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## Covalent Grafting Of Functional Oligo-Isoprenes Onto Silica-Based Surfaces To Achieve Robust Elastomeric Monolayers, Thin Films And Coatings

*Thi Nguyet TRAN, Arnaud NOURRY, Pamela PASETTO, Guillaume BROTONS\**

Institut des Molécules et Matériaux du Mans (IMMM), UMR 6283 CNRS – Le Mans Université,  
Avenue Olivier Messiaen, 72085 Le Mans Cedex, France

**KEYWORDS.** Natural rubber, polyisoprene and oligoisoprene, grafted polymer brushes, non-leaching sustainable coatings, bio-based elastomers, ultra-thin polymer films.

### ABSTRACT.

A new methodology is presented to covalently graft polyisoprene from natural or recycled rubber on hydroxylated and silicon-containing surfaces. For this purpose, we first synthesized novel functional telechelic oligomers from natural rubber, bearing a hydroxyl group at one chain end and a silane group at the other, which allowed their direct tethering on silicon-based and other materials. As alternative approach, we also synthesized bi-functional telechelic oligomers with a ketone and an aldehyde end-moieties and they reacted selectively with surface amino groups, introduced *via* a pre-functionalization step using commercial amino-alkoxysilanes. A high glass surface coverage density was reached and the oligoisoprenes free chain-ends were converted to acrylate functions, to possibly grow more polymer or to engage a photopolymerization process with other bio-based acrylate-terminated telechelic oligoisoprenes, in order to obtain thick films. In this way, ultra-thin oligomer layers, copolymer brushes, as well as grafted films and bulk materials were formed and characterized at sub-nanometer resolution using X-rays Reflectivity. A strong covalent grafting of polyisoprene coatings was achieved and resisted to long immersions in water and aggressive organic solvents under strong mechanical agitation. The robust molecular, thin films, and bulk sheathings are versatile polymeric constituents and represent a new family of sustainable coatings.

### INTRODUCTION

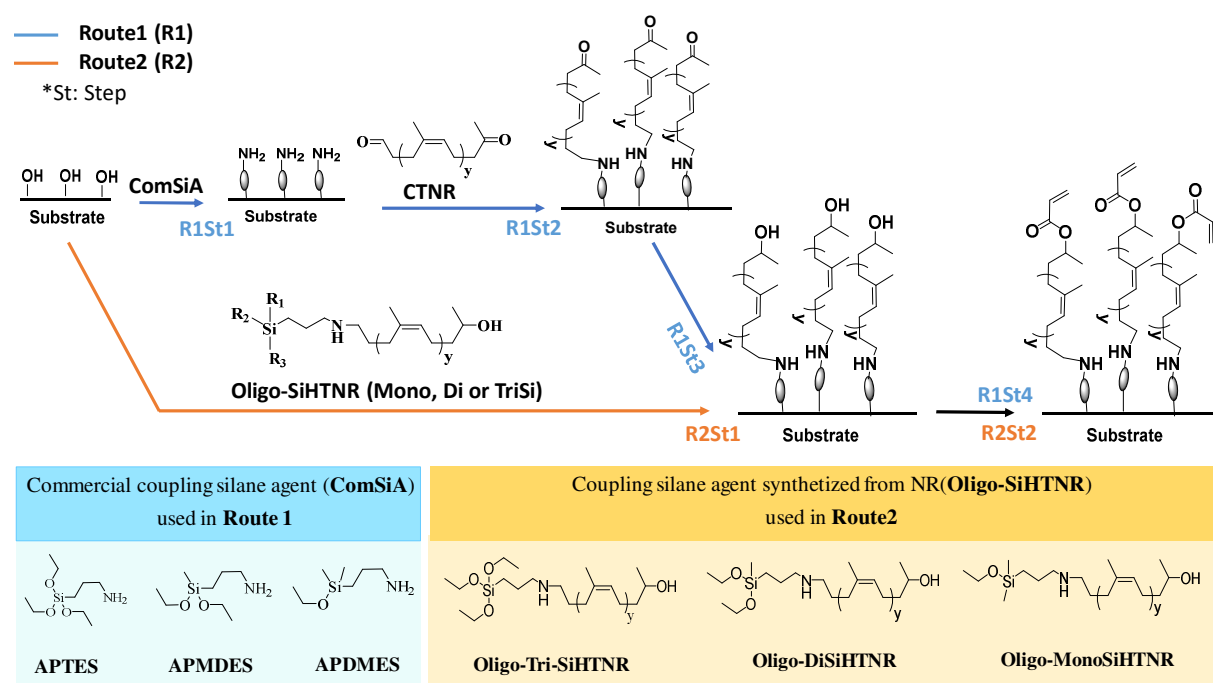
Hybrid inorganic substrate /organic polymer materials are extremely interesting because of the combination of features from both components and are nowadays integral part of many devices.<sup>1-7</sup> Two main strategies are followed to graft a polymer layer on bare or functionalized surfaces, called “grafting from” if the polymer grows from the surface by adding monomers;

“grafting to”, if the polymer chain already formed is tethered to the surface.<sup>8</sup> The development of controlled radical polymerization allowed the control over the polymer chain length and dispersity and the portfolio of available approaches and methodologies has been extensively covered.<sup>9-10</sup> In the form of polymer coatings on substrates, one of the major challenges is to increase the robustness and adherence so to guarantee a long lifecycle. To improve adhesion with rubbers, new technologies appeared, including surface treatments such as plasma etching (corona discharge) or chemical treatments such as bromination, fluorination, sulfonation and ozonolysis.<sup>11-13</sup> Surface treatments are expected to only affect the top few molecular layers and changes in the bulk are kept minimal. Nevertheless, elastomeric films that are just physically bound to their substrate in absence of covalent links, are often easily detachable by washing or calving. Therefore, the need to establish covalent anchoring protocols and functionalization routes at the inorganic/polymer interface is still a subject of interest.<sup>14-15</sup>

Natural Rubber (NR) is one of the most used polymers in many applications including tyres, since it is a renewable bio-sourced elastomer possessing excellent properties such as high elasticity, mechanical strength and fatigue resistance over a wide range of operating temperatures.<sup>16-17</sup> Thin polyisoprene (PI) films play also an important role in modern technologies including electronic applications and anti-fouling coatings.<sup>18-19</sup> D. Liu *et al.*<sup>19-20</sup> demonstrated that the adsorption of the protein bovine serum albumin was very low on surfaces of PI thin films and the patterning of adhesion of proteins on PI-copolymer surfaces influenced the biological cell attachment and spreading. K. Shiju *et al.*<sup>18</sup> pointed out that an iodine doped PI thin film could be used as an active channel in the organic switching devices. K. Ayche *et al.*<sup>21</sup> used PI thin films as possible protective layer for microelectromechanical system (MEMS) devices, as a water barrier. Nevertheless, in most of cases, PI thin films were just deposited on their substrate by spin or dip coating deposition techniques.<sup>22</sup> Derouet *et al.*<sup>23-24</sup> functionalized silica particles with polyisoprene, growing the chains from the surface *via* the very demanding technique of anionic polymerization of the oil-issued isoprene monomer. As in many applications the bio-sourced natural rubber could replace silicon-based coatings, for instance in the preparation of fouling release paints<sup>25</sup>, we choose to use this hydrophobic biopolymer for our model study.

We wanted to pursue the same objective of D. Derouet *et al.* but we could take advantage of the two methodologies later developed in our group to obtain telechelic oligomers from natural rubber or waste tyres.<sup>26,27</sup> Carbonyl Telechelic Natural Rubber oligomers (CTNR) can be obtained with a targeted molecular weight and reasonably narrow dispersity with an easily

upscalable process. Their chain ends can be transformed using the classical organic chemistry reactions to obtain building blocks for the synthesis of new materials, such as polyurethane films<sup>28</sup> or foams.<sup>29</sup> In this study, we developed a new methodology to tether covalently a thin film of PI on silicon-containing materials, choosing glass as model, *via* two approaches. The first one consisted on activating the surfaces containing free hydroxyl groups, and on grafting commercial amino-alkoxysilanes (APTES, APMDDES or APDMES, Figure 1, route 1) to obtain the amino group (-NH<sub>2</sub>) functionalization. Then Carbonyl Telechelic Natural Rubber oligomers were grafted *via* reductive amination reaction. Conversely, the second route consisted in the direct covalent grafting on the glass bare surface of a new bi-functional oligomer, Oligo-SiHTNR, synthesized from NR (Figure 1, route 2). Once all the chain-ends of the grafted oligomers were transformed into acrylate groups, we post-polymerized



oligoisoprene films and tested their resistance to solvents immersion [water and tetrahydrofuran (THF)]. In this way we built dense and tethered molecular PI layers, thin films and thick or bulk coatings.

**Figure 1.** Schematic presentation of the two routes used to covalently graft natural rubber oligomers on surface hydroxyl groups, to form a reactive polyisoprene coating with ketone, hydroxyl or acrylate end-moieties.

The grafted polymeric layers were in depth studied to determine the three-dimensional structure, the thickness, the polarity and to prove the covalent bonding and its resistance in

rough conditions as solvent immersion. As example of the versatility of our approach, the synthesis of amphiphilic copolymers brushes was also performed.

Previous work in our group demonstrated that CTNR oligomers can be obtained also from waste tyre granulates and powders<sup>30</sup>, so that the results presented in this research work could be extended and polyisoprene could also come from end-of-life tyres, thus transforming a waste into a new high-value raw material.

## EXPERIMENTAL SECTION

### 1) Chemicals and Materials

Natural rubber (STR5LCV60) was produced by Jana Concentrated Latex Co., Songkhla, Thailand. Periodic acid ( $\text{H}_5\text{IO}_6$ ,  $\geq 99\%$ ), acryloyl chloride ( $\geq 97.0\%$ ), triethylamine ( $\text{Et}_3\text{N}$ ,  $\geq 99.0\%$ ), methacryloxypropyl triethoxysilane (MAPTES,  $\geq 98.0\%$ ), toluene (dry,  $\geq 99\%$ ), (3-aminopropyl)(ethoxy) dimethylsilane (APDMES,  $\geq 97\%$ ), 3-aminopropyl(diethoxy) methylsilane (APMDES,  $\geq 97\%$ ), 3-aminopropyltriethoxysilane (APTES,  $\geq 99\%$ ), 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173,  $\geq 97.0\%$ ), AIBN (2,2'-Azobis-2-methylpropionitrile, 98%), anhydrous dimethyl sulfoxide (DMSO,  $\geq 99.9\%$ ) were purchased from Sigma Aldrich and used without any further purification. The purity information was provided by the manufacturer. Trifluoroacetic acid was purchased from Alfa Aesar. Sodium borohydride ( $\text{NaBH}_4$ ,  $\geq 98\%$ ), 4-aminobutan-1-ol ( $\geq 98\%$ ), N, N'-bis (tert-butoxycarbonyl)-1H-pyrazole-1-carboxamidine ( $\geq 98\%$ ) were purchased from Acros Organics. Sodium bicarbonate ( $\text{NaHCO}_3$ ) technical reagent grade, anhydrous magnesium sulfate ( $\text{MgSO}_4$ ) laboratory reagent grade, sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) and sodium chloride ( $\text{NaCl}$ ) general purpose grade were purchased from Fisher Scientific. Dichloromethane (DCM), tetrahydrofuran (THF), and toluene were purchased from Aldrich and dried in a dry solvent station GT S100 (Glass Technology). Ethyl acetate ( $\text{EtOAc}$ ), Cyclohexane, Ethanol ( $\text{EtOH}$ ), were purchased from Fisher Scientific and used after distillation. Water was deionized using Ultrapure Milli-Q Reagent Water System Millipore and used at  $18\text{M}\Omega$ . Concentrated HCl and NaOH solutions (research grade; Aldrich Chem. Co.) were diluted to obtain the desired concentrations. Microscope Slides (76x26 mm, ground edges  $45^\circ$ , white Glass, Thermo Scientific, two bathes used and named type 1 and 2) were purchased from Thermo Scientific. Guanidinium monomer was prepared following a procedure already described.<sup>31</sup>

## 2) Chemical Characterization

### 2.1) Nuclear magnetic resonance (NMR) Analysis

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were respectively recorded at 400 and 100.6 MHz on a Bruker<sup>TM</sup> spectrometer. The samples were dissolved in chloroform-*d* ( $\text{CDCl}_3$ ) or methanol-*d*<sub>4</sub> ( $\text{CD}_3\text{OD}$ ). The chemical shifts ( $\delta$ ) are expressed in part per million (ppm) relative to  $\text{Me}_4\text{Si}$  and the coupling constants (J) in Hertz.

### 2.2) Size Exclusion Chromatography (SEC) Analysis

Number-average molecular weight ( $\overline{M}_n$ ) and dispersity ( $\text{Đ}$ ) were measured by size exclusion chromatography using THF as eluent (flow 1 mL/min), at 35°C, on a Waters<sup>®</sup> chain 2707 autosampler equipped with a 1515 Isocratic Pump and a guard column (Styragel 30x4.6 mm) connected to a column (Styragel HR2 + HR4, 300x7.8mm). The Waters<sup>®</sup> 2996 PDA and Waters<sup>®</sup> 2414 Refractive Index Detector were used. Calibration was performed with polystyrene (PS) standards in the range from 580 g/mol to 483000 g/mol. The molecular weights of the oligoisoprenes were corrected according to the Benoit factor equal to 0.67.<sup>32</sup> The molecular weight of all oligomers was determined by SEC and by  $^1\text{H}$ -NMR. The  $^1\text{H}$ -NMR spectrum for the carbonyl telechelic oligomers was exploited according to equation (1) and the relative number-average molecular weight was referred to as  $\overline{M}_{n, \text{NMR}}$ .

$$\overline{M}_{n, \text{NMR}} = \left[ \frac{I_{5.13 \text{ ppm}}}{(I_{2.47 \text{ ppm}} / 4)} \times 68 \right] + 100 \quad (1)$$

where  $I_{5.13 \text{ ppm}}$  and  $I_{2.47 \text{ ppm}}$  were the integration values of the peaks at 5.13 ppm and at 2.47 ppm, respectively. 68 and 100 were the molar masses of the isoprene repeating unit and the chain ends of CTNR, respectively (g/mol).  $\overline{M}_{n, \text{NMR}}$  was used to calculate the molar concentration of the oligomers for the modification of the chains ends in the synthesis of hydroxy telechelic natural rubber (HTNR) and acrylate telechelic natural rubber (ACTNR).

### 2.3) Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectra were carried out with a Vertex 70V Bruker spectrometer with a deuterated triglycine sulfate detector, in ATR mode (attenuated total reflection). The absorption bands were recorded in the range of 400-4000  $\text{cm}^{-1}$  with 16 scans and a resolution of 2  $\text{cm}^{-1}$ . The data were analyzed using OPUS software.

### 3) Synthesis of oligomers from natural rubber

#### 3.1) Synthesis of carbonyl telechelic oligomers (CTNR)

The procedure to synthesize CTNR was developed in our laboratory.<sup>33-34</sup> In a 5L reactor, NR crumbs (50 g) were suspended in 1.250 L of THF for 15 h for dissolution, heating at 30°C under mechanical stirring. A solution 0.4 M of periodic acid (H<sub>5</sub>IO<sub>6</sub>) in THF was prepared separately, containing 24.22g of H<sub>5</sub>IO<sub>6</sub> and 275 mL of THF. This solution was added slowly to the NR solution using a dropping funnel and kept for 6h at 30°C under stirring. The obtained suspension was filtered. THF was eliminated under reduced pressure then the oligomers were dissolved in distilled dichloromethane (same volume as THF volume used to perform the reaction). The organic phase was washed twice with an aqueous solution composed by 70% vol of saturated NaHCO<sub>3</sub> (700 mL) and 30 % vol of saturated NaCl (300 mL). The second washing was performed twice with an aqueous solution composed by 50 % vol of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (20% w/w, 500 mL) and 50 % vol of saturated NaCl (500 mL). Then the organic phase was dried over MgSO<sub>4</sub> for 2h, filtered and evaporated in a rotary evaporator. The product was vacuum dried and an orange-yellow viscous liquid in 85% yield (42.5 g) was obtained.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>-d)  $\delta$  9.77 (s, 1H, CH<sub>2</sub>CHO), 5.10 (m, yH, CH<sub>3</sub>C=CH<sub>isoprene</sub> unit), 2.52-2.45 (m, 2H, CH<sub>2</sub>CHO), 2.43 (t, J=7.6 Hz, 2H, CH<sub>3</sub>COCH<sub>2</sub>), 2.34 (t, J=7.6 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CHO), 2.24-2.30 (m, 2H, CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>), 2.13 (s, 3H, CH<sub>3</sub>COCH<sub>2</sub>), 2.00-2.11 (m, 4yH, CH<sub>2</sub>, isoprene unit), 1.68 (s, 3yH, CH<sub>3</sub>CCH<sub>isoprene</sub> unit).

<sup>13</sup>C-NMR (101MHz, CDCl<sub>3</sub>-d)  $\delta$  (ppm): 208.6 (C=O<sub>ketone</sub>), 202.1 (C=O<sub>aldehyde</sub>), 135.2 (C=CH<sub>isoprene</sub> unit), 125.1 (C=CH<sub>isoprene</sub> unit), 44.0 (CH<sub>2</sub>COCH<sub>3</sub>), 42.4 (CH<sub>2</sub>CHO), 32.2 (CH<sub>2</sub>C=CH<sub>isoprene</sub> unit), 26.4(CH<sub>2</sub>CH=C<sub>isoprene</sub> unit), 24.3 (CH<sub>3</sub>CO), 23.5 (CH<sub>3</sub>, isoprene unit).

FTIR:  $\nu$  (cm<sup>-1</sup>): 3035 (H-C=C), 2959-2726 (CH), 1721 (C=O), 1665 (C=C), 834 (C=C-H).

$\overline{M}_{n, \text{NMR}} = 1260 \text{ g/mol}$

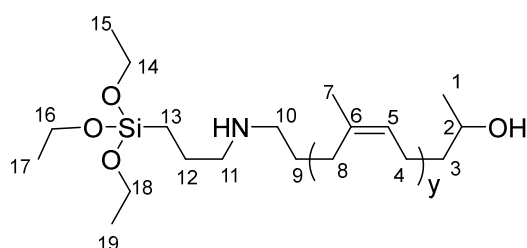
$M_{n, \text{SEC}} = 1600 \text{ g/mol}$ , Đ=1.89

#### 3.2) Synthesis of Oligo-SiHTNR

To a solution of CTNR (1.30 g, 1 mmol) in anhydrous chloroform (20 mL) was added, under Argon, the appropriate commercial coupling silane agent (1.0 mmol, 1 eq.). The reaction mixture was stirred for 24h at room temperature, concentrated under reduced pressure to give a colorless oil, which was diluted three times with chloroform (15 mL each time) then concentrated under reduced pressure again after each dilution. The residue was

subsequently taken up in a mixture of anhydrous chloroform (20 mL) and absolute ethanol (20 mL) and reacted with sodium borohydride (2 mmol, 2eq.) at room temperature for 30min. Solvents were evaporated to give a yellow-orange liquid. Excess borohydride was then hydrolyzed with water (60 mL). Oligo-SiHTNR were obtained by extraction with chloroform (40 mL). The organic phase was dried over  $\text{MgSO}_4$  then concentrated to provide the expected product: Oligo-DiSiHTNR (1.18 g, 80%) or Oligo-TriSiHTNR (1.23 g, 82%).

### Compound **Oligo-TriSiHTNR 3**



$^1\text{H-NMR}$ : ( $\text{CDCl}_3$ )  $\delta$  (ppm):  $\delta$  5.12 (t, yH, H-5), 3.89-3.75 (m, 7H, H-14, H-16, H-18 and H-2), 2.89-2.50 (m, 4H, H-10 and H-11), 2.11-1.98 (m, 4nH, H-8<sub>isoprene</sub> unit, H-4<sub>isoprene</sub> unit and 2H of H-9), 1.79-1.57 (m, 3nH of H-7<sub>isoprene</sub> unit and 2H, H-12), 1.24-1.13 (m, 12H, H-15, H-17, H-19 and H-1), 0.65-0.50 (m, 2H, H-13).

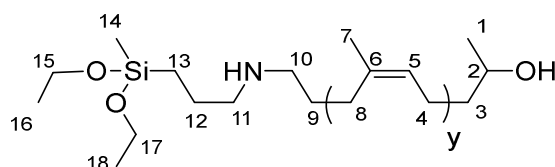
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ -d)  $\delta$ : 135.2 (C-6<sub>isoprene</sub> unit), 125.0 (C-5<sub>isoprene</sub> unit), 67.9 (C-2), 64.5 (C-10 or C-11), 58.5 (C-14, C-16, C-18), 32.2 (C-8<sub>isoprene</sub> unit), 26.4 (C-4<sub>isoprene</sub> unit), 23.4 (C-7<sub>isoprene</sub> unit), 18.3 (C-15, C-17, C-19).

FTIR : 3035  $\text{cm}^{-1}$  (H-C=C), 2959-2726  $\text{cm}^{-1}$  (C-H), 1589-1516  $\text{cm}^{-1}$  (C-N), 910-1187  $\text{cm}^{-1}$  (Si-O-C), 834  $\text{cm}^{-1}$  (C=C-H).

$$\overline{M}_{n, \text{NMR}} = 1470 \text{ g/mol}$$

$$M_{n, \text{SEC}} = 2200 \text{ g/mol}, D=1.84$$

### Compound **Oligo-DiSiHTNR 2**



$^1\text{H-NMR}$ : ( $\text{CDCl}_3$ )  $\delta$  (ppm):  $\delta$  5.12 (t, nH, H-5), 3.89-3.64 (m, 5H, H-15, H-17 and H-2), 2.89-2.48 (m, 4H, H-10 and H-11), 2.11-1.98 (m, 4nH, H-8<sub>isoprene</sub> unit, H-4<sub>isoprene</sub> unit and 2H of H-9), 1.79-1.57 (m, 3nH of H-7<sub>isoprene</sub> unit and 2H, H-12), 1.24-1.13 (m, 9H, H-16, H-18 and H-1), 0.65-0.45 (m, 2H, H-13), 0.22-0.03 (m, 3H, H-14).



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ -*d*)  $\delta$ : 135.2 (C-6<sub>isoprene</sub> unit), 125.0 (C-5<sub>isoprene</sub> unit), 67.9 (C-2), 64.5 (C-10 or C-11), 58.1 (C-15, C-17), 32.2 (C-8<sub>isoprene</sub> unit), 26.4 (C-4<sub>isoprene</sub> unit), 23.40 (C-7<sub>isoprene</sub> unit), 18.4 (C-16, C-18), -4.94 (C-14).

FTIR : 3035  $\text{cm}^{-1}$  (H-C=C), 2959-2726  $\text{cm}^{-1}$  (C-H), 1589-1516  $\text{cm}^{-1}$  (C-N), 910-1187  $\text{cm}^{-1}$  (Si-O-C), 834  $\text{cm}^{-1}$  (C=C-H).

$$\overline{M}_{n, \text{NMR}} = 1440 \text{ g/mol}$$

$$M_{n, \text{SEC}} = 2300 \text{ g/mol}, \text{Đ} = 1.86$$

#### 4) Experimental protocols to graft covalently oligoisoprene on glass

Two alternative routes were developed to reach a covalent grafting of NR oligomers bearing an acrylate at the chain-end on the surface of different supports: Route 1 and Route 2 (Figure 1). The first one (Route1) consisted in the immobilization of NR on glass surface using commercial silane coupling agents (ComSiA: APTES, APMDES or APDMES) to give the amino groups accessible on the surface (prefunctionalization step), before reaction with CTNR *via* reductive amination (functionalization step). Route 2 consisted in the one-step covalent grafting directly on the surfaces (Figure 1) of a new bifunctional oligomer, Oligo-SiHTNR, synthesized from NR with a silane group at one chain end.

All chemical structures and purity of the reagents used (APTES, APMDES, APDMES) were checked by NMR analysis. All glassware was cleaned in potassium hydroxide solution 0.1 M then in ethanol, rinsed with distilled water (3 times), and stored in a clean oven at 110°C until use. First, the glass surfaces (microscopy slides) were prepared through a series of cleaning procedures that removed contaminants. Freshly cleaned substrates were then activated in a UV-O<sub>3</sub> plasma for 15min (UVO-cleaner, Model N°42-420) and immediately placed in the reaction jar, which was closed and purged again extensively with Argon (over 10min).

##### 4.1) Description of functionalization conditions for Route 1

Route 1 consisted in the following steps: the activated glass surfaces were aminosilanized, thereby coated with amine groups that covalently coupled with CTNR compound *via* reductive amination reaction. The ketone groups were expected to be exposed to the air. Ketone groups were then chemically modified to hydroxyl groups *via* a reduction reaction. In the last step, an acrylate group was then introduced *via* an esterification reaction.

### Step 1: silanization, using commercial amino-silane coupling (R1St1)

To a 100 mL round bottomed flask, closed and purged extensively under Argon, anhydrous toluene (40 mL) was introduced and the appropriate volume of the reagent (APDMES, APMDES or APTES) was added to obtain the desired concentration. After 30 minutes of stirring at room temperature, a syringe was used to transfer 35 mL of this solution into a reaction vessel (a custom-designed microscopy slide-staining jar in glass with a Teflon screw cap and kept under Argon, see Figure 5). Then, the vessel was placed on an orbital shaker operated at 50 rpm. Different reactions were carried out at 22, 40 or 70°C for different times (all conditions tested are reported in Table 1). After this silanization step, the glass slides were rinsed individually with toluene (5min), water (5min), and ethanol (5min), all under *ultrasonic* agitation, and finally some were dried in an oven at 110°C for 15 min.

**Table 1.** Different conditions tested for the silanization step on glass surfaces (R1St1).

	APDEMS (MonoSi)	APMDES (DiSi)					APTES(TriSi)		
	S1(*)	S1	S2	S3-5	S7-8	S9-16	S1	S2	S3-4
[C] mol/L	0.086	0.086	0.086	0.030	0.086	0.086	0.086	0.086	0.030
Immersion temperature (°C)	RT	RT	RT	RT	70	40	RT	RT	RT
Argon flush / Sealed with a Teflon cap	Y / N	Y / N	Y / N	Y / N	Y / Y	Y / Y	Y / N	Y / N	Y / N
Immersion time (hours)	72	48	72	72	24	24	24	72	72
Dried at 110°C in an oven (in air if No)	N	N	N	N	Y	Y	N	N	N

\* S= Serie; S1: Serie 1; S3-5: from Serie 3 to Serie 5, RT for room temperature. Y=Yes, N=No.

### Step 2: immobilization of CTNR layer on aminated-silane surface via reductive amination reaction

All pre-functionalized surfaces obtained from step 1 were used for grafting CTNR *via* reductive amination reaction, following two different protocols (A and B) herein described. This step is the same for both protocols: a solution of different concentrations (described in Table 2) of CTNR in dry DCM or Toluene was prepared in a 100mL round bottom flask, under Argon. The desired volume of acetic acid was added, as described in Table 2. This

mixture was stirred at room temperature for 10 min. Five pre-functionalized microscope slides obtained from step 1 were placed in a custom-designed slide-staining jar, which was airtight closed and submitted to three cycles of *vacuum* and Argon. The slide-staining jar was then flushed with argon for 15 min before injecting 35 mL of the CTNR solution previously prepared *via* a syringe, and all was stirred for 10 min. The next step followed protocol A or B:

**Protocol A:** 8 mL of anhydrous EtOH were added via a syringe. This mixture was stirred for 5 min before adding 2 eq. of NaBH<sub>4</sub> (see Table 2, herein, considering that the CTNR corresponds to 1 eq.).

**Protocol B:** Without adding anhydrous EtOH, 4 eq. of reducing catalyst NaBH(OAc)<sub>3</sub> were immediately added. Similarly to protocol A, 4 equivalents of NaBH<sub>4</sub> was used (CTNR corresponding to 1 eq.).

The final mixture obtained was stirred under Argon for 10 min before being placed in an orbital shaker operated at 50 rpm. The reaction was carried out at different temperatures (RT, 40°C) for a desired time (described in Table 2). After reductive amination step, the microscope slides were rinsed individually in an *ultrasonic* bath using the reaction solvent (5min), water (5 min), ethanol (5 min) and they were dried in an oven at 80 °C for 3 min.

**Table 2.** Parameters varied for the reductive amination step 2 (R1St2).

	TriSi			DiSi				
	S1-2	S3	S4	S1	S2	S3	S4	S7-16
$\overline{M}_n$ , NMR (g/mol)	1500	1256	1256	1500	1500	1256	1256	1256
Anhydrous Solvent	Toluene/ EtOH	Toluene/ EtOH	Toluene/ EtOH	Toluene/ EtOH	Toluene/ EtOH	Toluene / EtOH	CHCl <sub>3</sub> / EtOH	CHCl <sub>3</sub>
[CTNR] (mol/L)	0.010	0.030	0.030	0.010	0.010	0.015	0.015	0.030
Ratio CH <sub>3</sub> COOH/ CTNR	0/1	20/1	20/1	0/1	0/1	0/1	20/1	2/1
Type of reducing agent	a	b	b	a	a	a	a	b
Ratio catalyst/CTNR	2/1	4/1	4/1	2/1	2/1	2/1	2/1	4/1
Reaction temperature (°C)	RT	RT	RT	RT	RT	RT	RT	40

<b>Reaction time (h)</b>	48	72	90	48	24	72	72	48
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\*(a): NaBH<sub>4</sub>; (b): NaBH(OAc)<sub>3</sub>

### Step 3: chemical modification of ketone terminal group, via reductive reaction

The microscope slides obtained from step 2 *via* reductive amination were placed in a custom-designed slide-staining jar, which was airtight closed and submitted to three cycles of *vacuum* and Argon. Then 25 mL of anhydrous CHCl<sub>3</sub> and 10 mL anhydrous EtOH were introduced, followed by adding 4 eq. of NaBH<sub>4</sub>. The mixture was stirred at room temperature for 10 min under argon before placing it in an orbital shaker operated at 50 rpm. The reaction was carried out at 40°C for a desired time (described in Table 3). Once the reaction finished, the microscope slides were rinsed individually in an *ultrasonic* bath with CHCl<sub>3</sub> (5 min), water (5 min), ethanol (5 min) and dried in an oven at 80 °C for 3 min.

**Table 3.** Different conditions to carry out selective reduction reactions -R1St3 (\*) based on the amount of CTNR used in the first step.

	DiSi		
	S1-2	S3	S4-16
<b>Ratio (*) CTNR/NaBH<sub>4</sub></b>	2	3	4
<b>Reaction Time (h)</b>	48	72	48
<b>Reaction temperature (°C)</b>	40	40	40

### Step 4: introduction of acrylate groups at the polymer chain-end

To a custom-designed slide-staining jar, airtight closed and purged under *vacuum* then rinsed with Argon (3 times), were successively introduced at 0°C, 35 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>3</sub>N (1.75 eq. compared to 1.0 eq. CTNR) and acryloyl chloride (1.5 eq.). The reaction mixture for series S12-15 was stirred at RT for 48 h, in an orbital shaker, operated at 50 rpm. Once the reaction was finished, the microscope slides were rinsed individually in an ultrasonic bath with CH<sub>2</sub>Cl<sub>2</sub> (5 min), water (5 min), ethanol (5 min) and dried in an oven at 80°C for 3 min.

### 4.2) Description of functionalization conditions for Route 2

The glass substrates were first cleaned and activated to remove contaminants and to introduce surface hydroxyl groups. Then, the surfaces were silanized with different Oligo-SiHTNR

compounds thereby forming a monolayer of polyisoprene containing hydroxyl groups at the chain-end that could be modified successively, first *via* selective reduction, then *via* esterification reaction to obtain acrylate group.

#### *Step 1: silanization of Oligo-SiHTNR*

The preparation of Oligo-SiHTNR solution was carried out following Step 1, route 1 (R1St1), as previously described (Section 1.4.1). Several conditions were tested and are presented in Table 4.

**Table 4.** Experimental conditions for Step 1 Route 2 (R2St1), using anhydrous toluene as solvent. The reactions were run under Argon atmosphere.

	Oligo-DiSiHTNR				Oligo-TriSiHTNR
	S1	S2	S3	S4	S1
[Oligo-SiHTNR] mol/L	0.01	0.03	0.03	0.03	0.03
Temperature of reaction solution (°C)	RT	40	40	40	40
Immersion time (hours)	24	48	72	120	48

### 4.3) Functionalization with MAPTES

The MAPTES (methacryloxypropyl triethoxysilane) solution for functionalization was prepared in the same way as in Step 1, route 1 (R1St1 for other aminosilanes as previously described). Activated glass substrates were functionalized with MAPTES, using the optimal conditions (C=0.086 mol/L, T=40°C, 24 h of immersion time and dried at 110°C in oven). A custom-designed slide-staining jar was used and it was airtight closed during reaction, after extensive purging with Argon.

### 4.4) Synthesis of polyisoprene - polyguanidinium brushes

The surfaces functionalized with NR-oligomers exhibiting acrylate groups at the free extremity were polymerized with a guanidinium monomer (Figure S17) to form copolymer brushes polyisoprene-polyguanidinium. Activated glass substrates were functionalized with alcoxysilanes oligomers, using the optimal conditions (C=0.086 mol/L, T=40°C, 24 h of immersion time and dried at 110°C in oven). The reaction took place inside a custom-designed slide-staining jar that was airtight closed and that was first extensively cleaned and purged with Argon under agitation.

The grafting of the guanidinium monomer was performed in DMSO solution, inserting the slides previously functionalized inside the slide-staining jar. The concentration of guanidinium monomer and AIBN were 0.08 mol/L in DMSO and 0.0068 mol/L, respectively. A small quantity of DMF (2 drops) was added in the reactive mixture, using its protons as internal reference to calculate monomer conversion by NMR. Different reaction times and temperatures were tested. The corresponding samples were collected and analyzed by  $^1\text{H}$  NMR. From these data, it was chosen to keep the reaction at 90°C for 19h because in this condition the total disappearance of the characteristic proton peaks of the acrylate group of the guanidinium monomer was obtained. Using longer times would thus not change the result. The slides were extensively washed with DMSO and water to eliminate unreacted monomer, then with DCM and finally they were dried under vacuum.

## **5) Surface and thin films characterization**

All X-ray reflectivity (XRR) and contact angle measurements were carried out at room temperature on glass microscopy functionalized slides.

### **5.1) Contact Angle measurements (CA)**

Contact Angle measurements were performed with a precision of 0.1° using a homemade set-up with a bright LED white source, and a telecentric lens on the source and camera (CMOS) pathways. For each sample, at least 5 drops of 1  $\mu\text{L}$  were deposited on separated regions over the surface to obtain an average value. To obtain robust values for a given surface state, errors bars are obtained from the cumulate values obtained from several samples (at least 3), identically prepared. A homemade software was used for image analysis.

### **5.2) X-ray reflectivity (XRR) of interfaces, molecular and thin films**

X-ray reflectivity measurements were performed using a PANalytical Empyrean X-Ray diffractometer running at 40 kV and 30 mA (Cu-K $\alpha$  radiation reflected on a parallel beam x-ray optics, acting as a monochromator at 0.154 nm). Reflectivity scans, data treatment and fitting analyses are presented in the supporting information section: *X-ray reflectivity measurements*.

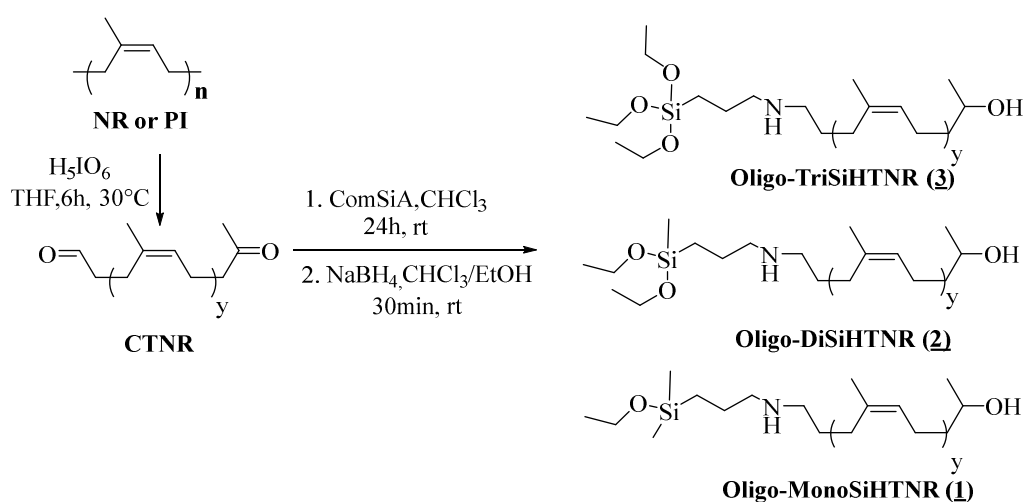
## **RESULTS AND DISCUSSIONS**

Novel telechelic NR oligomers were synthesized from the oxidative controlled degradation of natural rubber chains. In order to graft PI chains to surfaces for coating applications, the

functionalization of silicon-based materials was studied, starting with silicon dioxide from glass microscopy slides, made from a widely used class of glass and presenting an excellent starting surface roughness and flatness. The first idea was to synthesize a bi-functional molecule that would be covalently bound to the material and that could be polymerized at the other end with acrylated PI oligomers or other monomers. The second idea was the synthesis of new Oligo-SiHTNR for covalent binding to silicon-containing surfaces.

### 1) Synthesis of different Si-HTNR oligomers for surface functionalization

The silano-telechelic oligomers (Oligo-SiHTNR) could be obtained following the synthetic routes displayed in Scheme 1.



**Scheme 1.** Chemical pathways to synthesize three types of Oligo-SiHTNR oligomers.

The polyisoprene chains of natural rubber were cut by oxidative degradation to obtain Carbonyl Telechelic Natural Rubber oligomers (CTNR) using periodic acid. The molecular weight of CTNR was well controlled by choosing the concentration of periodic acid and reaction conditions optimized in the past in our team.<sup>33-34</sup> Two functional groups at the chain-end of CTNR oligomers were first generated: a ketone and an aldehyde. According to the strategy, only one end had to be functionalized with a silane group, whereas the other end should be converted in acrylate function. Having a superior reactivity, the aldehyde function was the only one to selectively react with the commercial silane coupling agents (ComSiA) to obtain the designed Oligo-SiHTNR used for the glass surface functionalization (Figure 1 and Scheme 1).

As shown in the literature<sup>35-36</sup>, the reducing agent  $\text{NaBH}(\text{OAc})_3$  allows the selective functionalization of the aldehyde CTNR chain-end without modification of the ketone moiety,

via a reductive amination reaction. Unfortunately, this reducing agent presents weak acidic properties and it can promote hydrolysis of ethoxy groups at the chain-end of the commercial silane coupling agent, giving unwanted products. To confirm the occurrence of this side reaction, a simple test was carried out in the same reaction conditions. A solution of commercial APMDES (0.5 mL, 1 eq.) in dry DCM (10 mL) was mixed to NaBH(OAc)<sub>3</sub> (2 eq., Entry B, Figure S1) or NaBH<sub>4</sub> (2eq., Entry A, Figure S1), or no reducing agent (Entry C, Figure S1). After treatment, the chemical structure of the obtained residue was analyzed by <sup>1</sup>H NMR. The spectra are presented in Supporting Information (Figure S1). They show clearly the disappearance of the signal of ethoxy groups in the case of NaBH(OAc)<sub>3</sub> but not in the case of NaBH<sub>4</sub>, meaning that the NaBH(OAc)<sub>3</sub> cannot be used as reductive agent in presence of aminosilanes. Therefore, to reduce this effect, the Oligo-SiHTNR was obtained by the reductive amination reaction of CTNR at room temperature using NaBH<sub>4</sub> as reductive agent. The oligomers CTNR were at first reacted with the appropriate aminosilane (one equivalent) for 24h in a mixture of CHCl<sub>3</sub>/EtOH (to enhance CTNR solubility), then two equivalents of NaBH<sub>4</sub> were added and the reaction was continued for 30min. In these conditions, Oligo-SiHTNR was generated with silane chain end (from the aldehyde) and a hydroxyl group by reduction of the ketone moiety, as orange-yellow viscous liquid in 80% yield for Oligo-DiSiHTNR (**2**) and 82% for Oligo-TriSiHTNR (**3**). In fact, APTES (tri-ethoxysilane) and APMDES (di-ethoxysilane) silanes are much more effective in coupling with a surface, in comparison with the APDMES (mono-ethoxysilane).<sup>37</sup> In our case, we faced the same difficulty mentioned in the literature and some characteristic proton signals of mono-ethoxysilane moieties of Oligo-MonoSiHTNR were very low in term of integration and were overlapped with the massif signals of polyisoprene. The structure was not clearly established for **1**, that is why, in this paper, we reported only the synthesis of the two silano oligomers **2** and **3** (see data in SI, section 2.1).

## 2) Grafting oligomers to hydroxylated and silicon-containing surfaces

Two routes were envisioned to obtain PI coatings on glass. The first one in three steps used a silanization of glass to generate -NH<sub>2</sub> groups (R1St1, R1St2, R1St3), on which CTNR oligomers were post-grafted. The pending ketone end-moiety was then reduced to alcohol function. The second route was a direct functionalization of glass in *one pot* from the Oligo-SiHTNR already bearing the hydroxyl end-moiety (R2St1). In both cases, the alcohol functions were converted in acrylate for further reactions (R1St4 and R2St2), among which



thicker PI coatings could be prepared by further polymerization of acrylate oligomers (ACTNR). To test the reactivity of CTNR on  $\text{-NH}_2$  surfaces (R1St2) *via* reductive amination reaction and oligo-SiHTNR (R2St1) with silicon-containing surfaces, activated glass microscopy slides were used exposing a high density of silanol groups after solvent cleaning and UV plasma treatment (see Experimental Section 4).

### 2.1) Grafting Oligo-SiHTNR on glass surfaces (Route 2)

All tested protocols used to graft Oligo-SiHTNR in *one pot* (route 2) by direct contact of the molecules solubilized in toluene are described in experimental section 4.2. As expected, the ethoxy silane groups of Oligo-SiHTNR were successfully grafted to glass surface (see XRR data presented in Figure S14 and Table S2), however, the only drawback of these macromolecules was their sensitivity. They had to be synthesized shortly before use as their solubility and stability evolved quickly. Our alternative method in two steps presented in (Figure 1 route 1), turned out to be much easier and robust with the possible storing of compounds for weeks before use.

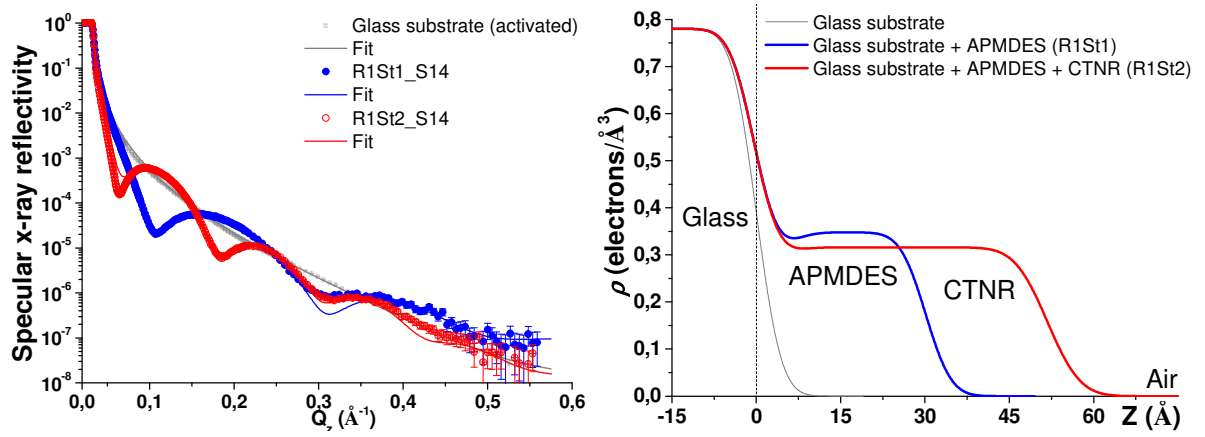
### 2.2) Grafting CTNR on amino-silanized glass surfaces (Route 1)

Aiming at obtaining a high grafting density of CTNR following the route 1 protocol, we tried three selected commercial silane coupling agents to get  $\text{-NH}_2$  groups at the surface of the glass substrates: APTES (tri-ethoxysilane), APMDES (di-ethoxysilane) and APDMES (mono-ethoxysilane). The most commonly used one, APTES (3-Aminopropyltriethoxysilane), is also the most reactive. It is known that a possible bulk polymerization or vertical polymerization from the substrate might occur in presence of water traces and this results in the growth of aggregates or multilayers with uncontrolled structures (3D).<sup>38</sup> Note that even in the case of a 2D surface silane polymerization, some conformations appear with pending molecules and a weak binding to the substrate. We thus always conducted extensive rinsing procedures with several solvents and under *ultrasonic* agitation at each step to eliminate materials with weak “hang time”. To measure the thickness, density and possible roughness of the aminosilane layer, we conducted specular X-ray reflectivity experiments as well as water contact angle measurements, at each step of the protocols. Results are discussed herein for different pre-functionalization conditions (described in see Experimental Section 4.1.1).

Concerning APTES pre-functionalization, the XRR data (SI section 3.2) demonstrated that the formation of APTES layers depends on the experimental conditions (APTES concentration, contact times, ...) but is also affected by more subtle parameters such as the air

relative humidity. APTES layers showed an excellent coating resistance to all cleaning treatments used to eliminate non-covalently bound molecules. However, the XRR curve measured after step 2 (consisting in a long contact with the CTNR molecule and sub-sequent cleaning, R1St2), did not change noticeably from the XRR curves measured just after the APTES pre-functionalization (R1St1). This indicated that CTNR<sub>1500</sub> oligomers did not react noticeably with the APTES layers. Even after several days of immersion, the absence of CTNR grafting was probably due to the intrinsic disorder of 3D APTES layers and to the lack of availability of embedded -NH<sub>2</sub> groups for their reaction with CTNR aldehydes *via* NaBH<sub>4</sub> (S1-S2) or NaBH(OAc)<sub>3</sub> reduction.

The same protocols were then optimized for APMDDES, the di-ethoxysilane molecule. Several experimental conditions were first tested at room temperature on activated glass surfaces (R1St1, S1 to S3). The first conditions (series S1) based on a 48h pre-functionalization step, gave the thinnest films obtained with only 1.15 nm in thickness and the electron density expected for pure APMDDES. A single monolayer of APMDDES should not exceed 0.9 nm in thickness<sup>39-41</sup>, therefore this layer surely included some disorder (R1St1\_S1) and did not effectively tether CTNR molecules during the functionalization step (R1St2\_S1). Increasing the contact time to 72h translated in an increase of the APMDDES layer to 1.9 nm (R1St1\_S2) and reducing the contact solution concentration did not give thinner films. The thick layers obtained in this way resulted in a dense coating (2.5 nm for R1St2\_S3) with an incomplete layer on top (1.3 nm and 34% of the compact layer density). All these layers were unreactive to CTNR grafting until we increased the reaction temperature to 40°C for the aminosilane prefunctionalization, obtaining also a better reproducibility. Note that at 70°C the reactivity was poor again (series S7 and S8, XRR not shown). Satisfying conditions for the aminosilane prefunctionalization (R1St1) were obtained following the protocol adopted for series S9 to 16 (see Table 1) and carrying out the CTNR functionalization step (R1St2) at room temperature, using NaBH(OAc)<sub>3</sub> in chloroform (conditions adopted for series S7 to 16 in Table 2). The Figure 2 (left) shows representative XRR data and best fits obtained (Table S4 for S14) at pre and functionalization steps (R1St1 and R1St2, respectively) with the clear formation of a robust and dense 2.2 nm thick CTNR coating grafted on top of a 3 nm APMDDES reactive and dense layer. The plotted electron density profiles (Figure 2, up) from these fits also evidence a quite small roughness at air (0.46 nm) that is similar to the one measured for the bare substrate (0.35 nm) and for the APMDDES pre-coating (0.36 nm).

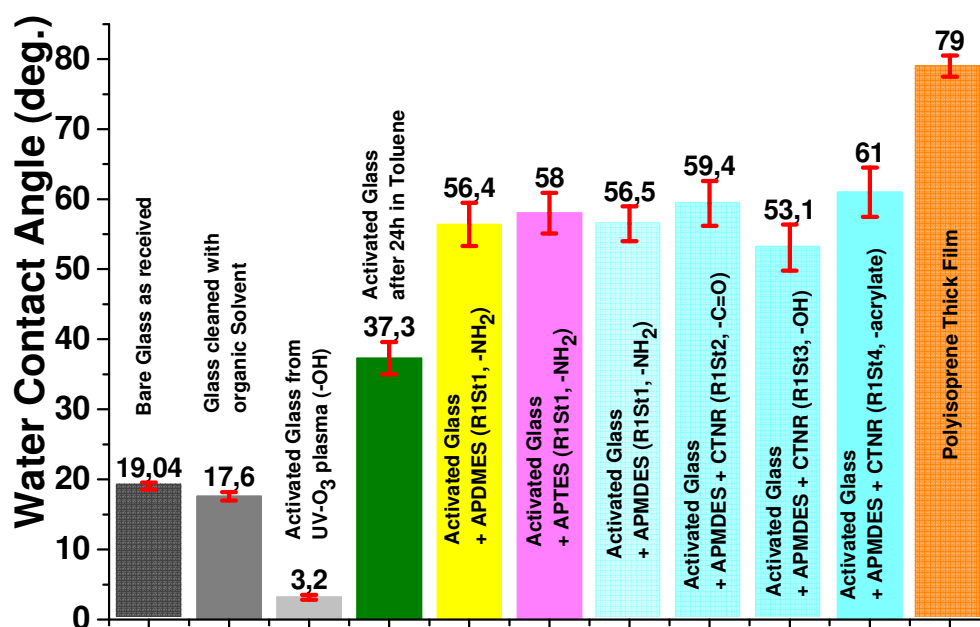


**Figure 2.** Up) Specular X-ray reflectivity (XRR) data with best fits to the data (solid lines) of a prefunctionalized glass substrate with APMDES (di-aminosilanes), before and after reaction with CTNR oligomers (respectively in plain blue and empty red marks). **Bottom** Electronic density depth profiles corresponding to the best fit to the XRR data (same color code, see text for experimental conditions).

Since the graft polymer flat layer exhibits the PI melt density ( $\rho = 0.93 \text{ g/cm}^3$ ), one can estimate from its thickness ( $h = 2.2 \text{ nm}$ ) the grafting surface density ( $\sigma_{\text{PI}} = h \rho N_A / M_n$ ) and the corresponding mean distance between grafting points ( $D = 2/\sqrt{\pi \sigma_{\text{PI}}}$ ), where  $M_n = 1240 \text{ g/mol}$  and  $N_A$  is the Avogadro number.<sup>42</sup> We obtained  $\sigma_{\text{PI}} = 0.98 \text{ chains/nm}^2$  (*i.e.*  $1.625 \cdot 10^{-10} \text{ mol/cm}^2$ ) so a mean distance between anchoring points of  $1.14 \text{ nm}$ . We considered that the chain is made of  $N \sim 20$  monomers, and we used a Kuhn length for *1,4*-polyisoprene of  $b = 0.82 \text{ nm}$ <sup>43</sup> that corresponds to the segment length in a freely jointed chain model. It is related to the real monomer length  $a$  ( $\sim 0.382 \text{ nm}$ ) *via* the flexibility Flory' characteristic ratio equal to  $(b/a)^2 = 4.6$ . Following the Alexander-de Gennes model of graft polymer chains, the adimensional grafting density  $(a/D)^2$  is here smaller than  $N^{-6/5}$ , so that each grafted oligomer can adopt the mushroom regime where other surrounding chains act like a good solvent with negligible inter-chain repulsions. In that case, the vertical extension of a grafted chain within the dense melt is equal to the Flory radius:  $R_F = a N^{3/5} = 2.31 \text{ nm}$ , that is here in perfect agreement with the layer thickness measured with X-rays ( $2.2 \text{ nm}$ ). The CTNR coating scales perfectly with a dense PI monolayer.

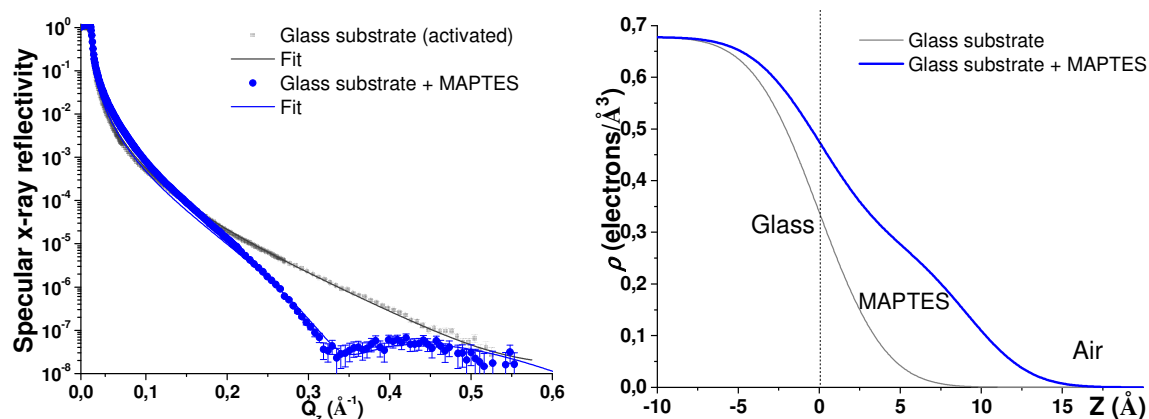
Contact angle measurements of water droplets ( $\theta_c$ ) were carried out as a simple and complementary method to check for surface chemical modifications. Figure 3 shows representative data for the different surface states with error bars including several measurements per sample on many samples. A high density of surface silanols was obtained after plasma treatment with  $\theta_c$  values below  $3^\circ$  (a regime where it becomes difficult to

measure precisely the angle). The silanization with amino ethoxysilanes (R1St1 prefunctionalization with a mono, di or tri-silane) always resulted in an increase up to  $56^\circ \pm 2^\circ$ <sup>40, 44</sup> well above the expected glass loss of hydrophilicity with time, after activation and immersion in organic solvents for days. At the functionalization step (R1St2), it was found that grafted CTNR only increased  $\theta_c$  of few degrees ( $\sim 59^\circ$ ), since layers have similar molecular interactions with water. The transformation of the chain-end ketone group solely into a hydroxyl group (R1St3) resulted in a slightly lower hydrophobicity ( $53^\circ$ ). The contact angle increased to  $61^\circ$  with the transformation into acrylate (R1St4). However, contact angles also depend on the thickness, roughness and organisation of the layer. Polyisoprene freestanding thick films with a high degree of crosslinking gave the highest values with  $\theta_c \sim 80^\circ$ , which was never reached with oligoisoprene ultra-thin films (bearing ketone, OH, acrylate chain-end) as expected.



**Figure 3.** Contact angle measurements of water droplets of 1 $\mu$ L deposited on bare glass, functionalized glass and polyisoprene thick films. The error bars come from measurements of many droplets per sample and at least 3 samples for each surface state. We also prepared glass slides functionalized with the commercial MAPTES molecule in order to generate the surface methacrylate function in *one pot*. The protocol optimized for APMDES was used in one-step (see Experimental Section 4.3) and we obtained stable MAPTES monolayers with a high reproducibility. XRR data representative of these samples are shown in Figure 4 with the best fitting parameters given in Table S5. We obtained a 0.9 nm monolayer that resisted to

washing procedures and which exhibited an electron density equal to 90% of the value expected for a total coverage of glass. Such samples correspond to a high surface density of methacrylate functions on glass and have been compared to the CTNR grafted oligomers with acrylate surface groups in the following section.



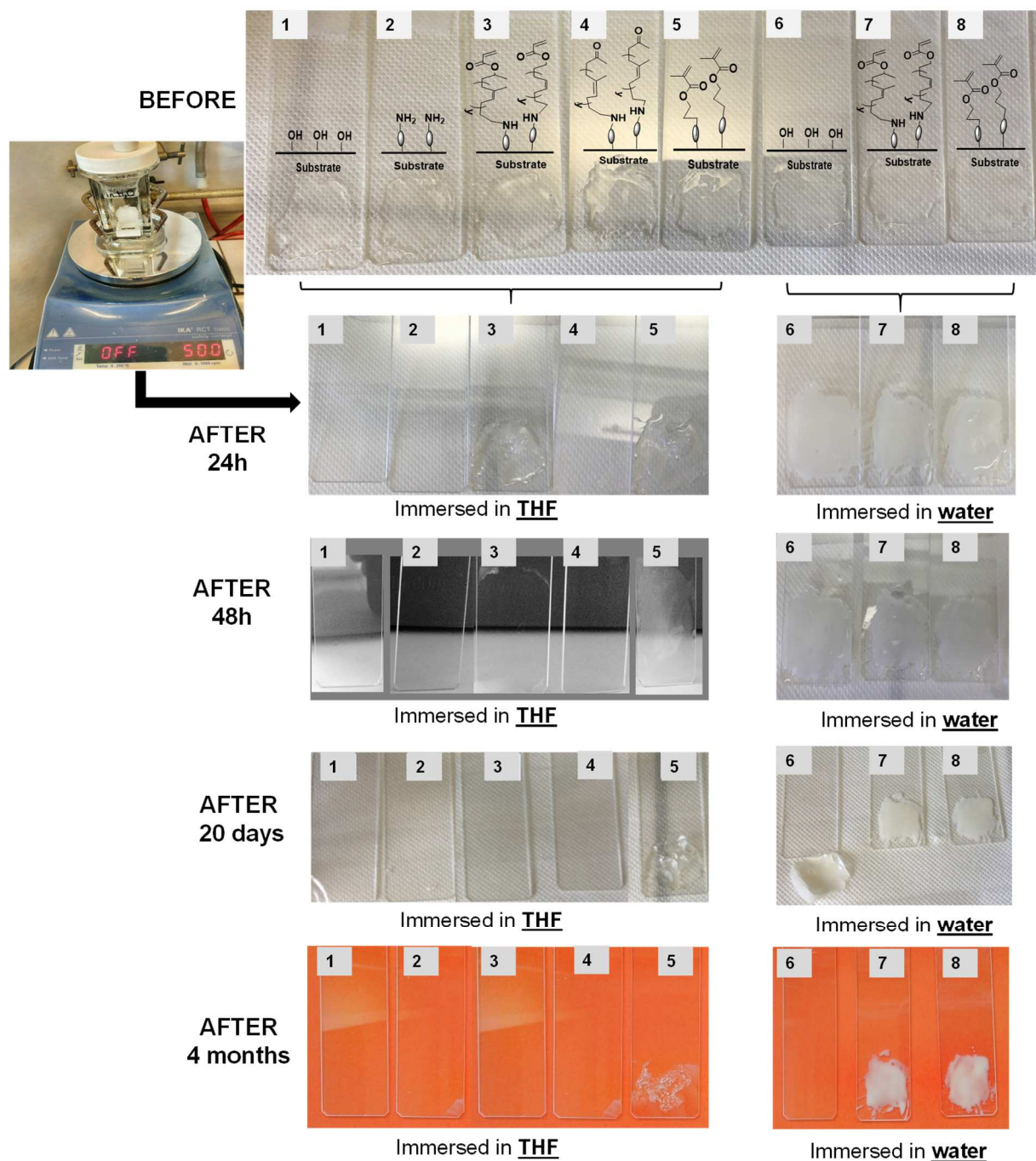
**Figure 4.** Left) Specular X-ray reflectivity (XRR) data with best fits to the data (solid lines) of a prefunctionalized glass substrate with MAPTES. Right) Electronic density depth profiles corresponding to the best fit to the XRR data (same color code, see text for experimental conditions).

### 2.3) Robustness and immersion tests of covalently grafted PI thick films on glass

The CTNR grafted layer resisted to our extensive cleaning protocols under ultrasonic shacking and was not noticeably affected by subsequent chemistry steps (R1St3 and St4) used to transform ketone groups in hydroxyl groups and then in acrylate groups. To further test the reactivity of the oligoisoprene coatings bearing a reactive acrylate group (R1St4), we then studied the post grafting of a thick layer obtained from a mixture of acrylate oligomers from NR and photoinitiator (Figure S16), which we used in the past in analogue formulations and conditions to prepare freestanding films.<sup>31, 45</sup> We compared the PI post-grafting on different reference surface states obtained at different steps of our protocols, including PI adhesion to bare glass surfaces. Figure 5 shows the different surfaces tested, namely: activated bare glass substrates, pre-functionalized surfaces with aminosilanes exhibiting  $-\text{NH}_2$  groups (R1St1), functionalized surfaces with PI oligomers exhibiting ketone groups (R1St3) or acrylate groups (R1St4), as well as functionalized glass with MAPTES. On all these surfaces, a thick film of pre-polymerization homogenized mixture composed by reactive ACTNR (97.5% w/w of ACTNR<sub>6000</sub>) and by 2.5% w/w of Darocur (photoinitiator) was deposited. UV-Curing was then carried out for 3 minutes (light intensity  $I = 29,4 \text{ mW/cm}^2$ ). Then all samples were either immersed in THF solvent (samples 1 to 5) or in water (samples 6 to 8), under strong magnetic

stirring (500 rpm) in sealed vials at room temperature, to demonstrate the formation of covalent bonds between the pre-functionalized surfaces and the thick cross-linked coating obtained after the photopolymerization of the acrylate oligomers. The surface attachment was regularly checked, and pictures are shown after 24h, 48h, 20 days and 4 months of immersion in the solvents. After 24h in THF, an efficient organic solvent for CTNR and ACTNR, the thick coatings only remained on surfaces bearing acrylate groups (samples 3 and 5). In THF, two days were needed to detach the bulk films from grafted CTNR coatings (R1St4) and 4 months for MAPTES coatings. For many applications, immersion in water is relevant and all PI thick films resisted much longer to water exposition, except on the highly hydrophilic activated glass surface in absence of covalent grafting (in this case, physisorption only was expected with surface silanol groups and it resisted just few days in water before total separation). The PI thick films formed on surfaces containing free acrylate or MAPTES monolayers resisted to vigorous stirring in water all the four months of the immersion experiment. To our knowledge, it is not possible to experimentally measure the fraction of acrylate functions that reacted with the surface coatings under UV exposition. Nevertheless, it was high enough to create a strong tethering of the PI thick film, comparable to the grafting to MAPTES monolayers known to expose a very high surface density of methacrylate groups. All these results including XRR, contact angles and immersion tests in different solvents confirmed that grafted CTNR oligomers on silicon-based surfaces, have a good chemical reactivity to allow tethering other oligoisoprenes or carrying out new chemistries .

Surface obtained after polymerization with the mixture (F1)  
before immersed in water/THF

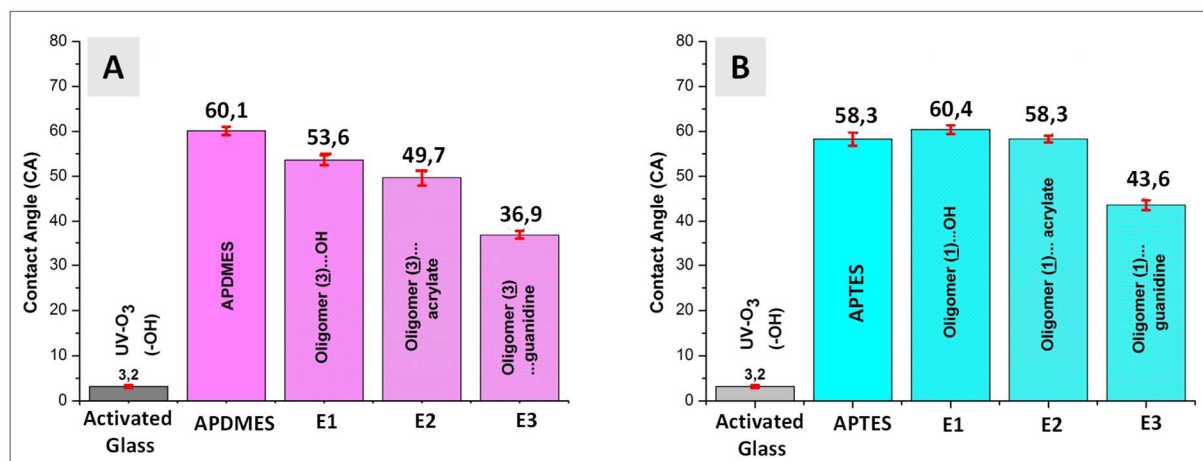


**Figure 5.** The pre-polymerization mixture (F1) containing 97.5% w/w of ACTNR6000 and 2.5% w/w of Darocur was deposited on different functionalized glass surfaces: (1&6) Raw activated glass; (2&7) pre-functionalized surface with  $-NH_2$ ; (3) target surface exhibiting acrylate functions; (4) functionalized surface exhibiting ketone groups, (5&8) MAPTES monolayers exhibiting meta-acrylate functions. All surfaces were cured under UV radiation for 3 minutes and then immersed in THF (1 to 5) and in water (6 to 8) at room temperature for several days as indicated.



## 2.4) Grafted di-block copolymers polyisoprene-co-polyguanidinium

To illustrate an application of our strategy, we prepared coatings with an antibacterial activity. Glass surfaces were functionalized with the alkoxy-silyl oligomers (mono and tri) and the free chain ends were turned into acrylate groups. An acrylate monomer bearing a guanidinium moiety was previously prepared in our group and showed its effectiveness against selected strains of pathogenic bacteria when inserted in the bulk of PI films.<sup>31</sup> It was polymerized from the acrylate chain ends of the grafted oligoisoprenes to form copolymer brushes polyisoprene-polyguanidinium (Figure S17). The free radical polymerization of the guanidinium monomer was performed in DMSO solution, where the functionalized slides were immersed in presence of AIBN initiator. A complete conversion of the guanidinium monomer in solution was reached after 19h at 90°C, confirmed by NMR data. The changes in surface polarity were monitored by measuring the contact angle after each functionalization step, after performing an extensive number of washings in order to extract unreacted monomers. The functionalization was checked at each step using contact angle measurements and we noticed a relevant decrease of contact angle values after the grafting of guanidinium monomers, as expected for the formation of copolymers in which the hydrophilic block is exposed at the air interface.



**Figure 6.** Contact angle values of glass slides functionalized at different steps including the formation of the polyisoprene-polyguanidinium brushes



## CONCLUSIONS

This paper describes different approaches developed to graft covalently polyisoprene (PI) on silica glasses and silicon surfaces, forming dense monolayers of polyisoprene chains (nano-sized coatings), thin (sub- $\mu\text{m}$ ) or thick (mm) films. Novel functional telechelic oligomers, bearing a hydroxyl group at one chain end and a silane group at the other, have been synthesized from solid natural rubber, by selectively breaking some of the carbon-carbon double bonds and modifying the chain ends. These oligoisoprenes (Oligo-SiHTNR) have been covalently tethered on silicon-based materials, opening a new strategy in the sustainable coatings research field. An alternative route started with a pre-functionalization of the support with commercial amino-alkoxysilanes (APTES, APMDES and APDMES), prior to PI immobilization, then oligomers obtained from natural rubber having carbonyl chains ends were reacted with the grafted amino groups. Modification of the oligoisoprenes free chain ends into acrylate groups allowed the formation of dense polyisoprene coatings by reaction with tailor-made oligomers with acrylate extremities, in presence of a photoinitiator and irradiating quickly with a UV-lamp. The choice of the best approach to follow to functionalize a surface depends strongly on the aimed application and PI thickness:

- the first route consists in only one grafting step of the Oligo-SiHTNR to a unfuctionalized surface. However, the synthesis of the sililated oligomers requires different steps and they have to be kept stable prior surface chemistry;
- in term of time and implementation, the second route seems more advantageous and it is highly robust. Only commercial precursors (amino silanes) are used for the surface functionalization, but two steps are needed to obtain a dense coating.

A third route was also proposed by grating methacryloxypropyl triethoxysilane (MAPTES) to the surface and then forming thick PI films by adding the acrylate oligoisoprenes, the photoinitiator and carrying out the polymerization to obtain crosslinked coatings. This route (creating a methacrylate monolayer) is excellent for covalent anchorage of polymer films. All the coatings showed excellent resistance to long exposures in water under strong stirring (over 4 months tests) and a good resistance to organic solvents including THF, whereas just physisorbed PI films detached rapidly from all surfaces. As example for future antibacterial applications, amphiphilic polyisoprene-polyguanidinium copolymer brushes were grafted to glass, obtained by reaction of the monomer containing the guanidinium group with the PI-

acrylate chain ends.<sup>31, 45</sup> The protocols optimized herein to reinforce the mechanical attachment of the hydrophobic PI to interfaces open the route to many industrial applications for the bio-based NR derivate building blocks and for the relative PI hybrid coatings.

## **ASSOCIATED CONTENT**

### **AUTHOR INFORMATION**

#### **Corresponding Author**

\* Guillaume.Brotons@univ-lemans.fr

#### **Author Contributions**

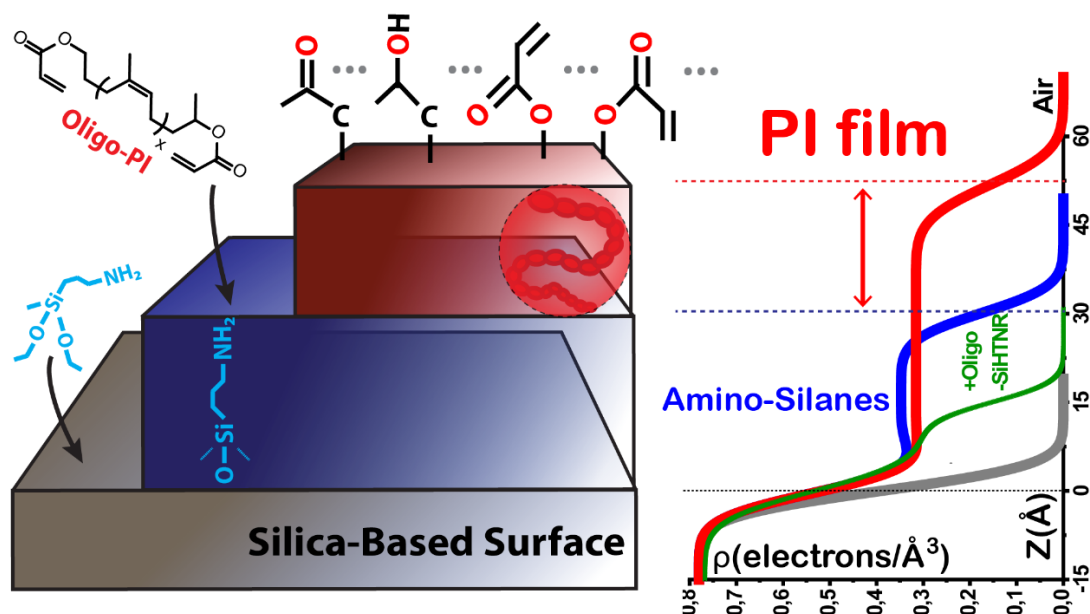
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## REFERENCES

1. Kickelbick, G., Hybrid Materials – Past, Present and Future. *Hybrid Materials* **2014**, *1* (1).
2. Sanchez, C.; Julián, B.; Belleville, P.; Popall, M., Applications of hybrid organic–inorganic nanocomposites. *Journal of Materials Chemistry* **2005**, *15* (35-36), 3559-3592.
3. Mullins, L., Determination of degree of crosslinking in natural rubber vulcanizates. Part I. *Journal of Polymer Science* **1956**, *19* (92), 225-236.
4. Srivastava, S.; Mittal, V., Recent Developments in Elastomer/Hybrid Filler Nanocomposites: Advances in Energy, Environment and Polymer Nanocomposites. 2017; pp 423-490.
5. Hoshian, S.; Jokinen, V.; Franssila, S., Robust hybrid elastomer/metal-oxide superhydrophobic surfaces. *Soft Matter* **2016**, *12* (31), 6526-6535.
6. Saveleva, M. S.; Eftekhari, K.; Abalymov, A.; Douglas, T. E. L.; Volodkin, D.; Parakhonskiy, B. V.; Skirtach, A. G., Hierarchy of Hybrid Materials-The Place of Inorganics-in-Organics in it, Their Composition and Applications. *Frontiers in Chemistry* **2019**, *7* (179).
7. Sajjad, H. M.; Larry, A. N.; Thomas, T.; Parvaneh, M. T.; Hidemitsu, F.; Ajit, K., Review-Organic-Inorganic Hybrid Functional Materials: An Integrated Platform for Applied Technologies. *J. Electrochem. Soc.* **2018**, *165* (8).
8. Rigoberto, C. A.; William, J. B.; Kenneth, C. C.; Jürgen, R., Polymer Brushes: Synthesis, Characterization and Applications. *Wiley-VCH, Book*. **2005**.
9. Barbey, R. I.; Lavanant, L.; Paripovic, D.; Schulz, N.; Sugnaux, C.; Tugulu, S.; Klok, H.-A., Polymer Brushes via Surface-Initiated Controlled Radical Polymerization: Synthesis, Characterization, Properties, and Applications. *Chemical Reviews* **2009**.

10. Zoppe, J. O.; Ataman, N. C.; Mocny, P.; Wang, J.; Moraes, J.; Klok, H.-A., Surface-Initiated Controlled Radical Polymerization: State-of-the-Art, Opportunities, and Challenges in Surface and Interface Engineering with Polymer Brushes. *Chemical Reviews* **2017**, *117* (3), 1105-1318.
11. Rezaeian, I.; Zahedi, P.; Rezaeian, A., *Rubber Adhesion to Different Substrates and Its Importance in Industrial Applications: A Review*. Journal of Adhesion Science and Technology, 2012; Vol. 26, p 721-744.
12. Achary, P. S.; Gouri, C.; Ramaswamy, R., Reactive bonding of natural rubber to metal by a nitrile-phenolic adhesive. *Journal of Applied Polymer Science* **2001**, *81* (11), 2597-2608.
13. Rezaeian, I.; Zahedi, P.; Loghmani, M. S., Formulation and curing characteristics of EPDM/NR and EPDM/SBR polyblends used in metallic surfaces rubber lining. *Journal of Applied Polymer Science* **2009**, *113* (2), 849-854.
14. Brittain, W. J.; Minko, S., A structural definition of polymer brushes. *Journal of Polymer Science Part A: Polymer Chemistry* **2007**, *45* (16), 3505-3512.
15. Edmondson, S.; Osborne, V. L.; Huck, W. T. S., Polymer brushes via surface-initiated polymerizations. *Chemical Society Reviews* **2004**, *33* (1), 14-22.
16. Mohd Azahar, N.; Hassan, N.; Putra Jaya, R.; Ab kadir, M. A.; Mohd yunus, N. Z.; Mahmud, M. Z. H., *An Overview on Natural Rubber Application for Asphalt Modification*. International Journal of Agriculture, 2016; Vol. 2.
17. Hirata, Y.; Kondo, H.; Ozawa, Y., 12 - Natural rubber (NR) for the tyre industry. In *Chemistry, Manufacture and Applications of Natural Rubber*, Kohjiya, S.; Ikeda, Y., Eds. Woodhead Publishing: 2014; pp 325-352.
18. Shiju, K.; Praveen, T.; Preedep, P., Elastomeric organic material for switching application. *AIP Conference Proceedings* **2014**, *1620* (1), 206-212.
19. Liu, D.; Wang, T.; Keddie, J. L., Protein Nanopatterning on Self-Organized Poly(styrene-*b*-isoprene) Thin Film Templates. *Langmuir* **2009**, *25* (8), 4526-4534.
20. Liu, D.; Che Abdullah, C. A.; Sear, R. P.; Keddie, J. L., Cell adhesion on nanopatterned fibronectin substrates. *Soft Matter* **2010**, *6* (21), 5408-5416.
21. Ayche, K.; Ventura, A.; Bardeau, J. F.; Minisini, B.; Pilard, J. F.; Delorme, N., Natural rubber based thin coating for MEMS encapsulation. *Progress in Organic Coatings* **2016**, *99*, 308-313.
22. Extrand, C. W., Spin coating of very thin polymer films. *Polymer Engineering & Science* **1994**, *34* (5), 390-394.
23. Derouet, D.; Forgeard, S.; Brosse, J.-C., Synthesis of alkoxysilyl-terminated polyisoprenes by means of “living” anionic polymerization, 1. Modeling of the termination step by studying the reaction of butyllithium with various alkoxysilane reagents. *Macromolecular Chemistry and Physics* **1998**, *199* (9), 1835-1842.
24. Derouet, D.; Forgeard, S.; Brosse, J.-C.; Emery, J.; Buzare, J.-Y., Application of solid-state NMR (<sup>13</sup>C and <sup>29</sup>Si CP/MAS NMR) spectroscopy to the characterization of alkenyltrialkoxysilane and trialkoxysilyl-terminated polyisoprene grafting onto silica microparticles. *Journal of Polymer Science Part A: Polymer Chemistry* **1998**, *36* (3), 437-453.
25. Hu, P.; Xie, Q.; Ma, C.; Zhang, G., Silicone-Based Fouling-Release Coatings for Marine Antifouling. *Langmuir* **2020**, *36* (9), 2170-2183.

26. Gillier-Ritoit, S.; Reyx, D.; Campistron, I.; Laguerre, A.; Singh, R. P., Telechelic cis-1,4-oligoisoprenes through the selective oxidolysis of epoxidized monomer units and polyisoprenic monomer units in cis-1,4-polyisoprenes. *J. Appl. Polym. Sci.* **2003**, 87 (1), 42-46.
27. Sadaka, F., Etude de la dégradation contrôlée de polydiènes : Application au recyclage des déchets pneumatiques. *thèse* **2010**.
28. Panwiriyarat, W.; Tanrattanakul, V.; Pilard, J.-F.; Burel, F.; Kébir, N., Elaboration and properties of renewable polyurethanes based on natural rubber and biodegradable poly(butylene succinate) soft segments. *Journal of Applied Polymer Science* **2016**, 133 (5), n/a-n/a.
29. Rattanapan, S.; Pasetto, P.; Pilard, J.-F.; Tanrattanakul, V. J. J. o. P. R., Preparation and properties of bio-based polyurethane foams from natural rubber and polycaprolactone diol. **2016**, 23 (9), 182.
30. Tran, T. K. N.; Pilard, J.-F.; Pasetto, P., Recycling waste tires: Generation of functional oligomers and description of their use in the synthesis of polyurethane foams. **2015**, 132 (1).
31. Tran, T. N.; Nourry, A.; Brotons, G.; Pasetto, P., Antibacterial activity of natural rubber based coatings containing a new guanidinium-monomer as active agent. *Progress in Organic Coatings* **2019**, 128, 196-209.
32. Busnel, J. P., Data handling in g.p.c. for routine operations. *Polymer* **1982**, 23 (1), 137-141.
33. Jellali, R.; Campistron, I.; Laguerre, A.; Pasetto, P.; Lecamp, L.; Bunel, C.; Mouget, J.-L.; Pilard, J.-F., Synthesis of new photocurable oligoisoprenes and kinetic studies of their radical photopolymerization. *Journal of Applied Polymer Science* **2013**, 127 (2), 1359-1368.
34. Kebir, N.; Campistron, I.; Laguerre, A.; Pilard, J.-F.; Bunel, C.; Jouenne, T., Use of telechelic cis-1,4-polyisoprene cationomers in the synthesis of antibacterial ionic polyurethanes and copolyurethanes bearing ammonium groups. *Biomaterials* **2007**, 28 (29), 4200-4208.
35. Kébir, N.; Morandi, G.; Campistron, I.; Laguerre, A.; Pilard, J.-F., Synthesis of well defined amino telechelic cis-1,4-oligoisoprenes from carbonyl telechelic oligomers; first studies of their potentialities as polyurethane or polyurea materials precursors. *Polymer* **2005**, 46 (18), 6844-6854.
36. Morandi, G.; Kebir, N.; Campistron, I.; Gohier, F.; Laguerre, A.; Pilard, J.-F., Direct selective reductive amination of carbonyl telechelic oligoisoprenes: elaboration of promising tri- and tetrafunctionalized oligoisoprene intermediates. *Tetrahedron Letters* **2007**, 48 (43), 7726-7730.
37. Weetall, H. H., Preparation of immobilized proteins covalently coupled through silane coupling agents to inorganic supports. *Applied Biochemistry and Biotechnology* **1993**, 41 (3), 157-188.
38. Caravajal, G. S.; Leyden, D. E.; Quinting, G. R.; Maciel, G. E., Structural characterization of (3-aminopropyl)triethoxysilane-modified silicas by silicon-29 and carbon-13 nuclear magnetic resonance. *Analytical Chemistry* **1988**, 60 (17), 1776-1786.

39. Moon, J. H.; Kim, J. H.; Kim, K.-j.; Kang, T.-H.; Kim, B.; Kim, C.-H.; Hahn, J. H.; Park, J. W., Absolute Surface Density of the Amine Group of the Aminosilylated Thin Layers: Ultraviolet–Visible Spectroscopy, Second Harmonic Generation, and Synchrotron-Radiation Photoelectron Spectroscopy Study. *Langmuir* **1997**, *13* (16), 4305-4310.
40. Yadav, A. R.; Sriram, R.; Carter, J. A.; Miller, B. L., Comparative Study of Solution Phase and Vapor Phase Deposition of Aminosilanes on Silicon Dioxide Surfaces. *Materials science & engineering. C, Materials for biological applications* **2014**, *35*, 283-290.
41. Aissaoui, N.; Bergaoui, L.; Landoulsi, J.; Lambert, J.-F.; Boujday, S., Silane Layers on Silicon Surfaces: Mechanism of Interaction, Stability, and Influence on Protein Adsorption. *Langmuir* **2012**, *28* (1), 656-665.
42. Gennes, P.-G., *P.-G. Scaling Concepts in Polymer Physics ; Cornell University Press : Ithaca, NY, USA, Book.* 1979.
43. Michael Rubinstein, R. H. C., *Polymer Physics, Book.* 2003.
44. Asenath Smith, E.; Chen, W., How to Prevent the Loss of Surface Functionality Derived from Aminosilanes. *Langmuir : the ACS journal of surfaces and colloids* **2008**, *24* (21), 12405-12409.
45. Tran, T. N.; Pasetto, P.; Pichon, C.; Bruant, D.; Brotons, G.; Nourry, A., Natural rubber based films integrating Zosteric acid analogues as bioactive monomers. *Reactive and Functional Polymers* **2019**, *144*, 104343.

