Manuscript Title : (Polymer-oligonucleotide) conjugate synthesis from an amphiphilic block copolymer; applications to DNA detection on microarray.

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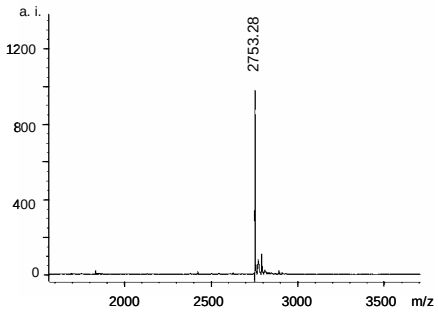
Supporting information :

a) MALDI-TOF MS analysis (in negative mode) of ODN population present in conjugate synthesis solutions (after collect of the peak eluted on HPLC at 25.8 min (Fig. 7)); a.i. = arbitrary intensity.



b) Capping study on HEG-CPG

Entry	Capping reaction	ODN synthesized from HEG-CPG (in % compared to experiment 1)
1	No capping	100 %
2	Ac_2O [a]	51 %
3	Ac_2O (in solution) [b]	25 %
4	Ac_2O[a] + DPP (0.1M)	18 %
5	Ac_2O (in solution) [b] + DPP (0.1M)	10 %
6	Ac_2O + DPP (0.5M)	7 %

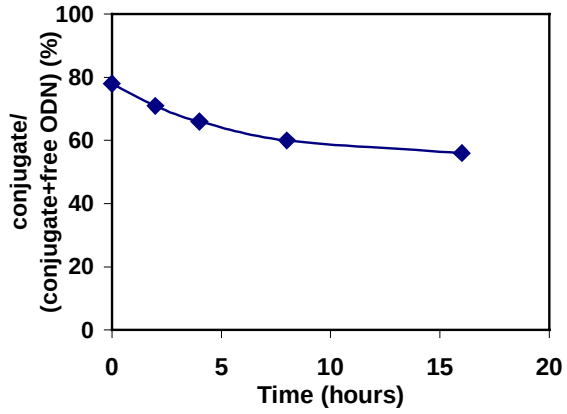
[a] Ac_2O reaction on HEG-CPG beads inside the synthesizer

[b] Ac_2O reaction on HEG-CPG beads carried out in a flask before introduction of the beads in the synthesizer

The reactivity of DPP in addition to acetic anhydride was first evaluated on HEG-CPG (without polymer). For different capping conditions, 25 mer polyT were synthesized from supports and resulting ODN population was analyzed by SEC.

On experiments 2 and 3, two protocols were compared for acetic anhydride capping reaction, i.e. reaction achieved inside the synthesizer (experiment 2) and reaction in a flask with a high amount of reagent (experiment 3). Results clearly evidenced that capping step with acetic anhydride inside the synthesizer was not efficient enough, since 51 % of ODN were obtained in comparison to experiment 1. When acetic anhydride reaction was carried out in a flask, it was more performing but not complete, 25 % of ODN still being initiated from the support. Adding a capping step inside the synthesizer with phosphoramidite reagent (DPP) further improved hydroxyl capping on surface (parasite ODNs decreased from 51% to 18%, experiments 2 and 4). Best results were obtained when achieving successively Ac_2O capping and DPP (0.5 M in acetonitrile) capping directly inside the synthesizer. A total reduction of 93 % of parasite ODN population was reached in these conditions (entry 6).

c) Stability study of (block copolymer-ODN) conjugate in ammonia.



The poly(TBAm-b-(NAM/NAS))-dT25) conjugate was previously purified up to 80% by filtration on membrane prior to carry out degradation kinetics in ammonia (30% NH_4OH/H_2O).