From the synthesis of functional RAFT agents to the design of functional latex particles

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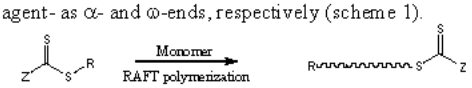
Introduction

The usual strategy to introduce a molecule of interest at a polymer chain-end consists in binding an appropriate derivative of that molecule onto a reactive group located at the polymer chain-end. However, the binding yield depends on the reactivity of the two counterparts and decreases with the increase in the polymer chain length. Another strategy relies on the introduction of the molecule of interest in a compound which will be used to initiate the polymer chains. Hence, each polymer chain will bear one molecule at the α-end. The development of Controlled Radical Polymerization techniques allowed producing such polymers with an additional control over the chain length and the ω-end. Among the most versatile approaches, the Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization is mediated by thiocarbonyl thio compounds (RAFT agents of the general formula Z-C(=S)–SR) and leads to chains that are characterized by the R and Z-C(=S)-S groups -from the RAFT agent- as α- and ω-ends, respectively (scheme 1).

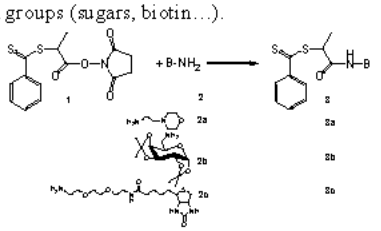


Scheme 1

Using an efficient and simple chemistry for the RAFT agent synthesis, it is possible to design the α-end according to a targeted application as long as the R group does not disturb the controlled RAFT polymerization. The transferring feature of the ω-end (incorporating the Z group) can for example be used to grow a second block.

Chain transfer abilities are sometimes advantageously used for stabilization during the synthesis of latexes. In dispersion polymerization for example, transfer along a polymeric chain during the polymerization leads to the grafting of these chains onto the forming particles conferring a steric stabilization to the final produced latex. In the same vein, thiol-ended PEOs were used as chain transfer agent/surfactant (transurf) for styrene polymerization in dispersed media (emulsion, dispersion) ensuring, however, partial stability since majority of the PEO chains mainly remains as hydrosoluble by-products. In all the cases, the efficiency of the stabilization strongly depends on the anchorage of the transferring stabilizing chains at the surface of the latex particles.

Considering these different points for the production of original latex particles, we first proposed a strategy for the synthesis of functional RAFT agents which relies on the design of a RAFT agent precursor, 1, bearing an activated ester in the R group (Scheme 1). As succinimidyl ester moieties readily react with nucleophiles in a one step reaction, a range of amino-based molecules of interest were successfully introduced as R groups (sugars, biotin…).



Scheme 2

We then took advantage of the chain transfer agent efficiency of the thiocarbonyl thio moiety. In that respect, polymer chains obtained by polymerization of N-Acryloylmorpholine (NAM), a hydrophilic monomer, mediated by functional RAFT agents depicted in scheme 2 were used in dispersion polymerization to produce latex particles incorporating hair of controlled chain length and functionality.

The strategy was further extended to a hydrophilic PEO carrying a thiocarbonyl thio end group (PEO-RAFT) which was synthesized according to the strategy depicted in scheme 2 and used as stabilizer in an *ab initio* emulsion polymerization of styrene. Besides, considering the very wide range of polymerizable monomers by the RAFT process including hydrophilic ones and the very recent work published by Charleux et al.[1], the additional use under acidic conditions of poly(dimethylaminoethyl methacrylate) (PDMAEMA) chains which we recently synthesized by the RAFT process was evaluated in conjunction with PEO-RAFT to prepare double stabilized (non ionic and cationic) latex particles.

Results and discussion

RAFT and MacroRAFT agents syntheses.

Functional RAFT syntheses. This synthetic approach[2] was first evaluated on a model compound, N-aminoethylmorpholine, 2a. A careful optimization led to the functional RAFT agent 3a with 68% yield after purification. Amino derivatives of biomolecules, a carbohydrate derivative, the 6-amino-6-desoxy-1,2:3,4-di-O-isopropylidene-6-α-D-galactopyranose, 2b, and a biotin derivative, the (+)-Biotinyl-3,6-dioxaoctanediamine, 2c were also successfully tested and pure RAFT agents 3b and 3c were isolated (66% and 72% yield, respectively). The controlled features of the polymerization of NAM mediated by 3a, 3b and 3c were showed and a range of R-PNAM-RAFT was obtained.

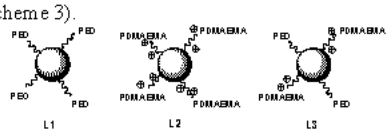
Synthesis of PEO-RAFT. PEO-RAFT was also synthesized according to scheme 2. Commercially available amino PEO (2000 or 5000 $g.mol^{-1}$) was reacted with a RAFT agent bearing an activated ester. The success of the reaction was showed by ^1H NMR analysis of the resulting PEO-RAFT.

Synthesis of PDMAEMA-RAFT. RAFT polymerization of DMAEMA was carried out under conditions depicted in reference 3. For the purpose of this study, PDMAEMA of 12000 $g.mol^{-1}$ (PDI = 1.09, SEC using light scattering detection[3]) was used under its hydrochloride form after treatment with hydrochloric acid.

Polymerizations in dispersed media.

Dispersion polymerization using R-PNAM-RAFT. Dispersion polymerization of butyl acrylate in a mixture of ethanol/water was performed in presence of R-PNAM-RAFT (4000 and 40000 $g.mol^{-1}$) and AIBN. Stable latexes were obtained and characterized by different techniques.

Ab initio emulsion polymerization using PEO-RAFT and PDMAEMA-RAFT. Water, Styrene and initiator (2,2'-azobis(2-amidinopropane) dihydrochloride,) were mixed with various amounts of PEO-RAFT, PDMAEMA-RAFT or a mixture of PDMAEMA-RAFT/PEO-RAFT (20/80 molar ratio). After degassing with argon and heating at 70°C for several hours, stable PS latex **L1**, **L2**, **L3** respectively were obtained (Scheme 3).



Scheme 3

They were characterized in terms of particle size but also particle structure by analyzing the latex by ^1H NMR after washing. Double stabilization was evidenced by comparing the stability of **L2** and **L3** first against pH. Whereas **L2** cationic latex is immediately destabilized when added to a 0.1M NaOH solution, no destabilization is observed for **L3**. When looking at the stability against freeze-thaw cycles (-18°C to 20°C), whereas **L2** is destabilized after one cycle, **L1** and **L3** remain stable after more than 3 cycles. This two last results evidence the beneficial contribution of the PEO-induced stabilization.

Conclusion

The design of a simple and efficient strategy to produce functional RAFT agents together with the use of the corresponding RAFT synthesized polymer chains in dispersed media allows us to take advantage of the chain transfer ability of the RAFT chain end to produce functional latexes achieving original properties.

References

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