UV-INDUCED SELF-ASSEMBLY OF AMPHIPHILIC POLYOXAZOLINE

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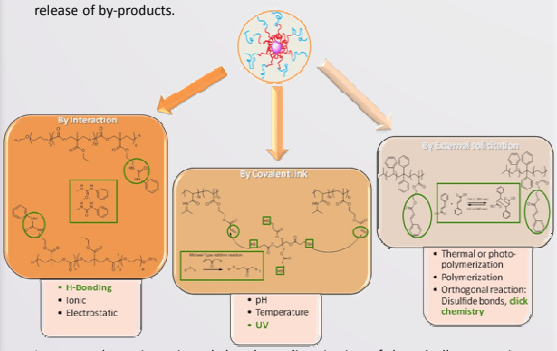
Context

The increasing interest of amphiphilic copolymers mainly arose from their ability to self-organize into a wide variety of morphologies in solution or in bulk giving objects such as micelles, vesicles, and nanotubes finding numerous applications such as surfactants, drug delivery systems, and surface coating technologies.

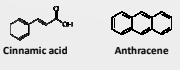
To stabilize the morphology and the size of the nano-objects, the cross-linking of the core or the corona can be used.[1] The cross-linking occured by interactions (H-bonding, ionic, and electrostatic), by covalent bonds according to selective reactions, or using external stimulus (pH, temperature…). Zhao has demonstrated the efficiency of the photo-cross-linking using UV-sensitive groups without incorporate external component.[2] This methodology avoids any release of by-products.



In our work, we investigated the photo-dimerization of the micelle core using UV-sensitive group: coumarin. Herein, the amphiphilic diblock polyoxazoline[3] bearing coumarin end-group was examined in details before studying amphiphilic heterografted copolymers based on polyoxazoline.

Focus on photo-sensitive groups

Photo-sensitive groups and the photo-dimerization[4]



-manifold functionalizations
-many applications (cosmetics, food industry)
-fast process
-cost-effective

Photo-dimerization of coumarin:

[2+2] photo-cyclization

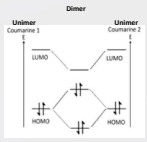
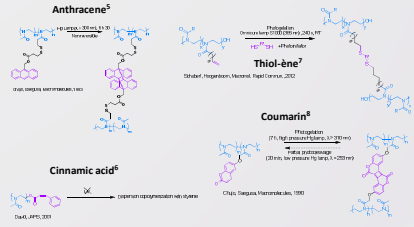
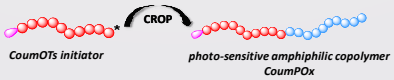


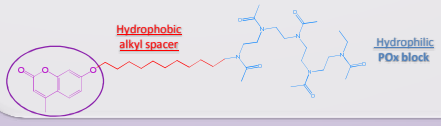
Photo-sensitive Polyoxazolines already described

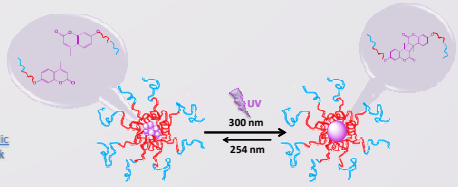


Strategy

In this study, the first step concerns the synthesis of cationic initiator based on tosylate group named CoumOTs. This active molecule in cationic ring-opening polymerization (CROP) of 2-oxazolines bears a long alkyl and hydrophobic chain terminated by a coumarin unit capable of photo-dimerization. The synthesis of amphiphilic and photo-active polyoxazoline copolymers was investigated before evaluating their ability of self-organization in solution. Finally, the photo-dimerization of pre-assembled CoumPOx in water was examined in order to estimate the modification drived by UV-process.

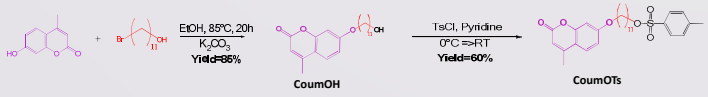


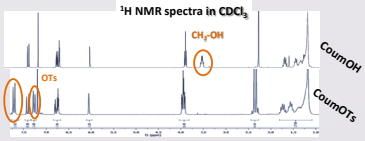




Synthesis of UV-sensitive amphiphilic copolymers based on POx and coumarin

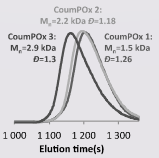
Initiator Synthesis:





- A Facile synthesis of UV-sensitive initiator coming from 7-hydroxy-4-methylcoumarin was described.
- Well-defined CoumPOx containing photo-dimerizable end group were prepared with molecular mass ranging from 1.5 to 2.9 kDa and Đ ≈ 1.2-1.3.

CROP of 2-methyl-2-oxazoline: Synthesis of amphiphilic copolymers (CoumPOx)

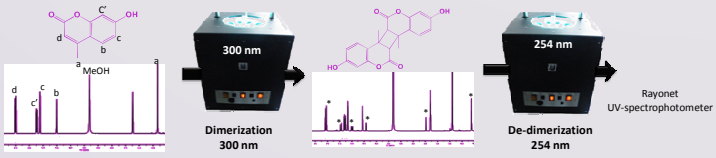


CoumPOx	yield (%)	$DP_{n\ th}$	$DP_{n\ NMR}$ [a]	$DP_{n\ GPC}$ [b]	Đ [b]	M_n/M_b [c]
1	45	12	22	12	1.26	3.2
2	42	21	24	25	1.18	6.5
3	62	35	30	34	1.30	8.8

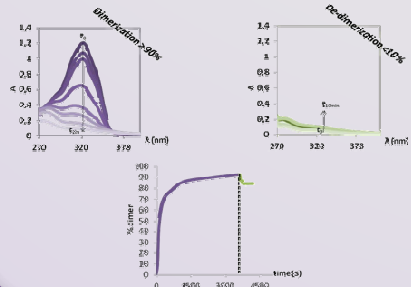
[a]: Calculated from ^{1}H NMR in $CDCl_3$ using $\int CH_{2\ POx} / \int CH_{Coum}$; [b]: Determined from GPC in DMF using PMMA standards; [c]: molecular weight of POx (Hydrophilic) / molecualr weight of Coum (hydrophobic)

UV-activity of coumarin derivatives and their self-organization

Preliminary study of 7-hydroxy-2-methylcoumarin dimerization

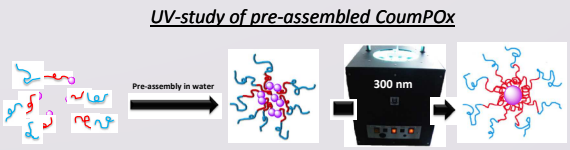


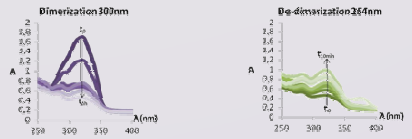
Rayonet UV-spectrophotometer

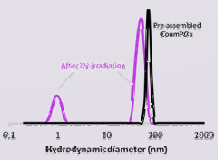


- To check the efficiency of the coumarin derivatives in photo-dimerization, the cyclization was first realized on 7-hydroxy-2-methylcoumarin. The kinetic study was monitored by Rayonet UV-spectrophotometer at 300 and 254 nm for the dimerization (1 h) and de-dimerization (10 min) of coumarin, respectively.
- The dimerization gave a conversion upper than 90 % whereas only 10 % de-dimerized.
- The reversible aspect of the photo-addition of coumarin was not observed in accordance to the litterature.

UV-study of pre-assembled CoumPOx





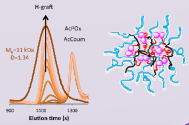


- CoumPOx was pre-assembled in acetone by direct precipitation and sonication (without any filtration). As evidenced by Dynamic Light Scattering (DLS), a single population of aggregates was observed around 70 nm.
- The dimerization of micelle core took place in high conversion close to 70 % whereas the core de-dimerized in poor conversion (15 %) as illustrated in the case of 7-hydroxy-2-methylcoumarin.
- The UV-irradiation of the micelles induced the formation of smaller nanoparticles (D_h=50 nm) as well as uni- and dimers (D_h=1 nm). This decrease in hydrodynamic diameter is consistent with the dimerization of the core and additionally suggested the surprising expulsion of uni- and dimers. The last phenomenon is currently under investigation.

Conclusions and Perspectives

- A series of UV-sensitive amphiphilic polyoxazolines was prepared by end-functionalization using coumarin group. They were pre-assembled in water by direct precipitation into well-defined aggregates.
- At 300 nm the dimerization of coumarin units occured in the micelle core whereas the reverse photo-reaction was inefficient at 254 nm. Even if a supplementary work is under investigation, the DLS study shown the limits of amphiphilic linear copolymers to stabilize micelles.

- We currently continue with amphiphilic heterografted copolymers based on acrylated-polyoxazoline and acrylated-coumarin to design core cross-linked micelles under UV-irradiation. Well-defined amphiphilic copolymers have already been synthesized.



Amphiphilic statistical heterografted copolymers

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