Design and synthesis of polymers containing a single mechanophore-based sacrificial bond embedded in a macrocycle

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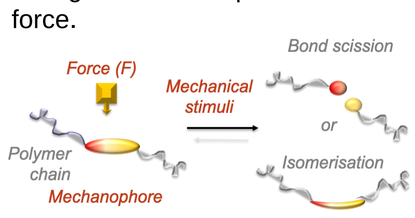
Context

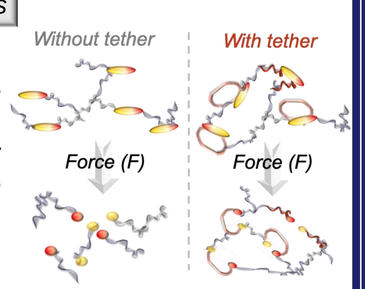
Mechanophores

Functional units that undergo structural and/or property changes when exposed to a force.



Tethered sacrificial groups

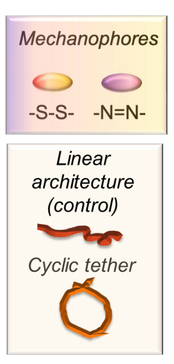
Weak bonds where the components stay linked and in close proximity after bond breakage (via the tether).



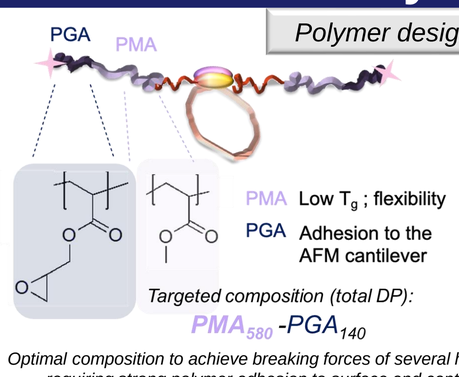
The tether keeps the material's integrity after the rupture of weak bonds since no connections are lost.

Objectives of the study

Two polymer systems with disulfide –S–S– and azo –N=N– mechanophores included in linear architectures (used as control) and cyclic tethers, with flexible (PMA) and adhesive (PGA) backbone blocks, were synthesized via SET-LRP and further analyzed by SMFS to probe bond rupture under mechanical force.



Polymer design

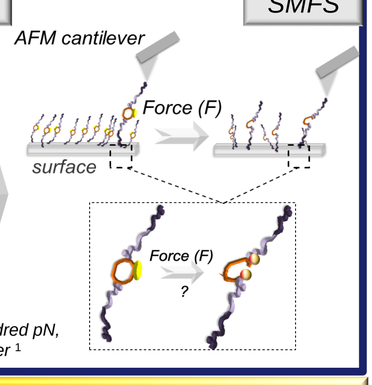


Targeted composition (total DP):

PMA_{580}-PGA_{140}

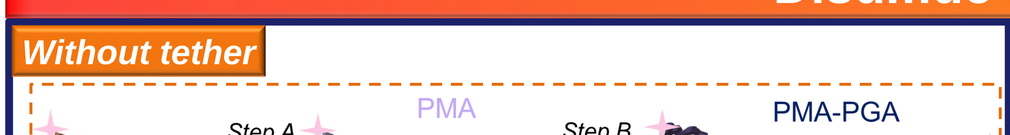
Optimal composition to achieve breaking forces of several hundred pN, requiring strong polymer adhesion to surface and cantilever [1]

SMFS

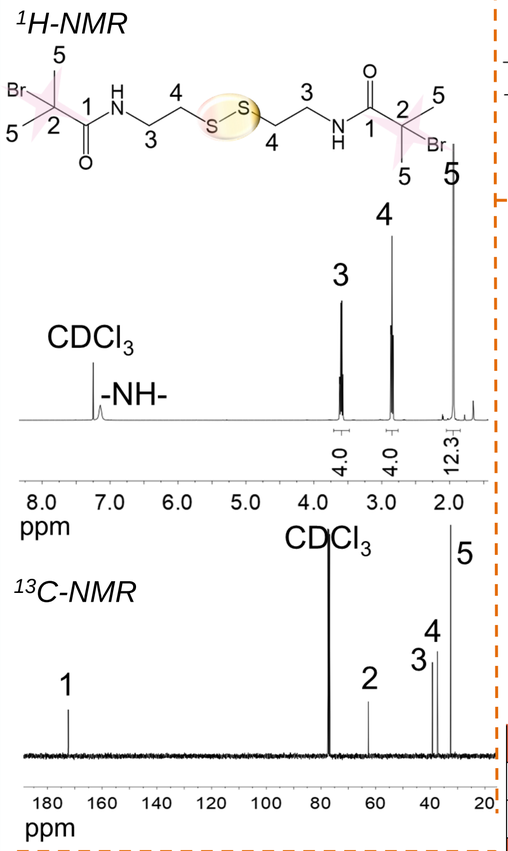


Disulfide mechanophore-based system

Without tether



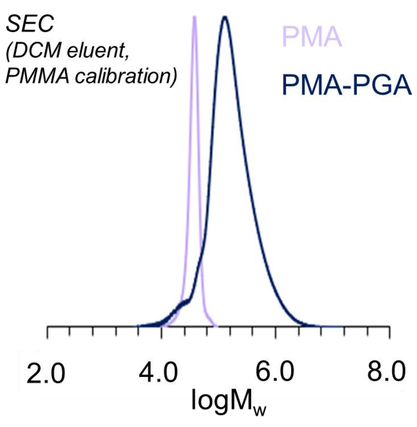
^{1}H-NMR



	Cu(0) wire	*$CuBr_2$ %	**Initiator/ Me_6TREN
Step A	5 mm length, 1 mm Ø	1	1/0.21
Step B			

*% molar (compared to the initiator), **molar ratio
[MA]:[initiator] = 580:1 ; [GA]:[macroinitiator] = 140:1

SEC (DCM eluent, PMMA calibration)

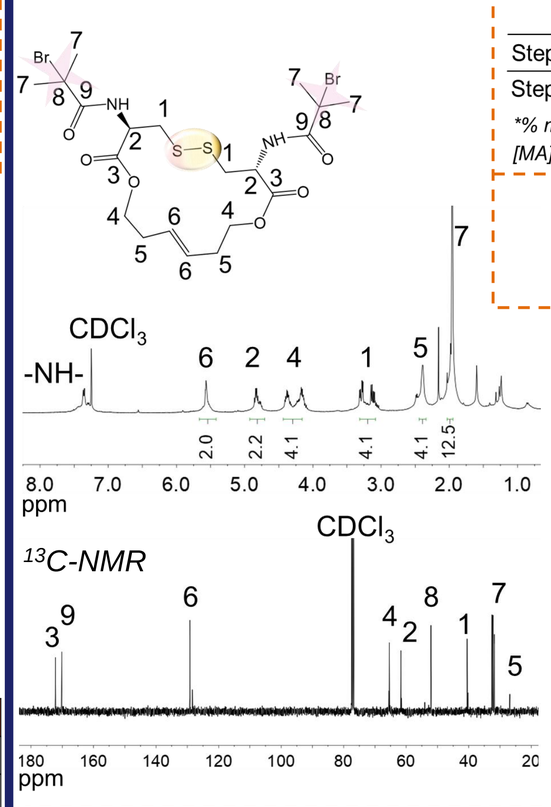


^{1}H-NMR data		PMA		PMA-PGA	
DP_{total}					
PMA	PGA	550	-	550	110
SEC data					
M_n (kg/mol)		40		95	
M_w (kg/mol)		52		144	
Đ		1.3		1.5	

The copolymers containing –S–S– mechanophore without tether were successfully synthesized with compositions close to those targeted.

Cyclic tether

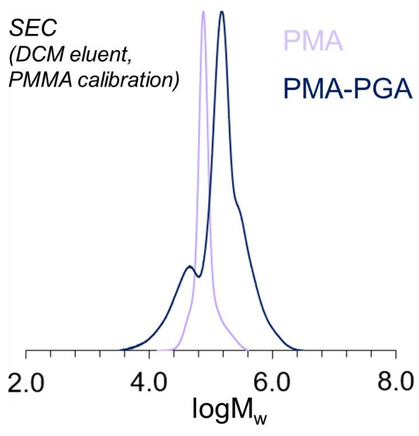
^{1}H-NMR



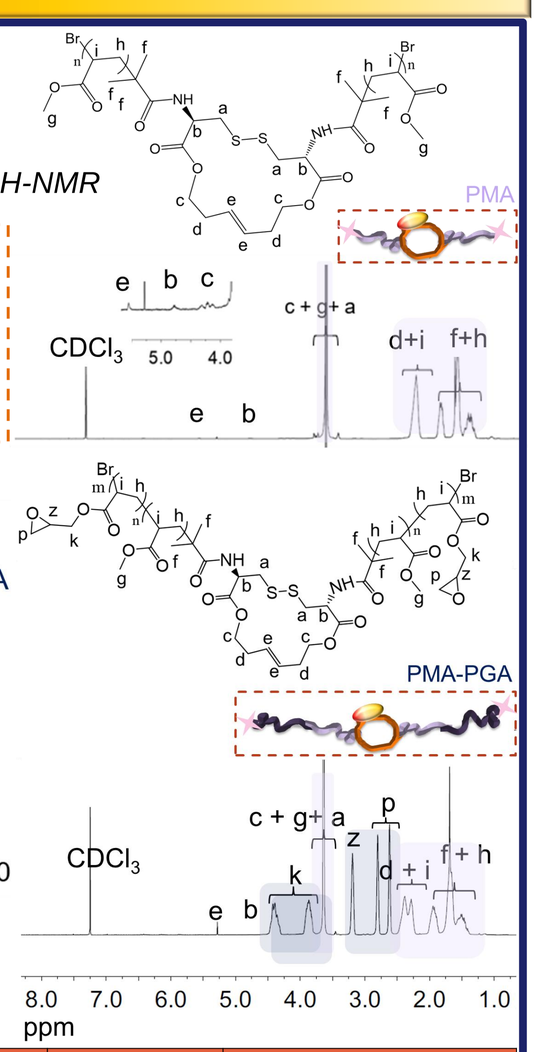
	Cu(0) wire	*$CuBr_2$ %	**Initiator/ Me_6TREN
Step A	5 mm length, 1 mm Ø	1.1	1/0.19
Step B		1	1/0.21

*% molar (compared to the initiator), **molar ratio
[MA]:[initiator] = 580:1 ; [GA]:[macroinitiator] = 300:1

SEC (DCM eluent, PMMA calibration)



^{1}H-NMR



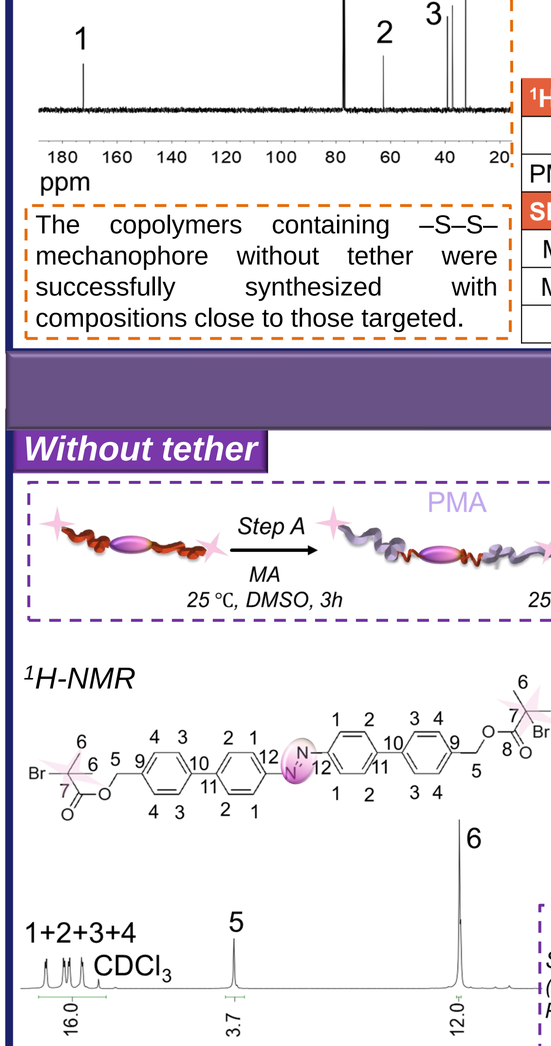
	^{1}H-NMR data		SEC data		
	DP_{total}		M_n (kg/mol)	M_w (kg/mol)	Đ
	PMA	PGA			
PMA	562	-	63	71	1.1
PMA-PGA	562	95	76	158	2.1

Formation of PMA block with narrow distribution and DP close to that targeted was noticed when using cyclic disulfide tethered initiator. PGA block extension resulted in a composition close to the target but showed broad MM distribution.

Azo mechanophore-based system

Without tether

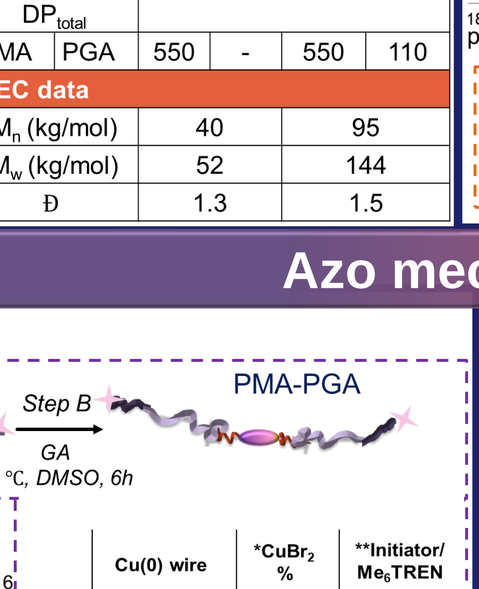
^{1}H-NMR



	Cu(0) wire	*$CuBr_2$ %	**Initiator/ Me_6TREN
Step A	5 mm length, 1 mm Ø	1.1	1/0.19
Step B		1	1/0.25

*% molar (compared to the initiator), **molar ratio
[MA]:[initiator] = 580:1 ; [GA]:[macroinitiator] = 300:1

SEC (DCM eluent, PMMA calibration)

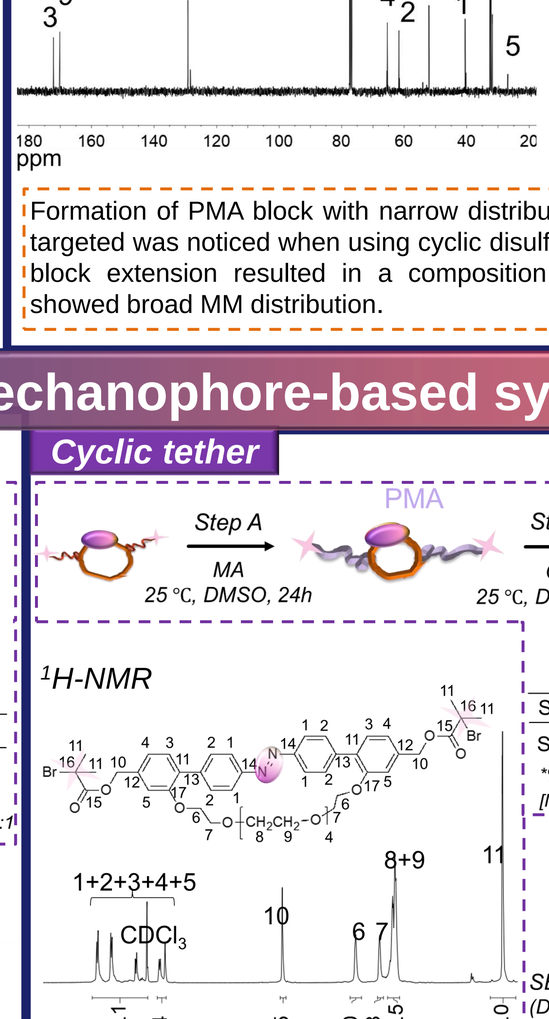


^{1}H-NMR data		PMA		PMA-PGA	
DP_{total}					
PMA	PGA	578	-	578	60
SEC data					
M_n (kg/mol)		42		56	
M_w (kg/mol)		63		79.4	
Đ		1.5		1.4	

Azo-based PMA was synthesized with composition close to the target. However, low PGA extension was achieved (compared to the target), which may result from reduced macroinitiator reactivity.

Cyclic tether

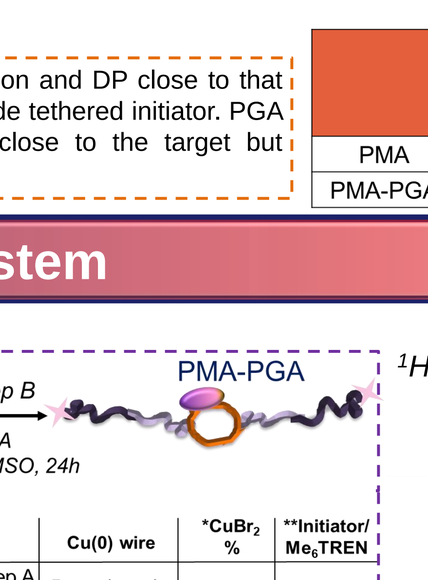
^{1}H-NMR



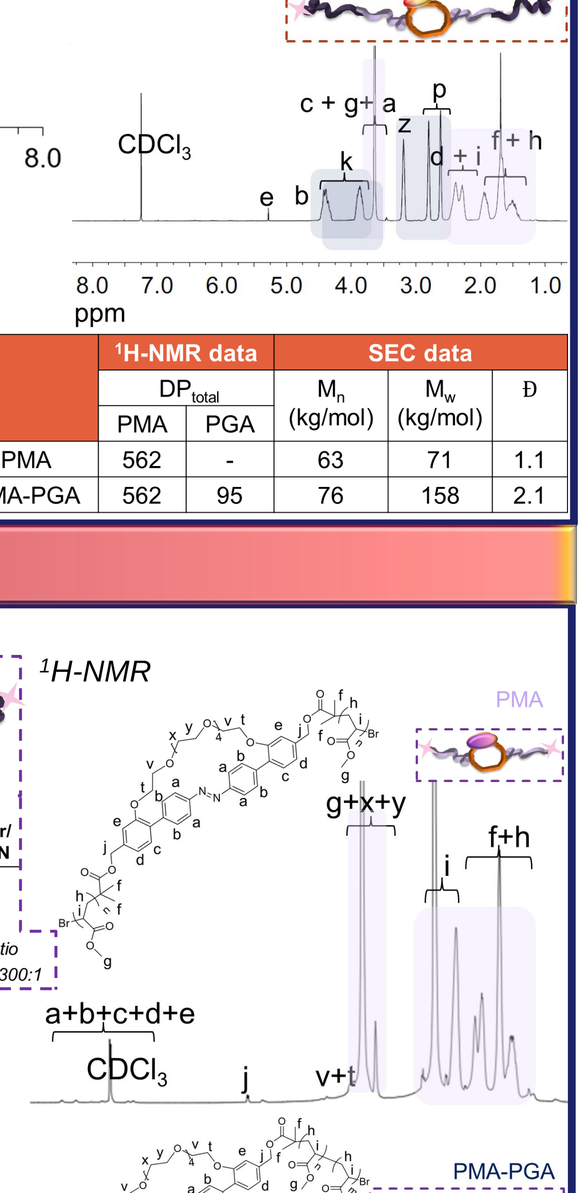
	Cu(0) wire	*$CuBr_2$ %	**Initiator/ Me_6TREN
Step A	5 mm length, 1 mm Ø	1	1/0.21
Step B			

*% molar (compared to the initiator), **molar ratio
[MA]:[initiator] = 580:1 ; [GA]:[macroinitiator] = 300:1

SEC (DCM eluent, PMMA calibration)



^{1}H-NMR

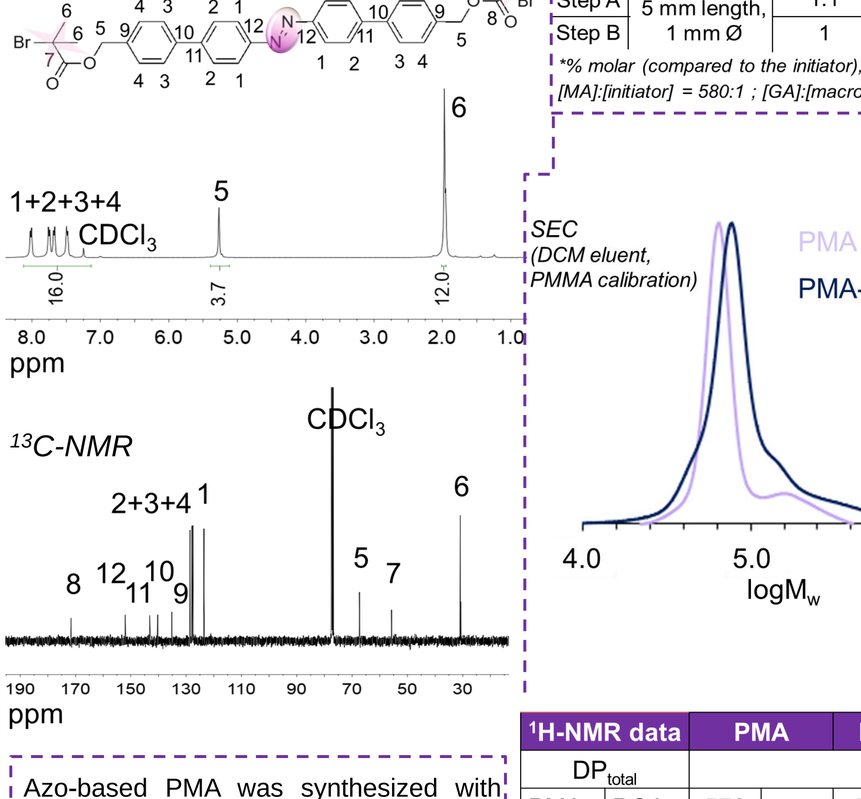


	^{1}H-NMR data		SEC data		
	DP_{total}		M_n (kg/mol)	M_w (kg/mol)	Đ
	PMA	PGA			
PMA	560	-	41.5	45.7	1.1
PMA-PGA	560	55	43.3	56.4	1.3

Azo-based cyclic tether initiator facilitated the formation of PMA and PMA-PGA architectures with generally well-defined distributions. Similar as when using the control azo initiator, PMA block formation proceeded efficiently, whereas PGA extension was lower than that targeted.

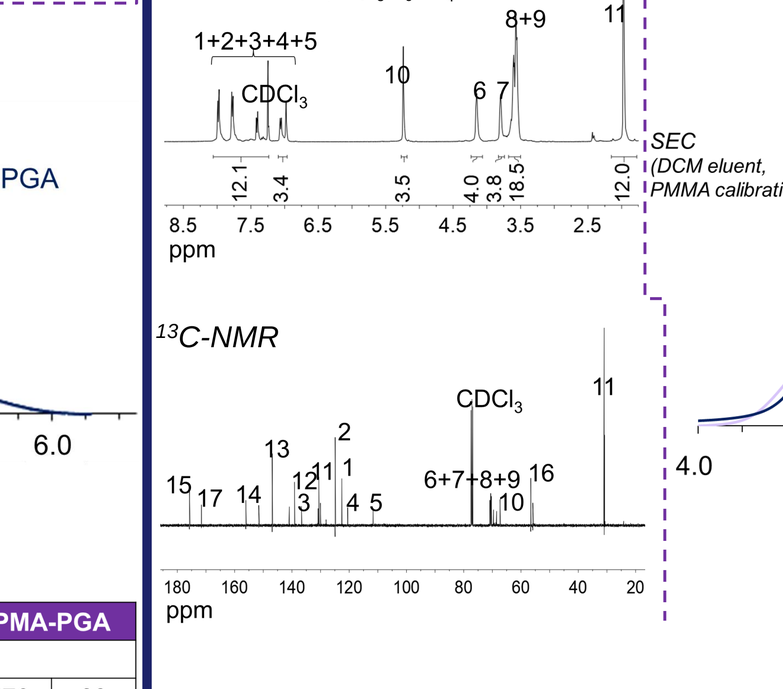
Single Molecule Force Spectroscopy (SMFS)

-S-S-



In the case of the cyclic –S–S– tether, a rupture event may be detected (region B).

-N=N-



The results indicate no significant difference in behavior between the polymer containing –N=N– bond and the reference polymer without the mechanophore group.

Conclusions and Perspectives

- The synthesis and characterization of SET-LRP initiators designed with two different mechanophore groups (–S–S– and –N=N–), as well as linear architectures and cyclic tethers was presented.
- PMA-PGA diblock copolymers were synthesized and characterized.
- SMFS results suggest that further optimization of the polymer structure is needed to better understand bond-breaking mechanisms under force (i.e., extend the –S–S– tether or, in the case of –N=N– system, increase the length of the PGA block).

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References:

1. Wang, J.; Kouznetsova, T.B.; Niu, Z.; Ong, M.T.; Klukovich, H. M.; Rheingold, A. L.; Martinez, T. J.; Craig, S. L. Nature Chem. 2015, 7, 323.
2. Willis-Fox, N.; Rognin, E.; Aljohani, T.A.; Daly, R. Chem. 2018, 4, 2499.
3. Sharma, A. K.; Malileni, J.; Box, S.; Ghiassinejad, S.; van Ruymbeke, E.; Fustin, C.A. Org. Chem. Frontiers. 2021, 8, 2383.
4. Deneke, N. ; Rencheck, M. L.; Davis, C. S. Soft Matter, 2020,16, 6230.