Glycosylated Nanoparticles by SET-LR-PISA

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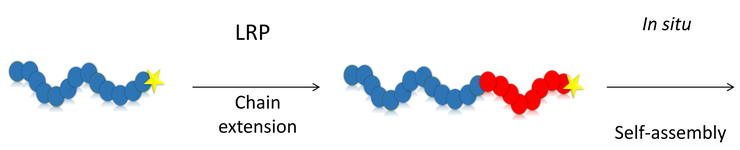
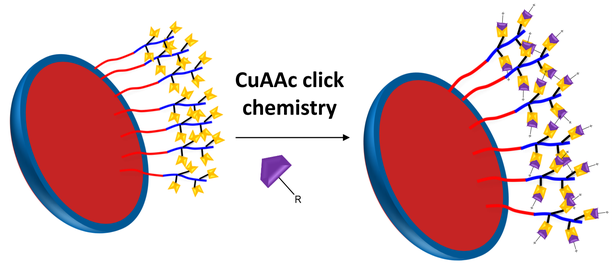
Introduction

The possibility to functionalize NPs surfaces allowed their implementation into many fields, *i.e.* cosmetics, agricultural, diagnostics. In medicine, they can be use as drug carrier for the encapsulation of hydrophobic and toxic drugs. Herein, the introduction of a propargylic moiety within the hydrophilic shell of the NPs provides a versatile framework for the surface functionalization of NPs *via* copper catalysed alkyne-azide cycloaddition (CuAAc).

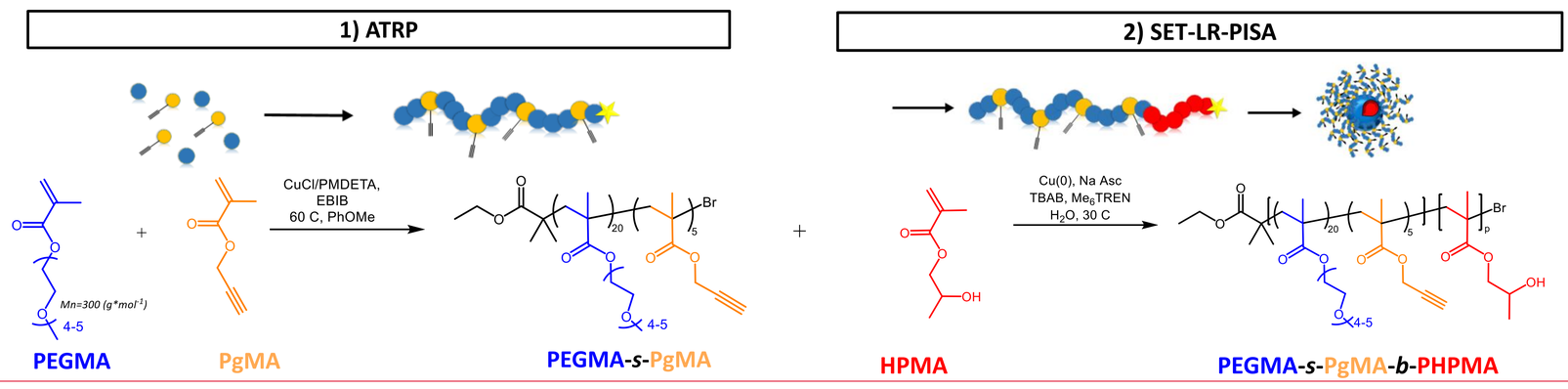
1. Polymerization-Induced Self Assembly **(PISA)** allows for the simultaneous chain extension of a macro precursor and *in situ* self assembly in a solvent suitable for the precursor and the second monomer.



2. Alkyne-azide copper catalyzed cycloaddition **(CuAAC)** allows for the binding of two building blocks, selectively yielding 1,2-disubstituted 1,2,3-triazole.



Synthesis of NPs: SET-LR-PISA



➢Solid content= 10%

➢DP_{PHPMA}= 150, 300,450

Sample ID	Mw_{GPC}	M_n	$Đ_M$
PEGMA-s-PgMA-b-PHPMA150	1800	13600	1.34
PEGMA-s-PgMA-b-PHPMA300	26000	14900	1.37
PEGMA-s-PgMA-b-PHPMA450	18600	13000	1.43

SET-LRP monomer conversion study

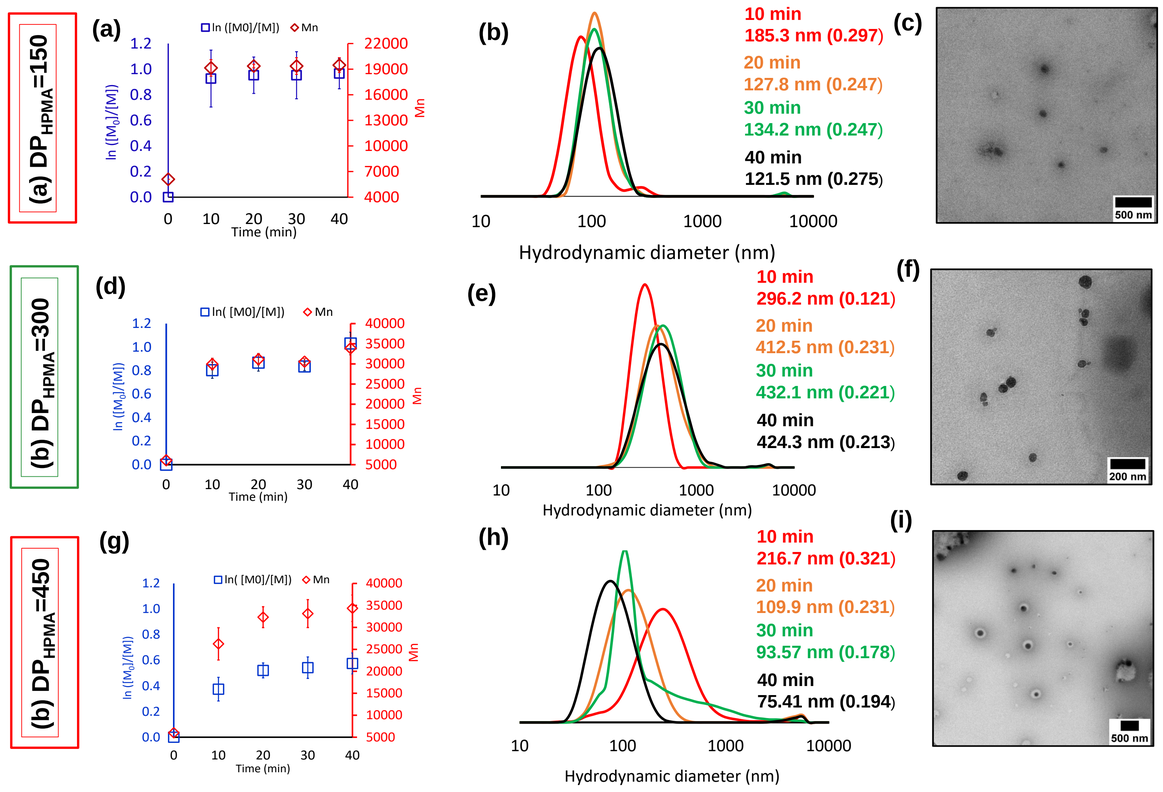


Figure 1. Linear plots of ln (M0/M) vs time and Mn vs time when targeting (a) DP_{HPMA}= 150, (d) DP_{HPMA} =300 and (g) DP_{HPMA} =450. Hydrodynamic diameter evolution vs time in case of (b) DP_{HPMA}= 150 , (e) DP_{HPMA}= 300 and (h) DP_{HPMA} =450. TEM images of (a) DP_{HPMA}= 150, (d) DP_{HPMA} =300 and (g) DP_{HPMA} =450.

Click reaction with various compounds with DP_{HPMA}=300

- Shell functionalization with fluorescein
- Shell functionalization with PEG-azide

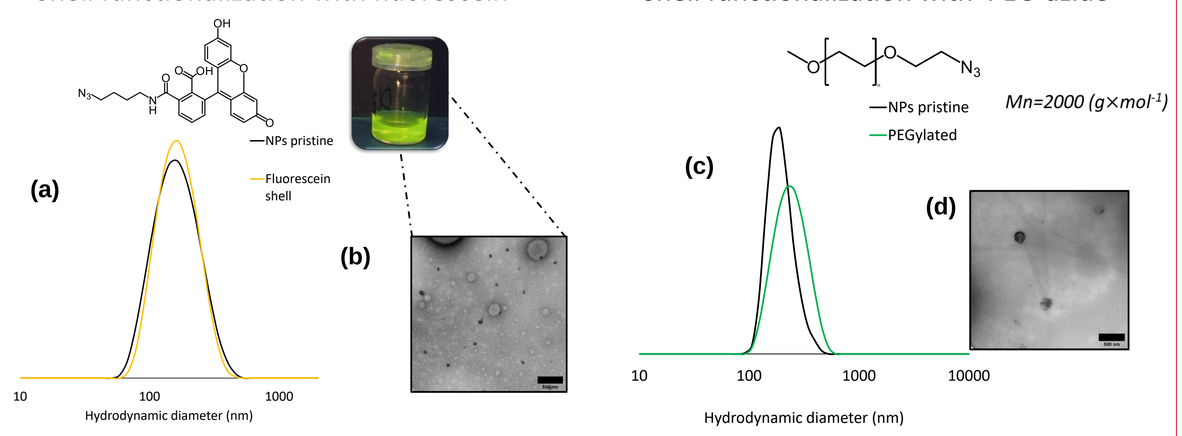


Figure 2. Hydrodynamic diameter of PEGMA-s-PgMA-b-PHPMA NPs before and after shell functionalization with (a) fluorescein azide and (c) methoxypolyethylene glycol azide. TEM images of the NPs with presenting (b) fluorescein or (d) PEGylated shell.

Sample ID	D_H	PDI	Z
NPs	148.1	0.179	-7.35
NPs + fluorescein	176.9	0.261	-20.6

Sample ID	D_H	PDI	Z
NPs	214.8	0.233	-5.94
PEGylated NPs	216.2	0.132	-9.33

- The functionalization **with Azido-2-ethyl-bromoisobutyrate** (ATRP initiator) allowed for the **shell extension** with **poly(NIPAM)**

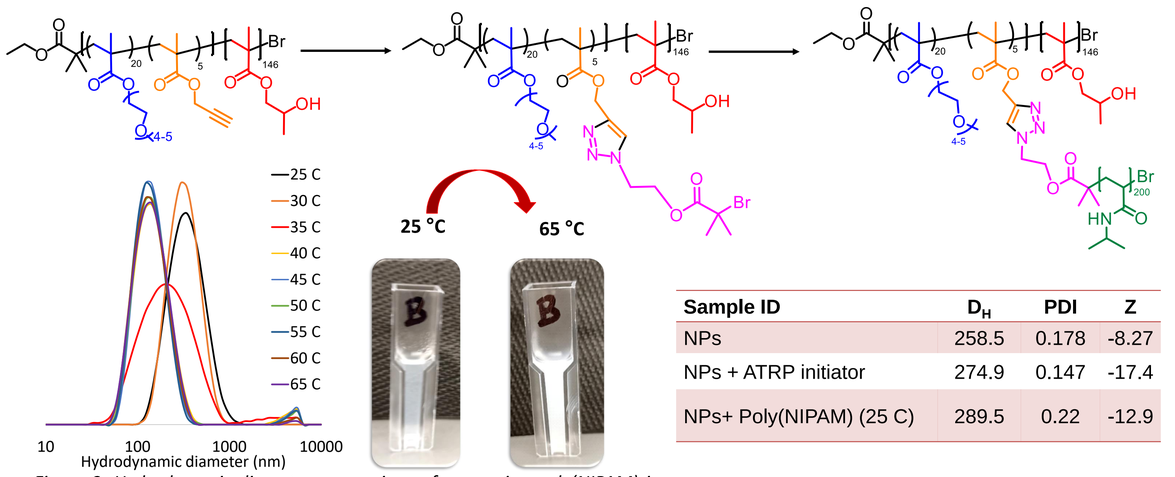
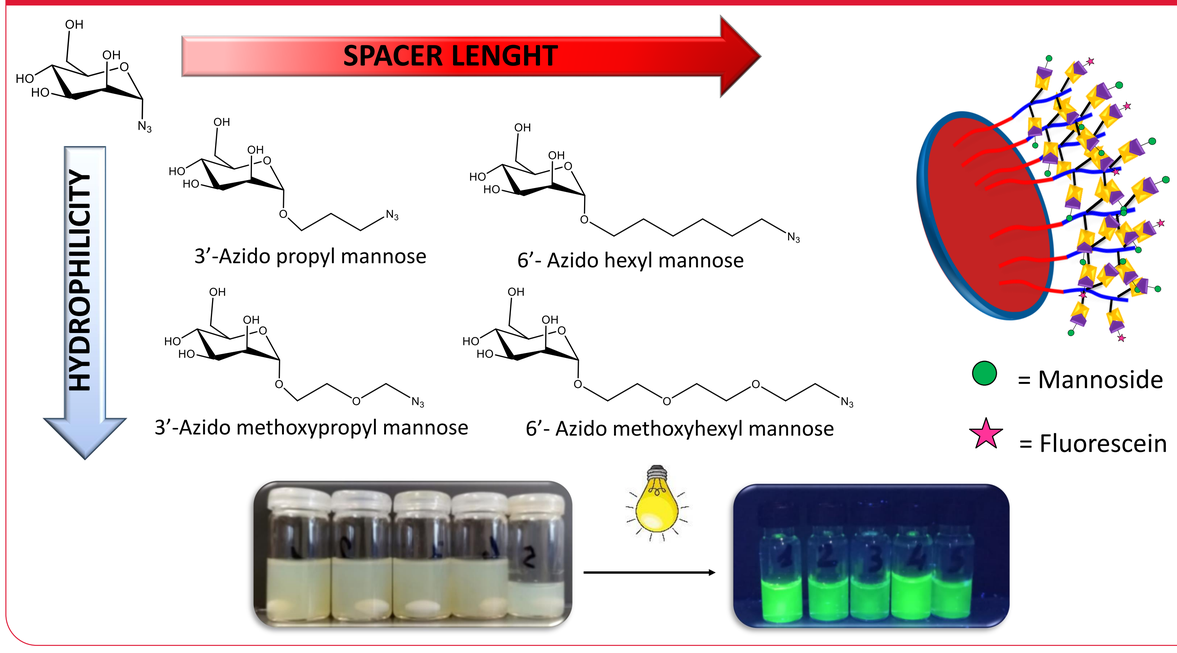


Figure 3. Hydrodynamic diameter comparison of presenting poly(NIPAM) in the shell in a temperature range of 25 C-65 C

Sample ID	D_H	PDI	Z
NPs	258.5	0.178	-8.27
NPs + ATRP initiator	274.9	0.147	-17.4
NPs+ Poly(NIPAM) (25 C)	289.5	0.22	-12.9

Mannosylated NPs



Summary and conclusion

- **$[P(PEGMA)_{18}$-*s*-$P(PgMA)_5]$-*b*-$[PHPMA]_n$ spherical NPs** were prepared *via* **SET-LP-PISA** in aqueous condition.
- The alkyne moiety along the backbone allows for the versatile functionalization *via* **Cu AAc** reaction with a variety of compounds (fluorescein, PEG-azide, mannosides)
- By functionalizing the NPs shell with azido-2ethy-bromoisobutyrate, the shell chain extension with poly(NIPAM) was successfully achieved.
- Future works will aim in investigating the bio interactions of the glycosylated NPs

References

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