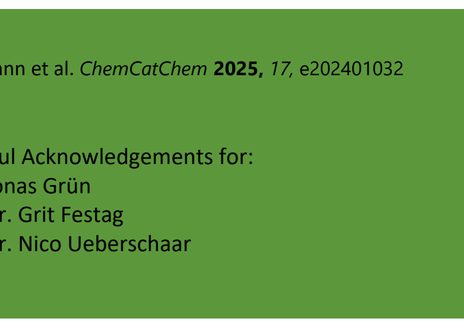


r_H = 26±3nm r_H = 32±3nm

0.65 eq Crosslinker, 2mg/ml Polymer



High-MW crosslinkable blockcopolyethers

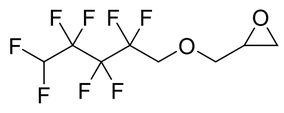


Crosslinker

DTME

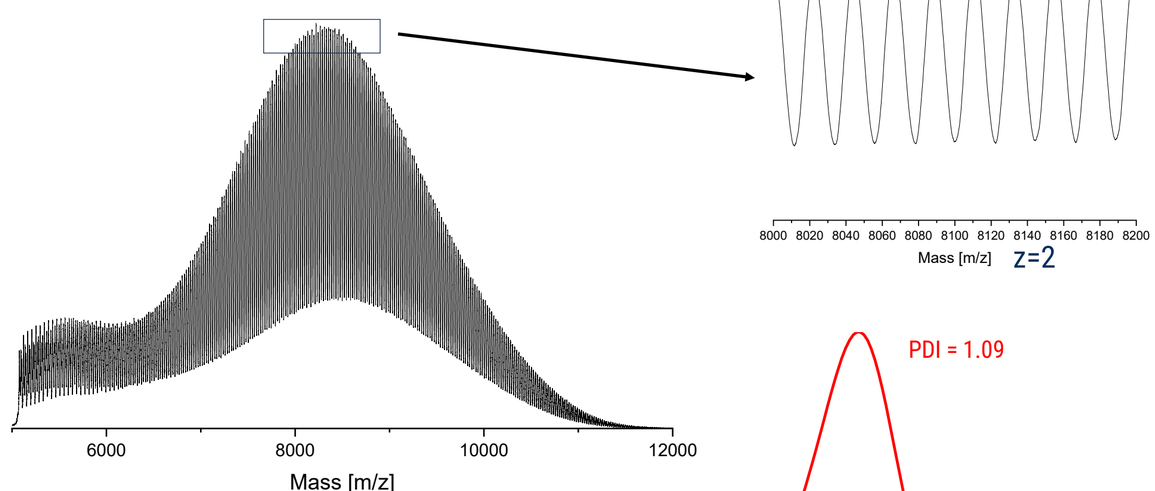
Reversible by reduction of disulfide

Fluorophilic polymer blocks



Glycidyl-octafluorpentylether (**GOFPE**)
- **Fluorophilic** polymer sections
- Commercially available
- AROP homopolymerization not published

mPEG5k, 100eq. GOFPE, 2eq. bisborane



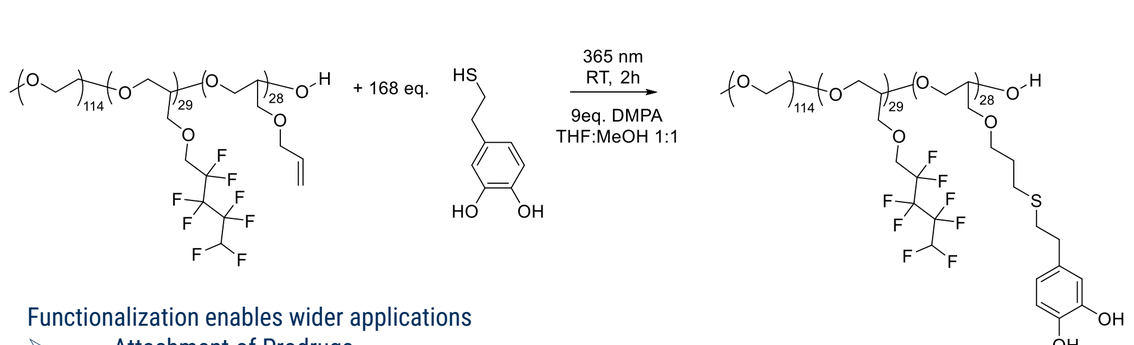
MALDI-ToF: DP = 35-40

Copolymerizations

Eq. GOFPE	Comonomer	M_n [kg/mol][a]	Formula[a]	PDI[b]
50	50eq. AGE	16.5	$mPEG_{114}$-*b*-P($GOFPE_{29}$-*co*-AGE_{28})	1.14
70	30eq. FGE	18.2	$mPEG_{114}$-*b*-P($GOFPE_{39}$-*co*-FGE_{13})	1.17

a) as determined by ^{1}H-NMR (300 MHz, $CDCl_3$), b) as determined by SEC (THF, PEG standards)

Functionalization by Thiol-en Click

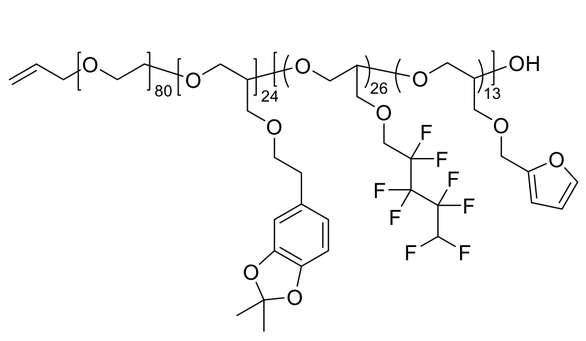


Functionalization enables wider applications
- Attachment of Prodrugs
- Surface coating
- Different crossliking mechanisms

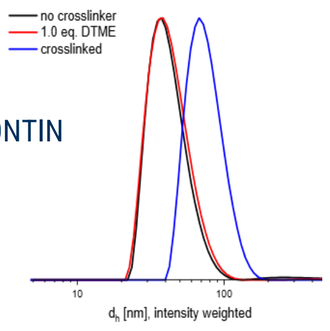
Triblock copolymers

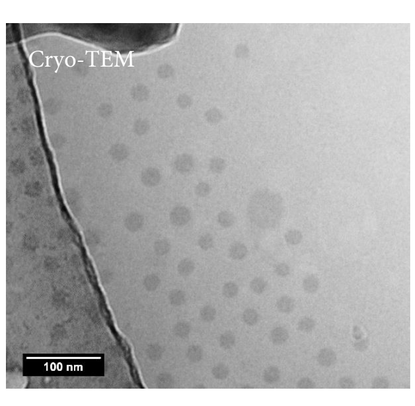
#	Initiator	M_n [kg/mol][a]	Formula[a]	PDI[b]
1	$APEG_{80}$	19.0	$APEG_{80}$-b-$PCAGE_{24}$-b-P($GOFPE_{26}$-co-FGE_{13})	1.18
2	$APEG_{80}$	17.4	$APEG_{80}$-b-$PCAGE_{27}$-b-P($GOFPE_{19}$-co-FGE_{11})	1.11
3	$mPEG_{114}$	19.2	$mPEG_{114}$-b-$PCAGE_{36}$-b-P($GOFPE_{15}$-co-FGE_6)	1.05
4	$mPEG_{114}$	16.8	$mPEG_{114}$-b-P($CAGE_{23}$-co-$tBGE_9$)-b-P($GOFPE_{15}$-co-FGE_6)	1.06

a) as determined by ^{1}H-NMR (300 MHz, $CDCl_3$), b) as determined by SEC (THF for #1, DMAc + 0.21% LiCl for #2, $CHCl_3$:iPrOH:NEt_3 94:4:2 for #3 and #4, PEG standards)

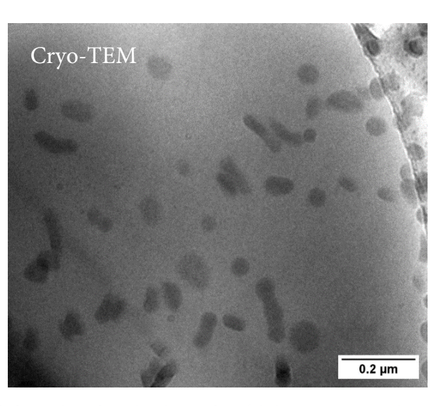


DLS-CONTIN





allyl-PEG_{80}-*b*-$PCAGE_{27}$-*b*-P($GOFPE_{19}$-*co*-FGE_{11})
No CL



allyl-PEG_{80}-*b*-$PCAGE_{21}$-*b*-P($GOFPE_{26}$-*co*-FGE_{13})
1.0 eq. DTME crosslinked

[1]Naumann et al. *ChemCatChem* **2025,** *17,* e202401032

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