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RAFT polymerization of an alkoxyamine bearing acrylate, towards a well-defined redox active polyacrylate†

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A new strategy for the synthesis of a well-defined redox active polymer, a polyacrylate bearing TEMPO, and its grafting onto a gold substrate is described. It consists of polymerizing an acrylate bearing an alkoxyamine by RAFT, followed by aminolysis of the trithiocarbonate chain-end into a thiol that is exploited for the polymer grafting onto the gold sensor. Thermal activation of the alkoxyamine under air provides the redox polymer with a high yield. Its electroactivity is evaluated by an electrochemical quartz crystal microbalance (EQCM).

Macromolecules with aliphatic backbones bearing pendant stable radical groups (like nitroxides) have attracted much attention in applications as cathode materials for lithium ion rechargeable batteries in which high charge/discharge efficiencies are targeted.¹ Several types of these redox polymers have previously been reported.^{2–4} The advantages of these redox polymers are that they are designable, environmentally friendly and mechanically flexible.^{4–7} Poly(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl methacrylate), PTMA, is one of the most promising redox polymers for application in organic radical batteries. It consists of a polymethacrylate bearing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in the repeating unit. This nitroxide presents a reversible two-couple redox activity: oxidation to oxoammonium cation at around 3.6 V (vs. Li/Li⁺) and reduction to an aminoxy anion at around 2.6 V (vs. Li/Li⁺).^{8–10} The theoretical capacity of PTMA approaches 111 mA h g⁻¹, which is slightly lower than some inorganic cathode materials, such as LiFePO₄.¹¹

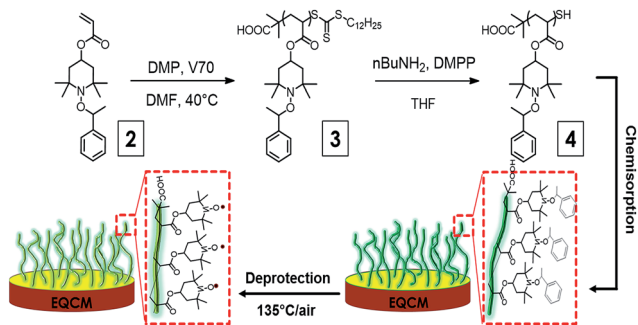
Several polymerization methods have been reported to synthesize nitroxide bearing polymers (radical polymers), including: (i) reaction of 2,2,6,6-tetramethyl-4-aminopiperi-

dinyloxy with poly(methyl methacrylate) or poly(pentafluorophenyl acrylate),¹² (ii) free radical polymerization (FRP) of 2,2,6,6-tetramethylpiperidin-4-yl methacrylate (TMPM) monomer, with a subsequent oxidation of the secondary amine^{13,14} or (iii) direct anionic polymerization of a nitroxide bearing monomer.^{9–16} While the first route is marked by a low degree of functionalization (<25%), anionic polymerization permits good functionalization but requests stringent reaction conditions. As radical polymerizations are uncomplicated in their general handling, they are preferred over ionic procedures. Nevertheless, an intrinsic drawback of free radical polymerization is the lack of control over the molar mass and the dispersity (PDI) of the polymer due to irreversible termination and transfer reactions. Low molar mass fraction of the radical polymers (resulting from these side reactions) may dissolve into electrolytes, leading to batteries with low energy capacity and poor cyclability.^{17,18} Moreover, radical synthetic procedures generate nitroxides at the last stage of the process by chemical oxidation of the secondary amine precursor (poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate); PTMPM).^{19,20} Unfortunately, this oxidation process requires the use of strong oxidizing agents such as 3-chloroperoxybenzoic acid^{9–17} or hydrogen peroxide in the presence of sodium tungstate^{18–21} that often lead to side reactions (cross-linking, over-oxidation) and consequently decrease the radical concentration that only reaches 65 to 81% of the theoretical amount of redox active nitroxides.⁹ As an alternative, we present for the first time a new approach toward redox polymer by Reversible Addition Fragmentation Transfer (RAFT) polymerization of an alkoxyamine bearing acrylate (4-acryloyloxy-1-((1'-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine; 2) (Scheme 1). The alkoxyamine moieties of the resulting polymer, 3, are then cleaved under aerobic condition to provide the corresponding TEMPO functionalized polyacrylate with a high yield in nitroxide. The ω-functionality of the polymer chain is then exploited for the preparation of surface-tethered redox polymer brushes on the surface of electrochemical quartz crystal microbalance (EQCM) sensors. Besides quantifying the mass loading of surface-attached polymers,^{22–24} EQCM

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Scheme 1 Synthetic strategy for the formation of a polyacrylate bearing TEMPO and its grafting onto a gold surface.

technique is also exploited to study the electrochemical behavior of redox active polymer brush.

Scheme 1 summarizes the synthetic strategy envisioned for the polymer-bearing TEMPO. It consists in polymerizing an acrylate bearing an alkoxyamine by RAFT polymerization using a trithiocarbonate (2-dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid; DMP) as RAFT agent. Additionally to enable the precise control over the molar mass of the polymer and its dispersity, this RAFT technique permits to provide a polyacrylate end-functionalized by a trithiocarbonate group that will be later exploited for the polymer grafting onto a gold surface. The alkoxyamine group is nothing else but a precursor of nitroxide by thermal cleavage of the C–ON bond of the alkoxyamine under aerated conditions, as it will be discussed later.

The acrylate bearing the alkoxyamine 2 was prepared by atom transfer radical addition (ATRA) of 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl with 1-bromoethyl benzene,^{25,26} followed by esterification of alcohol function with acryloyl chloride (Scheme S1†). ¹H NMR spectroscopy of products 1 and 2 confirms their structure (Fig. 1).

RAFT polymerization of 2 was then carried out using DMP as RAFT agent in the presence of 2,2'-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V70) as free radical initiator in DMF at

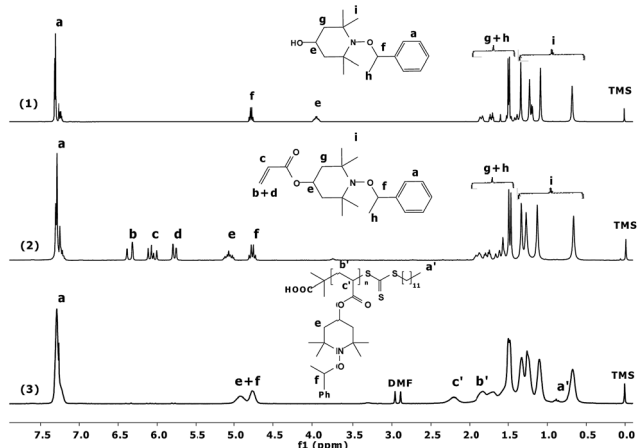


Fig. 1 ¹H NMR spectra (in CDCl₃) of (1), (2) and (3).

40 °C. V70 was used in order to perform the polymerization at a low temperature that was required to avoid the C–ON bond cleavage of the alkoxyamine. After optimizing the experimental conditions, especially the [DMP]/[V70] ratio, a controlled polymerization of 2 was noted with [DMP]/[V70] = 1/0.15 (Fig. 2). The molar mass of the polymer increased linearly with the monomer conversion, the dispersity was low all along the polymerization process until high conversion and the time dependence of $\ln([M]_0/[M])$ was linear; all these observations are in line with a controlled process. Fig. 3 shows that the SEC chromatograms are monomodal and shift towards the higher molar mass side with the course of the polymerization.

Fig. 1, spectrum (3), shows the ¹H-NMR spectrum of the purified polymer obtained in DMF at 40 °C using the [2] : [DMP] : [V70] ratio of 30 : 1 : 0.15 ([2] = 0.5 M, 6 h polymerization time, 98% conversion). The characteristic signals of the repeating units are found at 2.2 ppm for –CH–CO, and the –CH₃ groups of the ω-chain end at 0.88 ppm. Integration of the signal at 4.6 to 5.1 ppm corresponding to the two proton “e + f” of the repeating unit and at 0.88 ppm of the –CH₃ group of the ω-chain-end enables to calculate the molar mass of the polymer. This molar mass ($M_{n,NMR} = 9800 \text{ g mol}^{-1}$) is very close to the theoretical one ($M_{n,th} = 10\,000 \text{ g mol}^{-1}$) for the polymer formed after 98% monomer conversion (Fig. 1).

In order to enable the chemisorption of the redox active polymer onto gold, its precursor 3 was treated by an excess of

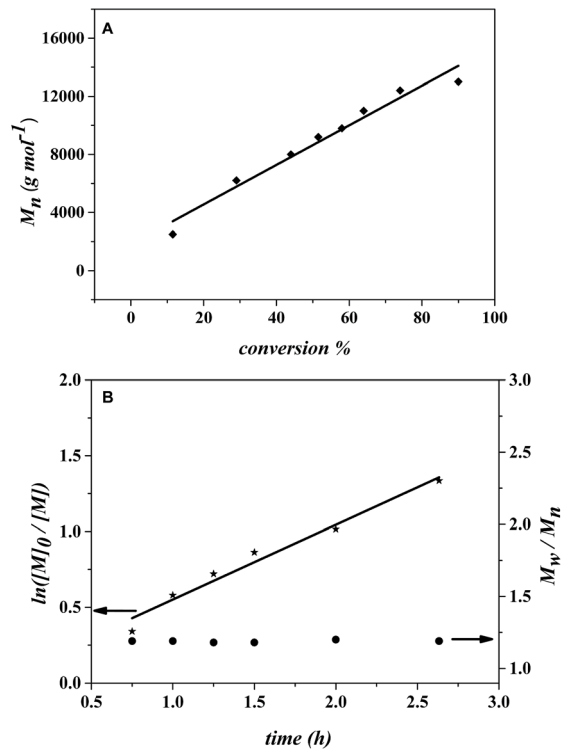


Fig. 2 (A) Evolution of molar mass of the polymer with the monomer conversion, and (B) semilogarithmic plot for RAFT polymerization of 2 in THF at 45 °C. Conditions: [2] : [DMP] : [V70] = 100 : 1 : 0.15, [2] = 0.5 M. Experimental M_n 's were measured by size exclusion chromatography (SEC) in THF using polystyrene calibration.

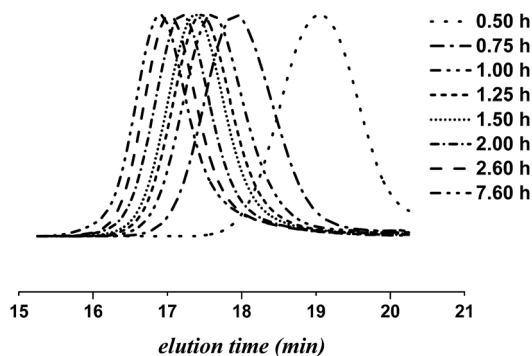


Fig. 3 Size exclusion chromatography (SEC) traces for the RAFT polymerization of **2** carried out in DMF at 40 °C against PS standards at a flow rate of 1 ml min⁻¹.

1-hexylamine. The trithiocarbonate end-group was therefore converted into thiol by aminolysis.^{27,28} The addition of a small amount of a reducing agent dimethyl phenyl phosphine (DMPP), suppressed the undesired side reaction, resulting from the interpolymeric oxidative coupling of the thiol end groups into disulfide.²⁹ Fig. S1a† shows the absence of any detectable high molar mass contamination in the GPC profile of **3** and **4**. During aminolysis, the characteristic yellow colour of the solution disappeared, consistent with the cleavage of RAFT end group (Fig. S2†). UV-visible analysis of the purified polymers confirms the disappearance of the C=S band at 310 nm (Fig. S3†). ¹H NMR analysis of the polymer before and after aminolysis highlights the success of the reaction with typical signals of the methyl group of the trithiocarbonate terminal end-group at 0.88 ppm that disappeared after aminolysis (Fig. S4†). Ability of thiol-based compounds to form dense and ordered self-assembled monolayers (SAMs) onto a gold surface was well known.^{30,31} The deposition of the redox polymer onto gold was then carried out using a QCM-d gold sensor. The thiol end-functionalized polymer **4** was immobilized to the sensor by drop casting a dilute solution of the polymer in THF (1 mg mL⁻¹), followed by intensively rinsing the coated substrate by THF to remove physisorbed polymer (Scheme 1).

The polymer-bearing TEMPO was then produced by heating (**4**) at 135 °C in *tert*-butylbenzene under aerated conditions (Scheme 1). At this temperature, the C-ON bond of the alkoxyamine cleaved, releasing TEMPO on the polymer chain while oxygen avoided the back reaction by deactivation of ethyl benzyl radical.³² A conversion of 90% was determined for polymer chain in solution by UV-vis spectroscopy (at 461 nm) using a calibration with TEMPO standards (Fig. S5†). The EPR spectroscopy of the so-formed polymer in *tert*-butyl benzene presents a broad central signal related to the fast spin exchange mechanisms due to the close distance among the polymer-bound radical sites (Fig. S6†).^{8,33} Fig. S2.B† displays the GPC traces before and after thermal treatment, and evidences that the low PDI of the starting polymer is preserved. The thermogravimetric analysis of the deprotected polymer performed under oxygen, show high stability until 180 °C, which prove their stability during thermal process (Fig. S7†). When applying the

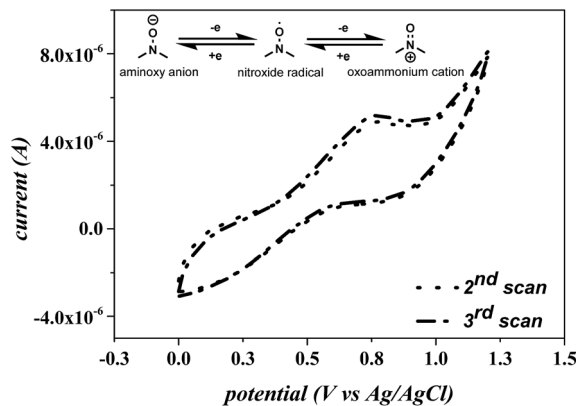


Fig. 4 Cyclic voltammogram of redox polymer layer on a gold disk EQCM electrode in a 0.5 M solution of *n*-Bu₄NClO₄ in acetonitrile at a scan rate of 10 mV s⁻¹.

same thermal treatment to the QCM-d sensor coated by **4**, the corresponding redox active polymer was formed on the sensor. The high frequency shift ($\Delta f_7 = 611.1$ Hz) that was monitored after deposition and thermal activation of **4** indicated the formation of an adherent polymer layer because it was not removed after intensive rinsing. According to the Sauerbrey equation,^{24,34} the calculated chemisorbed amount of redox polymer was 10.71 $\mu\text{g}\cdot\text{cm}^{-2}$.

Cyclic voltammetry was then recorded on the so-modified gold sensor to evaluate the electroactivity and redox reversibility of the chemisorbed redox active polymer film (Fig. 4). Two pairs of chemically reversible redox peaks were observed. The first pair of peaks less defined is in the range of 0–0.3 V, corresponding to the redox reaction between the nitroxide and aminoxy anion (n-type doped state). The second pair of peaks is at around 0.75 V, attributed to the redox reaction between the nitroxide and oxoammonium cation (p-type doped state). The two-electron redox reaction behaviour of PTA is similar to that of the reported PTMA redox activity.⁶ The specific capacitance of the polymer was calculated by the following equation:^{35–37}

$$C = \frac{1}{m\nu(V_a - V_c)} \int_{V_a}^{V_c} I(V) dV$$

where $\int_{V_a}^{V_c} I(V) dV$, m , ν and $(V_a - V_c)$ states for the integrated area of oxidation peak in cyclic voltammograms, the mass of the film, the sweep rate and the potential window respectively.

The specific capacity was found to be 103 mA h g⁻¹, corresponding to 87% of the theoretical capacity of this redox polymer³⁸ (119 mA h g⁻¹) (see ESI†).

Conclusions

This work presents the controlled synthesis of a redox polymer, a polyacrylate bearing TEMPO, by RAFT polymerization of an alkoxyamine monomer, followed by the thermal activation of the alkoxyamine pendant groups of the so-formed polymer under aerated conditions. The formation of a redox active polymer film onto the gold surface of a QCM-d sensor is also demonstrated by

the chemisorption of the polyacrylate bearing alkoxyamine that has been end-functionalized by a thiol group, followed by thermal activation of the alkoxyamines. Coupling data from QCM-d and electrochemical measurement provides a powerful approach to calculate the specific capacitance (mA h g^{-1}) of the redox polymer that is 87% of the theoretical value.

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