

Combination of Electrografting and Ring-Opening Metathesis Polymerization: An Efficient Way to Prepare Polynorbornene Brushes on Conducting Substrates

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Nowadays, increasing attention is paid to films of polymer chains covalently bonded to solid surfaces. [1, 2] This strategy is very useful to modify the surface properties of inorganic materials, to improve the interfacial bonding in composites, and to prepare novel inorganic – organic hybrids.[3,4] In addition to this technique that consists of the chemical bonding of preformed end-reactive chains to the surface ("grafting onto" method), polymer brushes can be formed by the "grafting from" method, that is, the initiation and growth of the chains from the solid surface. When this substrate is electrically conducting, electropolymerization has proved to be a powerful method to deposit polymers that highly adhere to the substrate. [5-7] Indeed, the electroreduction of monomers of the (meth)acrylate type at an appropriate potential leads to the rapid formation of an homogeneous polymer film on the cathode whatever its shape (plate, fiber) and nature (metal, carbon, indium tin oxide (ITO) glass).[8,9] That the polymer is chemisorbed onto the substrate is confirmed by insolubility in a good solvent for the polymer and by peeling tests.[10,11].

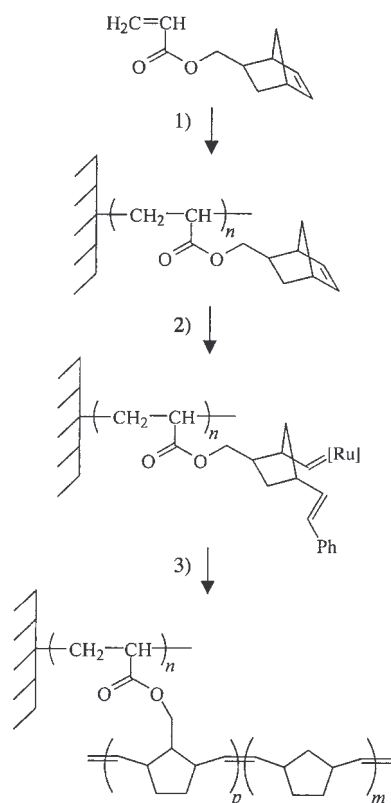
However, as a result of the formation of an insulating poly(meth)acrylate film on the cathode, the substrate is rapidly passivated (rendered inactive) which limits the film thickness (< 100 nm). Moreover, monomers that contain protic functions (alcohol, amine, carboxylic acid, etc.) cannot be electrografted because of their reduction at the same or at a less cathodic potential than the (meth)acrylate.

The recent development of well-defined and highly active catalysts by the groups of Schrock[12] and Grubbs,[13] has also reactivated interest in the ring-opening metathesis polymerization (ROMP) of cycloolefins, particularly for applications in solid-phase chemistry.[14-17] Therefore, a combination of living ROMP and electrografting appears to be a promising strategy to overcome the limitations of the electrografting process. Indeed, the thickness of the polymer film "grafted" to the electrode could be easily tuned by a second step of "grafting from" polymerization of cycloolefins. Moreover, advantage can be taken of the compatibility of the Grubbs catalyst with a wide-range of functional norbornenes to impart additional functionality to the surface of the conducting substrate.

The first step of the new process of surface modification reported herein relies on the electrografting of an acrylate, the ester group of which can be further used to initiate the ROMP of a cycloolefin. Scheme 1 shows the whole process that has been tested first for norbornenyf methylene acrylate (NBE-A).

Figure 1 compares the voltammogram recorded for the reduction of norbornene (NBE; curve A) and NBE-A (curve B) using a Cu wire as the cathode in DMF treated with tetraethyl ammonium perchlorate (TEAP). Two distinct phenomena are observed in the case of NBE-A as is usually reported for the electroreduction of acrylates, these are, electrografting of PNBE-A to the cathode at the less cathodic potential (peak I), and initiation of the polymerization in solution concomitant to the degrafting of the originally formed film (peak II).[18] The cathode is thus passivated as soon as the reduction occurs, which results in the dramatic decrease of the current intensity beyond peak I. For NBE, no reduction occurs (curve A) which confirms the stability of NBE in the potential range of interest for this process.

Whenever the applied potential is that corresponding to the top of peak I, the electrode is passivated after a few seconds, since peak I is no longer observed during a second potential scan (inset in Figure 1).



Scheme 1. Reaction scheme for the entire process. 1) Electrografting of NBE-A by cathodic polarization of the conducting substrate in DMF/TEAP mixture. 2) Grubbs initiator fixation by 5 min immersion in a dichloromethane solution; $[\text{Ru}]$ = ruthenium complex. 3) ROMP by dipping in the NBE solution at room temperature.

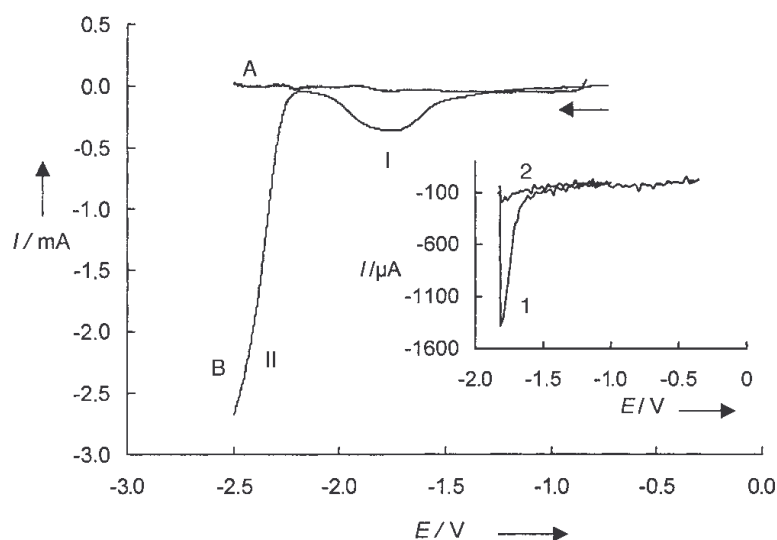
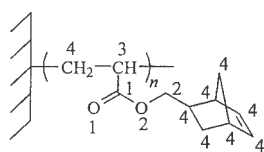


Figure 1. Cyclic voltammogram of A) NBE (0.75 M) and B) NBE-A (0.75 M) and TEAP (0.05 M) solution in DMF I) Grafting peak. II) Polymerization in solution. Inset: enlargement of the peak I recorded on steel plate cathode 1) first scan, 2) second scan.

Table 1. XPS data of the grafted P(NBE-A).



Atom	Position [eV]	Width	Area	%[a]	Theoretical amount[%]
C1	288.85	2.35	298	8.65	9.09
C2	286.83	1.26	298	8.65	9.09
C3	286.01	1.21	298	8.65	9.09
C4	285.05	1.40	2550	74.04	72.73
O1	533.34	2.27	778.9	50.00	50.00
O2	532.20	1.69	778.9	50.00	50.00

[a] Atomic experimental amount [%].

The deposition of the insulating film, which is not visible to the naked eye, has been confirmed by X-ray photoemission spectroscopy (XPS; Table 1); the experimental C1 and O1 curves are nicely fitted by taking into account the chemical structure of the expected grafted poly(norbornenylmethylene acrylate).

To attach the polymerization catalyst to the poly(NBE-A) coated surface, the modified electrode was dipped in a solution of the Grubbs catalyst (40 mg of Grubbs catalyst in 10 mL CH_2Cl_2) for five minutes and then rinsed three times with pure dichloromethane to remove any excess catalyst. Finally, the exposure of this modified substrate to a solution of NBE in CH_2Cl_2 (concentrations ranging from 0.1M to 0.5M), for a period of 10 to 30 minutes resulted in the "grafting from" polymerization.

The poly(NBE) (PNBE) grafted steel electrodes were washed extensively with dichloromethane, a good solvent for PNBE, and dried. Since only half of the electrode surface was dipped into the NBE-A solution during electrografting, only this part of the surface could initiate the NBE polymerization. Accordingly this part of the surface was covered by a white film of PNBE, visible to the naked eye, which confirms at least qualitatively the successful grafting of polyNBE from the P(NBE-A) grafted film.

The FT infrared reflection absorption spectroscopy (IR-RAS) analysis of the PNBE film shows three characteristic peaks of high intensity at 2955, 2860, and 964 cm^{-1} . The absorption at 964 cm^{-1} is typical of the *trans* double bonds of PNBE. Additional peaks of lower intensity are also observed at 1467, 1423, and 742 cm^{-1} . The *cis* double bonds of PNBE actually absorb at 742 cm^{-1} . [19] Figure 2 A shows that the intensity of the FTIR-RAS peaks of PNBE in the 3200 — 2500 cm^{-1} range increases with the NBE monomer concentration at constant polymerization time, which indicates a parallel increase in the PNBE film thickness.

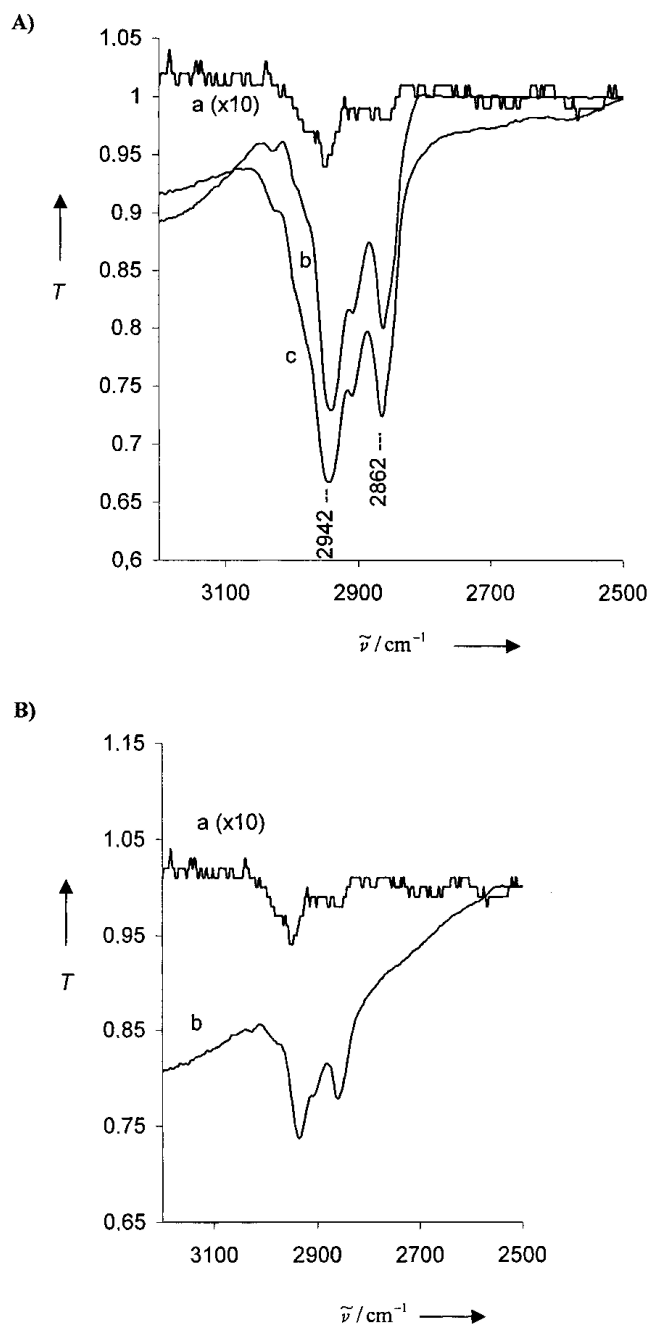


Figure 2. FTIR-RAS spectra of grafted PNBE films on steel, A) after 10 min polymerization from a CH_2Cl_2 solution with various NBE monomer concentrations: a) 0.1M, b) 0.25 M, c) 0.5 M. B) From a 0.1M NBE solution in CH_2Cl_2 after various polymerization times at room temperature: a) 10 min, b) 30 min.

The same observation holds whenever the polymerization time is increased at constant monomer concentration (Figure 2B).

Evaluation by SEM (scanning electron microscopy) of the film prepared from the 0.1M NBE solution in 10 min shows the film to be about 6 μm thick.

Figure 3 is a comparison of the surface of the steel electrode before and after grafting as observed by SEM. The PNBE film covers completely and homogeneously the treated surface to the point where the roughness of the original surface is totally masked.

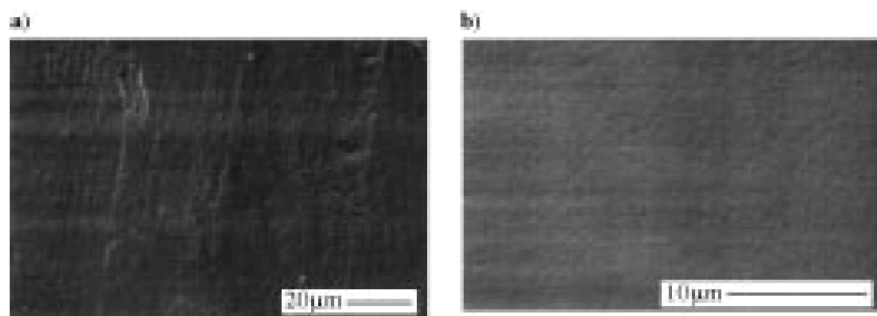


Figure 3. SEM images of a) neat steel, b) PNBE grafted onto steel.

The adhesion of the PNBE film onto steel has also been estimated by peeling tests. The surface adhesion, that is the peeling energy required to detach a standard scotch tape (3M-Acrylic foam 4930) from the neat surface is 1850 Jm^{-2} . This adhesion increases to 2400 Jm^{-2} when the test is repeated in case of the PNBE grafted surface. This value is however smaller than the actual adhesion energy, since the polymer film remains attached to the substrate after peeling.

The versatility of the electrochemical technique allows this coating method to be extend to various types of solid substrates. Electrografting of NBE-A followed by ROMP of NBE has been found successful not only on steel but also on copper wires, carbon plates, and carbon fibers. Figure 4 illustrates the SEM image of PNBE-modified fibers after extensive washing of the PNBE with dichloromethane in a Soxhlet apparatus for 13 days.

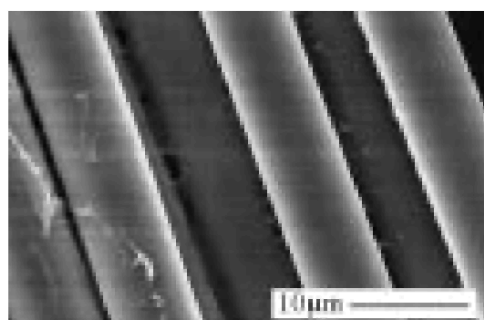


Figure 4. SEM image of PNBE grafted onto carbon fibers.

The electrografting of a conducting substrate by a poly-acrylate film (such as poly(NBE-A)) which can be used further to initiate the growth of a polymer brush (e.g. of PNBE) is thus an efficient technique to control the thickness of well-adhering polymer films. Advantage can be taken of the brush in the development of electrochemical sensors. Moreover, the coating of steel, for example, by a thick hydrophobic polymer film is a very useful way to impart corrosion protection. For instance, the PNBE coating has proved highly successful in protecting steel against corrosion (copper test). Indeed, whenever a drop of an acidic aqueous solution of CuSO_4 is deposited onto neat steel and on steel coated by PNBE, the oxidation of the neat surface is immediate as evidenced by the very fast formation of metallic Cu. In contrast, the coated surface remains unchanged at least for 12 h (Figure 5).

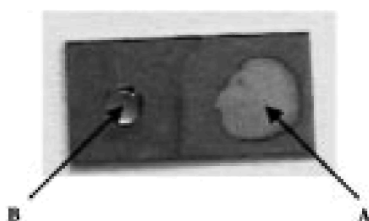


Figure 5. Steel plate after application of two drops of a CuSO_4 solution: A) neat steel: copper from the reaction with CuSO_4 ; B) PNBE grafted steel: the drop of CuSO_4 solution does not react.

Modification of carbon fibers by well-adhering polymer chains that contain reactive double bonds is also of importance in the field of composite materials. Finally the general concept illustrated in this paper can be extended to the ROMP of functionalized NBE, so paving the way to functionalized surfaces with tunable properties.

1. Experimental Section

NBE-A was prepared by reaction of 5-norbornene-2-methanol (41 mmol) with excess acryloyl chloride (123 mmol) in the presence of triethylamine (123 mmol), and dried before use.

Monomers, solvents, and conducting-salt were dried before use. Electrochemical experiments were carried out in a one-compartment cell with a platinum pseudoreference counter-electrodes with a PAR EG&G poten-tiostat (Model 273A). All the experiments were carried out in a glovebox under a dried inert atmosphere.

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