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Investigation and optimization of surface modification protocols to attach sequence defined oligomers onto silica substrates

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Introduction

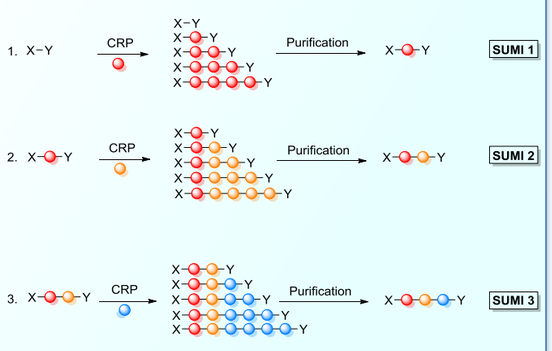
Sequence defined (SD) oligomers are synthesized by single unit monomer insertion controlled radical polymerization (SUMI-CRP) and elaborate purification which is holding back the development. Multiple hydrogen bond (MHB) SD oligomers are similar to biopolymers since they recognize their complementary part. This ability can be exploited by covalently grafting these oligomers onto silica substrates and therefore simplify the purification. For a proof of principle study grafting of SD oligomers onto silica particles is investigated.

SUMI procedure

Monomer 1:
Monomer 2:
Monomer 3:

RAFT agent or specific initiator: X−Y

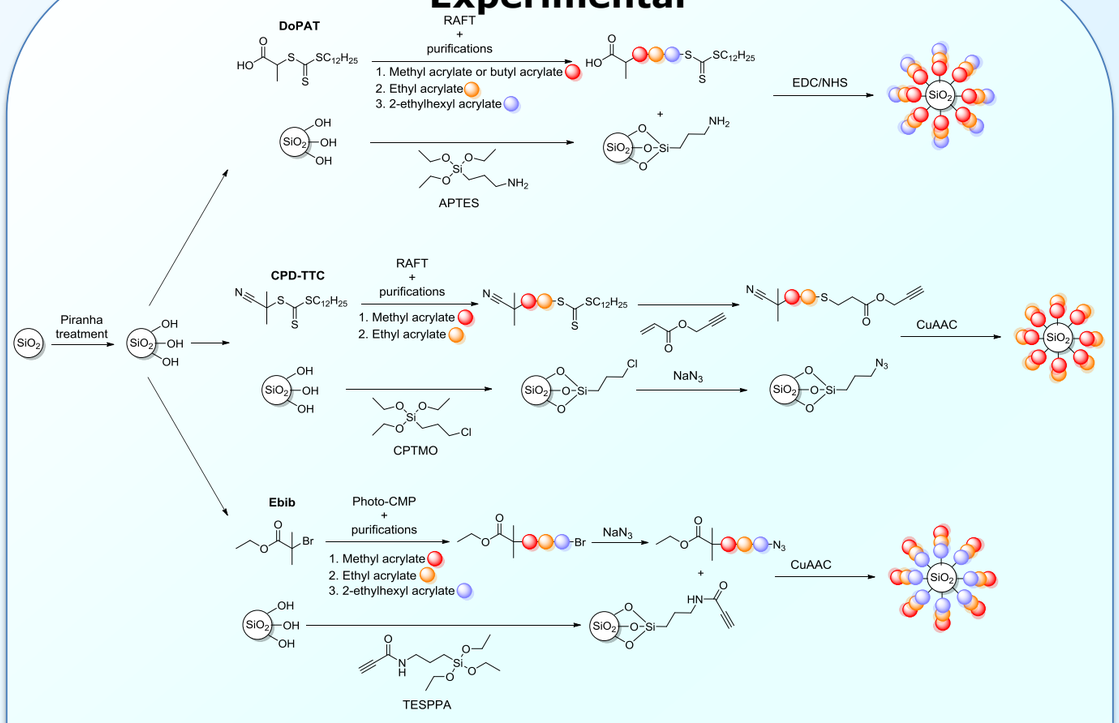
Synthesis of SD trimer



Scheme 1: Synthesis of SD oligomers through SUMI-CRP

Difficult and time-consuming purification to obtain desired molecules

Experimental



Scheme 2: Experimental procedures

1. Pre-treatment
2. Functionalization silica particles
3. Synthesis of SD oligomer
4. Coupling reaction

Yields and rec-SEC trace

Table 1: Experimental yields.

*** Too low yield to perform next controlled polymerization**

	SUMI 1	SUMI 2	SUMI 3
RAFT (first insertion = methyl acrylate)	7%	*	*
RAFT (first insertion = butyl acrylate)	25%	26%	*
Photo-CMP	40%	36%	17%

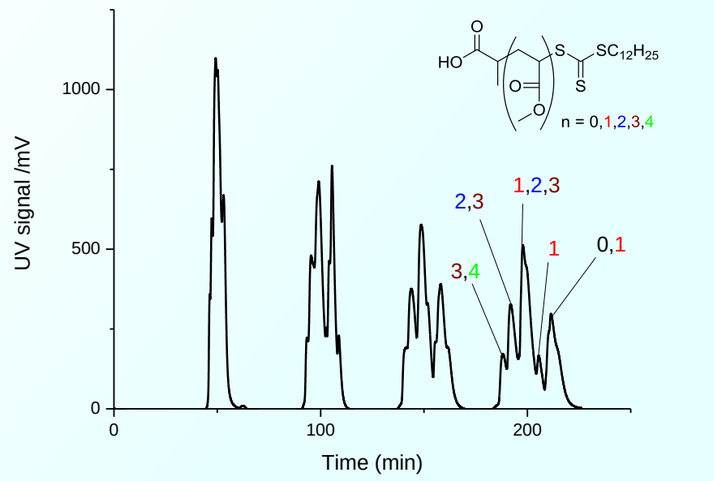


Figure 1: rec-SEC trace recorded during consecutive purification cycles of the statistical mixture after the first RAFT SUMI reaction (methyl acrylate) with DoPAT as transfer agent

Grafting results of functionalized silica particles

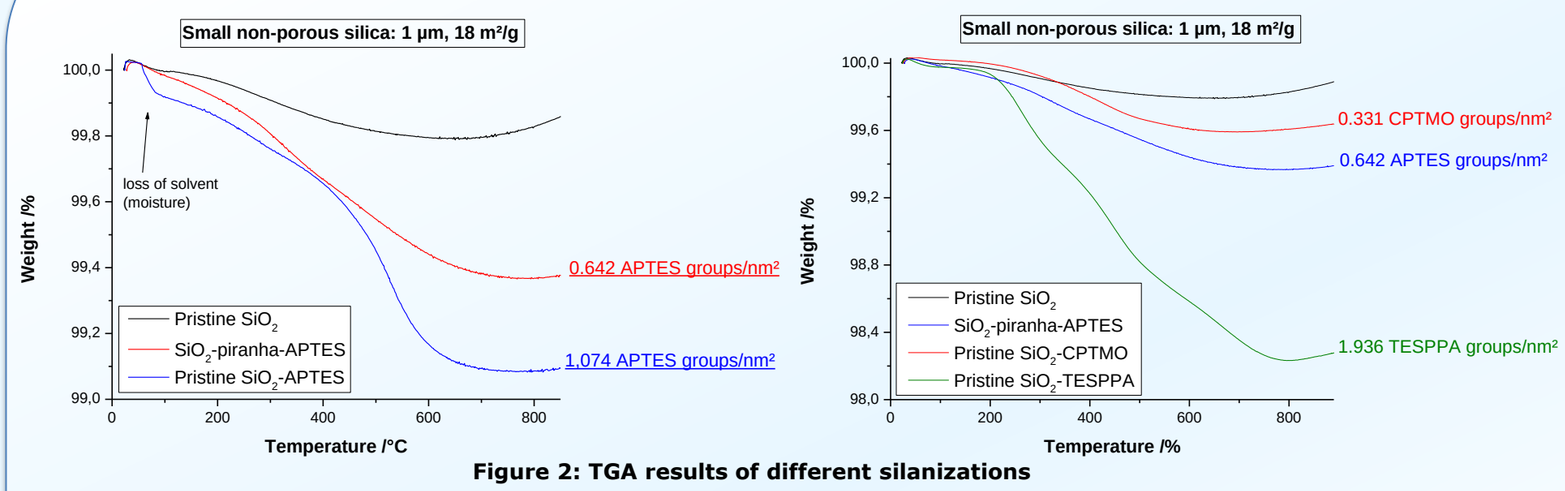


Figure 2: TGA results of different silanizations

Piranha treatment proved to be unnecessary and even has a negative effect on the surface grafting density. It increases the hydrophilic character of the particles which results in the repelling of APTES. According to literature grafting densities between 1.69 to 2.50 APTES groups/nm² should be achieved. Therefore, silanization with TESPPA is the most promising procedure.

Grafting results of CuAAC coupling

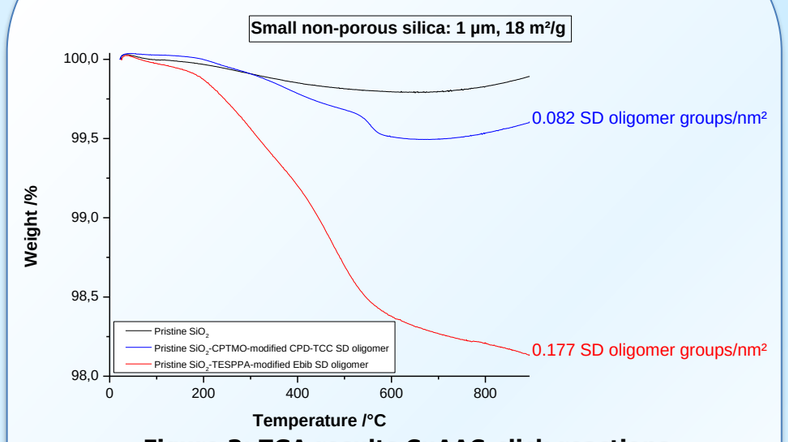


Figure 3: TGA results CuAAC-click reactions

- EDC/NHS coupling did not work
- Highest grafting density obtained by coupling azide modified photo-CMP SD oligomers onto alkyne functionalized silica particles

Conclusion

The results show that synthesizing SD oligomers with DoPAT RAFT agent is not recommended since the acid groups stick to chromatographic columns, deteriorating purification (Figure 1). More promising is using CPD-TTC RAFT agent, followed by trithiocarbonate modification and attachment of the alkyne SD oligomers with CuAAC onto azide-silica (0.082 oligomer groups/nm²). Also, SD oligomers synthesized by photo-CMP is successful (17% yield of MA-EA-EHA-Ebib). The bromides are modified into azides and grafted-to alkyne-silica (0.177 oligomer groups/nm²). In comparison with the CPD-TTC RAFT procedure, synthesizing SD oligomers via photo-CMP followed by azide modification and attachment onto alkyne-silica is preferred because better yields and a higher SD oligomer grafting density are obtained. As outlook, optimization of the CPD-TTC RAFT procedure and Ebib photo-CMP procedure is suggested. Also, MHB SD oligomers can be investigated.

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References

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PRD POLYMER REACTION DESIGN

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