

Mussel-Inspired Hydrophobic Coatings for Water-Repellent Textiles and Oil Removal

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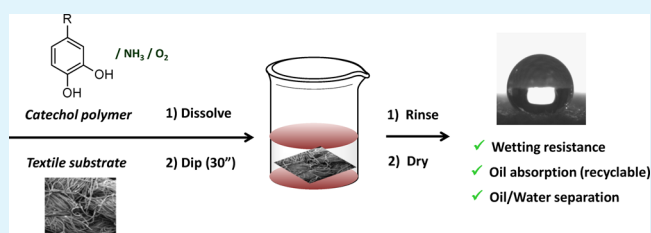
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S Supporting Information

ABSTRACT: A series of catechol derivatives with a different number of linear alkyl chain substituents, and different length, have been shown to polymerize in the presence of aqueous ammonia and air, yielding hydrophobic coatings that present the ability to provide robust and efficient water repellency on weaved textiles, including hydrophilic cotton. The polymerization strategy presented exemplifies an alternative route to established melanin- and polydopamine-like functional coatings, affording designs in which *all* catechol (adhesive) moieties support specific functional side chains for maximization of the desired (hydrophobic) functionality. The coatings obtained proved effective in the transformation of polyester and cotton weaves, as well as filter paper, into reusable water-repellent, oil-absorbent materials capable of retaining roughly double their weight in model compounds (*n*-tetradecane and olive oil), as well as of separating water/oil mixtures by simple filtration.

KEYWORDS: catechol, mussel-inspired, coating, hydrophobic, textile, pollutant removal



1. INTRODUCTION

In the last decades, biomaterials have inspired the design and development of novel functional materials to scientists working in a broad variety of research fields.^{1–3} One example of this fruitful approach has been the fabrication of new bioinspired materials based on catechol structures.^{4,5} These aromatic molecules bearing two *o*-hydroxyl groups are ubiquitous in nature, where they display an impressive diversity of functional roles. For instance, catecholic amino acids are found in mussel byssus proteins, where their presence is essential to their critical adhesive function in wet environments.⁶ In addition, alkyl-substituted catechols have also been identified as the main constituents of natural sap precursors of the polymeric glossy lacquers⁷ used as naturally sourced protective coatings in Eastern Asia for centuries.^{8,9} In the past years, researchers have been actively working in the development of simplified synthetic counterparts that take advantage of the remarkable adhesive and coating character of catechol-based materials.^{4,5} This is the case of mussel-inspired catechol-based polymers, which have emerged as versatile materials acting as protective layers,^{10,11} water-resistant adhesives,^{12–14} and primers for functional adlayers.^{15,16} Among all of the different potential applications, one of the most widely explored is that of catechol-based coatings for control of the wettability of surfaces and interfaces.¹⁷

Different synthetic approaches have been used for the fabrication of catechol-based polymeric materials. One such strategy consists of grafting catechol moieties as adhesive side groups in polymeric backbones to obtain (multi)layered films.^{18–23} Inspired by the pioneering work of Messersmith et al.,^{24,25} the most widespread methodology for control of the surface wettability has been the melanin-like oxidative polymerization of dopamine into a polydopamine (PDA) primer coating, followed by its functionalization with appropriate side chains.^{26–32} In PDA, catechols and quinones are assumed to play complementary roles: on the one hand, *o*-dihydroxyl groups in nonoxidized catechol moieties presumably confer adhesion to substrates; on the other hand, residual, highly electrophilic *o*-quinones act as reactive points for the covalent attachment of functional side chains. PDA has accordingly been used to surface-modify carbon nanotubes and carbon fibers for high-performance polymer composites^{33,34} and foams and mesh for high separation efficiency of oil/water mixtures^{35,36} and bioalcohols.³⁷ In addition, PDA has been used, combining biomimetic principles, to obtain superhydrophobic surfaces.^{38–40} Despite its versatility and simplicity, PDA modification relies on the existence of a sufficient amount of reactive

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groups in the primer coating, which cannot be accurately controlled and, because of PDA insolubility, restricted to in situ polymerization methodologies.

Recently, we have reported the development of an alternative, simpler approach to fabricate catechol-based materials.⁴¹ In this novel strategy, a single monomer bearing both a catechol ring and at least one desired functional side chain (i.e., designed to carry a maximum amount of functional groups) is first synthesized and then polymerized by means of a simple and inexpensive procedure consisting of treatment with ammonia in aerobic conditions. As would be the case of melanin-like materials, polymerization also takes place by means of a complex mechanism involving oxidation of the catechol ring, introduction of a nitrogen atom by covalent binding to this moiety, and further oxidation/cross-linking of the catechol unit, which, once aminated, is rendered more prone to oxidation. Compared to PDA, the main differences would be, first, the nitrogen source—which is endogenous in the case of catecholamines and external in our case (ammonia)—and, more importantly, the fact that this novel approach does not rely on uncontrolled residual reactivity in order to introduce a specific functionality in the coating because it is already built in the catecholic monomer. Regardless of the functional moiety, the polymerization mechanism is thus unique and generalizable provided that it is tolerant of the reaction conditions (the presence of ammonia, moderately basic pH, and contact with air).

Preliminary results showed that this approach can be used to modify the surface tension of a representative variety of substrates, at both the nano- and macroscale, by quick and ex situ deposition of robust coatings and without any surface pretreatment. As a follow-up to this study, here we present the practical application of this new strategy to optimization of a robust hydrophobic coating by choice of the side functional chain length, number of chains, and coating conditions of a series of 4-alkylcatechols (1–4). The catechol starting materials and the synthetic methodology followed are schematically showed in Figure 1. Remarkably, we found that all coatings tested were soluble in a few common organic solvents, thus side-stepping the need to coat surfaces by in situ procedures: polymeric materials could be isolated first and subsequently applied to different substrates by dissolving them in an appropriate medium and systematically evaluating the deposition conditions for optimal performance.

2. EXPERIMENTAL SECTION

Commercially available reagents were purchased from Sigma-Aldrich and used as received. Solvents were dried by distillation over appropriate drying agents. Chemical reactions involved in the synthesis of monomers were carried out under nitrogen, avoiding moisture by standard procedures, and were monitored by analytical thin-layer chromatography using silica gel F254 precoated aluminum plates (0.25 mm thickness). Silica gel 60 (particle size 35–70) was used for purification by flash column chromatography.

Chemical Characterization. ¹H NMR spectra were recorded on a Bruker DP550 spectrometer (250 MHz, CDCl₃, δ 7.26 ppm). ¹³C NMR spectra were recorded on a Bruker DP550 spectrometer (62.5 MHz; CDCl₃, δ 77.2 ppm; acetone-*d*₆, δ 39.5 ppm) with complete proton decoupling. IR spectra were recorded on a Sapphire-ATR spectrophotometer. High-resolution mass spectrometry (HRMS) spectra were recorded with a Micromass-AutoSpec using positive-ion electrospray ionization (ESI⁺). X-ray photoelectron spectroscopy analyses were conducted in order to identify the chemical states of the elements with a Phi 5550 multisystem spectrometer with monochromatic Al Kα radiation (1486.6 eV).

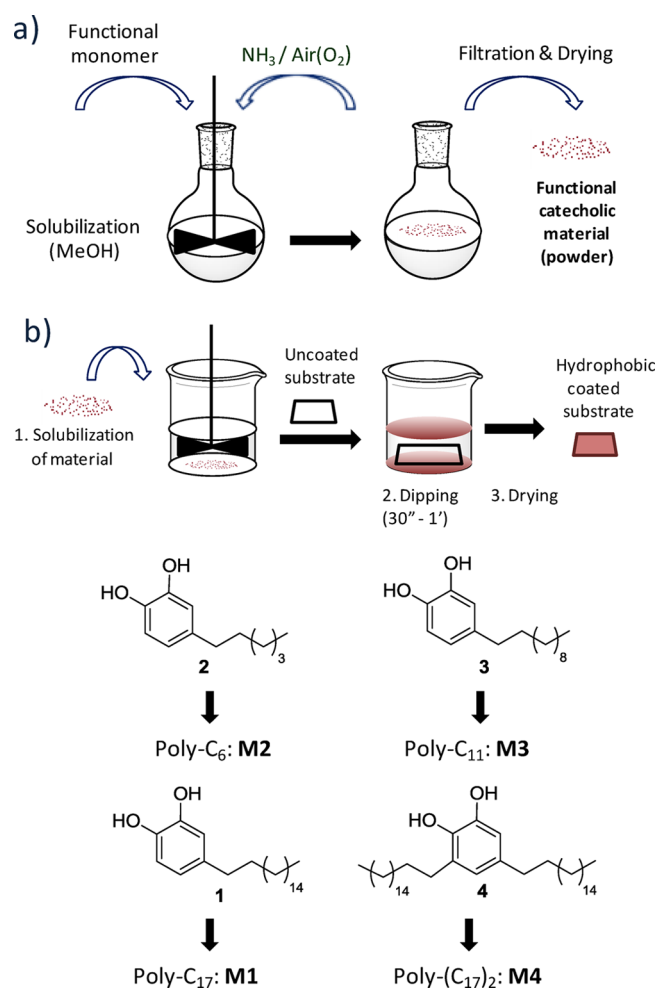


Figure 1. (a) Synthetic procedure for materials M1–M4 from the corresponding catechols 1 (C17 alkyl chain), 2 (C6 alkyl chain), 3 (C11 alkyl chain), and 4 (two C17 alkyl chains), respectively. (b) General coating procedure.

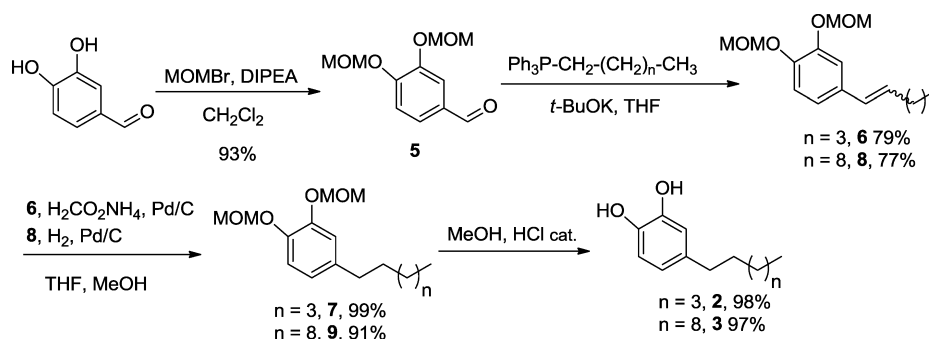
Contact Angle (CA). The CA of Milli-Q water droplets (ca. 5 μL) on coated substrates was used to evaluate the hydrophobicity of coated samples at room temperature by means of the sessile-drop technique. An Easy Drop Standard analyzer and the Drop Shape Analysis DSA 10 software (Krüss, Hamburg, Germany) were used throughout. The reported values arise from averaging CA measurements on five different spots of each sample.

Optical Microscopy. Optical microscopy images were obtained with an Axio Observer Z1m (Zeiss) inverted optical microscope, equipped with five different magnification lenses (5×, 10×, 20×, 50×, and 100×) and an XY motorized sample holder. The excitation source used was a short-arc high-pressure mercury lamp (HBO 103/2, 100 W).

Scanning Electron Microscopy (SEM). SEM measurements were carried out with Hitachi S-570 and Quanta FEI 200 FEG-ESEM microscopes, both operating at 15 kV. Coated glass and textile substrates were fixed on SEM holders using adhesive carbon tape. Prior to observation with SEM, all samples were metalized with a thin layer of gold using a K550 sputter coater (Emitech).

Synthesis of (Z)- and (E)-1,2-Bis(methoxymethoxy)-4-(hex-1-enyl)benzene (6). Pentyltriphenylphosphonium bromide (10.69 g, 22.11 mmol) was dissolved in anhydrous tetrahydrofuran (THF; 105 mL) under nitrogen, and potassium *tert*-butoxide (*t*-BuOK; 4.29 g, 38.23 mmol) was added portionwise. After stirring for 10 min, a solution of **5**⁴² (4.55 g, 0.020 mmol) in anhydrous THF (35 mL) was added to the reaction mixture, which was stirred for 3 h at the reflux temperature. After cooling, the reaction was quenched with water (80

Scheme 1. Synthesis of Target Catechols 2 and 3



mL), the phases were separated, and the aqueous layer was extracted with ethyl acetate (EtOAc; 3 × 10 mL). The combined organic phases were dried over magnesium sulfide (MgSO₄) and concentrated under reduced pressure to afford crude material, which was purified by column chromatography (hexanes–EtOAc, 15:1) to give a mixture (10:1) of (*Z*)- and (*E*)-6 (4.43 g, 15.80 mmol, 79% yield) as an oil. IR (ATR): ν 3002, 2954, 2825, 1603, 1578, 1508, 1465, 1395, 1252, 1225, 1201, 1151, 1126, 1071, 987, 921, 821 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 7.12 (d, *J* = 2.4 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.89 (dd, *J* = 8.4 and 2.2 Hz, 1H), 6.31 (d, *J* = 11.6 Hz, 1H), 6.10 (dt, *J* = 15.8 and 6.7 Hz, 1H-*E*), 5.60 (dt, *J* = 11.6 and 7.3 Hz, 1H-*Z*), 5.23 (s, 4H), 3.52 (s, 6H), 2.33 (m, 2H), 1.40 (m, 4H), 0.90 (t, *J* = 7.07 Hz, 3H). ¹³C NMR (62.5 MHz, CDCl₃): δ 146.8, 145.8, 132.5, 132.4, 128.0, 123.0, 117.4, 116.3, 95.5, 95.4, 56.2, 56.1, 32.2, 28.4, 22.5, 14.0. HRMS (ESI⁺). Calcd for C₁₆H₂₄O₄Na ([M + Na]⁺): *m/z* 303.1567. Found: *m/z* 303.1564.

Synthesis of 1,2-Bis(methoxymethoxy)-4-hexylbenzene (7).

To a stirred solution of a mixture of (*Z*)- and (*E*)-6 (4.41 g, 15.76 mmol) in a mixture of MeOH (32 mL) and THF (63 mL) were added palladium/carbon (418 mg) and ammonium formate (3.20 g, 50.0 mmol). The mixture was heated to reflux for 15 h, allowed to cool to room temperature, filtered through Celite, and concentrated under reduced pressure to afford 7 (4.37 g, 99% yield). IR (ATR): ν 2926, 2854, 1588, 1508, 1378, 1258, 1226, 1200, 1151, 1127, 1071, 989, 922, 812 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 7.07 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 1.9 Hz, 1H), 6.79 (dd, *J* = 6.4 and 1.5 Hz, 4H), 5.24 (s, 2H), 5.22 (s, 2H), 3.55 (s, 3H), 3.54 (s, 3H), 2.55 (t, *J* = 7.5 Hz, 2H), 1.61 (m, 2H), 1.32 (m, 6H), 0.92 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (62.5 MHz, CDCl₃): δ 147.1, 145.1, 137.6, 122.2, 117.0, 116.8, 95.6, 95.5, 56.1, 56.1, 35.5, 31.7, 31.6, 29.0, 22.6, 14.1. HRMS (ESI⁺). Calcd for C₁₆H₂₆O₄Na ([M + Na]⁺): *m/z* 305.1726. Found: *m/z* 305.1726.

Synthesis of 4-Hexylcatechol (2).

Compound 7 (4.46 g, 15.8 mmol) was dissolved in methanol (MeOH; 208 mL) and 1.5 mL of concentrated hydrochloric acid (HCl) were added. The mixture was heated to reflux for 3 h. Evaporation of the solvent under reduced pressure provided a solid residue, which was dissolved in EtOAc (10 mL) and washed with a NaHCO₃-saturated solution (3 × 30 mL). The organic phase was dried over MgSO₄ and concentrated under vacuum to afford 2 (3.01 g, 15.5 mmol, 98% yield) as an oil. IR (ATR): ν 3492, 3454, 3346, 2953, 2925, 2851, 1605, 1519, 1468, 1442, 1355, 1331, 1274, 1254, 1183, 1114 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 6.75 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 1.9 Hz, 2H), 6.59 (dd, *J* = 8.0 and 1.9 Hz, 1H), 2.47 (t, *J* = 7.5 Hz, 2H), 1.53 (m, 2H), 1.28 (m, 6H), 0.86 (t, *J* = 6.5 Hz, 3H). ¹³C NMR (62.5 MHz, CDCl₃): δ 143.5, 141.4, 136.1, 120.7, 115.6, 115.3, 35.3, 31.8, 31.6, 29.0, 22.6, 14.1. HRMS (ESI⁻). Calcd for C₁₂H₁₇O₂ ([M - H]⁻): *m/z* 193.1234. Found: *m/z* 193.1232.

Synthesis of (*Z*)- and (*E*)-1,2-Bis(methoxymethoxy)-4-(undecyl-1-enyl)benzene (8). Decyltriphenylphosphonium bromide (9.60 g, 19.86 mmol) was dissolved in anhydrous THF (110 mL) under nitrogen, and *t*-BuOK (4.23 g, 37.69 mmol) was added portionwise. After stirring for 10 min, a solution of 5 (4.49 g, 19.85 mmol) in anhydrous THF (30 mL) was added to the reaction mixture, which was stirred for 3 h at the reflux temperature. After cooling, the

reaction was quenched with water (90 mL), the phases were separated, and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic phases were dried over MgSO₄ and concentrated under reduced pressure to afford crude material, which was purified by column chromatography (hexanes–EtOAc, 10:1) to give a mixture (9:1) of (*Z*)- and (*E*)-8 (5.32 g, 77% yield) as an oil. IR (ATR): ν 2923, 2853, 1581, 1509, 1465, 1397, 1257, 1225, 1202, 1152, 1125, 1072 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 7.14 (d, *J* = 2.5 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 6.92 (dd, *J* = 8.5 and 2.2 Hz, 1H), 6.34 (d, *J* = 11.6 and 6.7 Hz, 1H), 6.12 (dt, *J* = 15.8 and 6.7 Hz, H_E), 5.62 (dt, *J* = 11.6 and 7.3 Hz, H_Z), 5.25 (s, 4H), 3.55 (s, 6H), 2.34 (m, 2H), 1.30 (m, 14H), 0.91 (t, *J* = 6.6 Hz, 4H). ¹³C NMR (62.5 MHz, CDCl₃): δ 146.79, 145.78, 132.53, 128.01, 122.98, 117.36, 116.24, 95.52, 95.41, 56.16, 56.12, 31.91, 30.02, 29.60, 29.57, 29.45, 29.33, 29.25, 22.70, 14.13. HRMS (ESI⁺). Calcd for C₂₁H₃₄O₄Na ([M + Na]⁺): *m/z* 373.2349. Found: *m/z* 373.2349.

Synthesis of 1,2-Bis(methoxymethoxy)-4-undecylbenzene (9).

To a stirred solution of a mixture of (*Z*)- and (*E*)-8 (5.32 g, 15.18 mmol) in EtOAc (135 mL) was added palladium/carbon (610 mg). The mixture was hydrogenated under a flow of H₂ overnight. The mixture was filtered through Celite and concentrated under reduced pressure to afford 9 (5.07 g, 14.4 mmol, 91% yield). IR (ATR): ν 2923, 2853, 1589, 1509, 1465, 1398, 1259, 1225, 1201, 1152, 1128, 1072 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 7.05 (d, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.76 (dd, *J* = 8.2 and 2.0 Hz, 1H), 5.22 (s, 2H), 5.19 (s, 2H), 3.52 (s, 3H), 3.51 (s, 3H), 1.58 (t, *J* = 7.4 Hz, 2H), 2.53 (m, 2H), 1.30–1.23 (m, 16H), 0.88 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (62.5 MHz, CDCl₃): δ 147.15, 145.16, 137.62, 122.16, 116.99, 116.83, 95.66, 95.50, 56.13, 56.06, 35.49, 31.92, 31.62, 29.68, 29.64, 29.63, 29.53, 29.35, 29.25, 22.75, 14.17. HRMS (ESI⁺). Calcd for C₂₁H₃₆O₄Na ([M + Na]⁺): *m/z* 375.2506. Found: *m/z* 375.2509.

Synthesis of 4-Undecylcatechol (3).

Compound 9 (3.78 g, 10.7 mmol) was dissolved in MeOH (175 mL), and 1.4 mL of concentrated HCl was added. The mixture was heated to reflux for 3 h. Evaporation of the solvent under reduced pressure provided a solid residue, which was dissolved in diethyl ether (75 mL) and washed with a NaHCO₃-saturated solution (3 × 30 mL). The organic phase was dried over MgSO₄ and concentrated under vacuum to afford 3 (2.75 g, 10.4 mmol, 97% yield) as an oil. IR (ATR): ν 3451, 3339, 2952, 2915, 2850, 1601, 1520, 1472, 1357, 1336, 1278, 1184, 1146, 1117, 1091 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 6.79 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 1.9 Hz, 1H), 6.63 (dd, *J* = 8.0 and 2.0 Hz, 1H), 2.51 (t, *J* = 7.2 Hz, 2H), 1.29 (m, 16H), 0.90 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (62.5 MHz, CDCl₃): δ 143.25, 141.14, 136.35, 120.81, 115.50, 115.21, 35.25, 31.93, 31.62, 29.68, 29.64, 29.61, 29.53, 29.35, 29.25, 22.71, 14.10. HRMS (ESI⁻). Calcd for C₁₇H₂₈O₂ ([M - H]⁻): *m/z* 263.2017. Found: *m/z* 263.2013.

Synthesis of Polymers. General Procedure. A solution of catechol (0.5 g) in 50 mL of MeOH (1% w/v) was heated to 40 °C and a 100 M excess of ammonia (25% aqueous solution) was added dropwise over 5 min. After stirring for 24 h at 40 °C, the dark solution was diluted with 60 mL of water, and the excess of ammonia and MeOH was removed under reduced pressure. The resulting aqueous solution was treated with concentrated HCl until the pH was slightly

acidic and extracted with hexane (3 × 80 mL). The combined organic phases were dried over MgSO₄ and concentrated under reduced pressure to afford a slightly brown solid material, which was used without further purification.

3. RESULTS AND DISCUSSION

3.1. Synthetic Route for Functional Catechol Precursors. The synthesis and characterization of long-chain 4-heptadecylcatechol (**1**) and 3,5-diheptadecylcatechol (**4**) have already been reported elsewhere.^{43,44} Short- and medium-chain-length alkylcatechols **2** and **3** were obtained by means of an analogous synthetic route, as depicted in Scheme 1. Briefly, the hydroxyl groups of commercial 3,4-dihydroxybenzaldehyde were protected as the corresponding methoxymethyl ethers, yielding aldehyde **5**. At this point, synthetic pathways diverged toward target compounds **2** and **3**. The Wittig reaction of aldehyde **5** with pentyltriphenylphosphonium bromide and *t*-BuOK in dry THF afforded olefin **6** in 79% yield as a 10:1 mixture of *Z* and *E* isomers, which was hydrogenated using ammonium formate under palladium catalysis to afford **7** in almost quantitative yield. Finally, cleavage of the methoxymethyl ethers in refluxing MeOH with acidic catalysis provided the target **2** in quantitative yield. An analogous set of reactions starting from aldehyde **5**, but using decyltriphenylphosphonium bromide as the phosphorane precursor and H₂ instead of ammonium formate in the hydrogenation step, led to the synthesis of **3**. Overall yields from the starting aldehyde were 71% and 63% for **2** and **3**, respectively.

3.2. Preparation and Characterization of Catechol-Based Polymeric Materials. The new polymeric catechol derivatives, **M2–M4**, derived respectively from precursors **2–4**, were prepared following a previously reported protocol for the preparation of ammonia-polymerized 4-heptadecylcatechol (**M1**) with an 85% yield.⁴¹ In all cases, the reaction was essentially quantitative within a few hours, as evidenced by the formation of turbid dark-brown dispersions and the disappearance of the starting monomeric catechol. In order to isolate the polymeric materials, the reaction mixture was diluted with water, MeOH and ammonia were removed under reduced pressure, and the aqueous suspension was acidified to pH 5 and extracted with *n*-hexane. **M1–M4** were obtained by evaporation from dry *n*-hexane phases as dark-brown solids and characterized by NMR and IR (see the Supporting Information, Figures S1 and S2). As previously reported for **M1**,⁴¹ ¹H NMR spectra of the new polymeric materials **M2–M4** only exhibit clear signals corresponding to part of the aliphatic nuclei of the alkyl chains, with only very broad, weak, and unstructured features in other areas of the ¹H NMR spectrum. This observation is consistent with the hypothesis that isolated materials are likely mixtures of oligomers under strong dynamic effects at room temperature. The presence of significant amounts of free radicals in the polymeric materials as a possible explanation for this anomaly was already ruled out in a previous study of **M1**⁴¹ by electron paramagnetic resonance and SQUID magnetization measurements.

IR spectra of **M2** and **M3** show distinctive peak profiles, in which two new signals not present for the starting catechol monomers stand out, namely, a medium peak around 1676 cm⁻¹, which could be assigned to carbonyl groups in *o*-quinone moieties, and a strong peak near 1575 cm⁻¹, which could be attributed to electronically poor olefins, although in both cases, peaks might be also assigned to imine bonds arising from Schiff-base condensations between ammonia/amines and *o*-

quinone carbonyl groups. On the basis of these and previously reported data on polymer **M1**, a plausible pathway for the polymerization reaction would start with the oxidation of the parent catechol by aerobic oxygen in basic media to the corresponding *o*-quinone, followed by 1,2 or 1,4 addition of ammonia to form either a Schiff base or a Michael-type adduct, respectively (see the Supporting Information for details). The simultaneous occurrence of any of these reactions and subsequent tautomerization processes and reactions between all of these intermediates in different oxidation states would lead to highly disordered oligomeric systems presenting both *o*-quinone and catechol moieties. Overall, the difficulties encountered in the elucidation of the molecular structures of isolated materials are not surprising but reminiscent of those encountered in previous and ongoing research on other catechol polymeric compounds obtained by melanization, such as natural and synthetic eumelanins⁴⁵ and PDA.^{46,47}

3.3. Coating Properties. In stark contraposition to natural and synthetic melanins⁴⁵ and PDA,^{46,47} which are essentially insoluble in common organic solvents, all materials herein described (**M1–M4**) were soluble in certain common organic solvents, such as *n*-hexane or chloroform. This allowed us to use a simple *ex situ* methodology for its application as coatings on different surfaces without any prior priming or pretreatment of the woven surfaces. In a typical experiment, a 25 cm² sample of the surface to be coated was immersed for 1 min in a 0.1–1% (w/v) solution of the polymeric material in chloroform, rinsed with a clean solvent, and dried. The hydrophobicity of the coated samples was characterized by CA measurements with water droplets (Table 1).

Table 1. CA Values Obtained with Water Droplets on Different Substrates after Treatment for 1 min with a 1% (w/v) Chloroform Solution of Polymeric Material

material	functional substitution pattern	glass	polyester	cotton
M1	4-C17	88.3 ± 4.8	134.1 ± 8.1	133.8 ± 5.3
M2	4-C6	79.2 ± 6.2	129.7 ± 7.8	0
M3	4-C11	81.1 ± 5.7	128.2 ± 6.4	0
M4	4,5-bis(C17)	102.3 ± 6.3 ^a	135.3 ± 7.2	129.3 ± 6.7

^a*n*-Hexane was used as the solvent.

We studied first the effect of the alkyl side-chain length on the performance of the resulting hydrophobic coatings. Glass slides treated with solutions of materials **M2** and **M3** showed very similar CA values, around 80°, regardless of the length of the linear alkyl chain present in the starting catechols (C6 and C11, respectively) but slightly below that of **M1** (88°),⁴¹ derived from long-chain (C17) catechol **1**. Polyester fabric coated with **M2** and **M3** showed similar CA values, around 130°, close to that reported for **M1** (134°). These CAs are substantially higher than those measured on glass surfaces and fully consistent with the general observation that the surface roughness exacerbates the intrinsic hydrophobicity of ideally flat substrates.⁴⁸ Remarkably, coating layers applied in this fashion are still thin enough so as not to smear the textile with a continuous layer; i.e., coated fibers remain instead fully detached from each other, an essential precondition to preserve the breathability, flexibility, and touch of the original textile material (Figure 2).

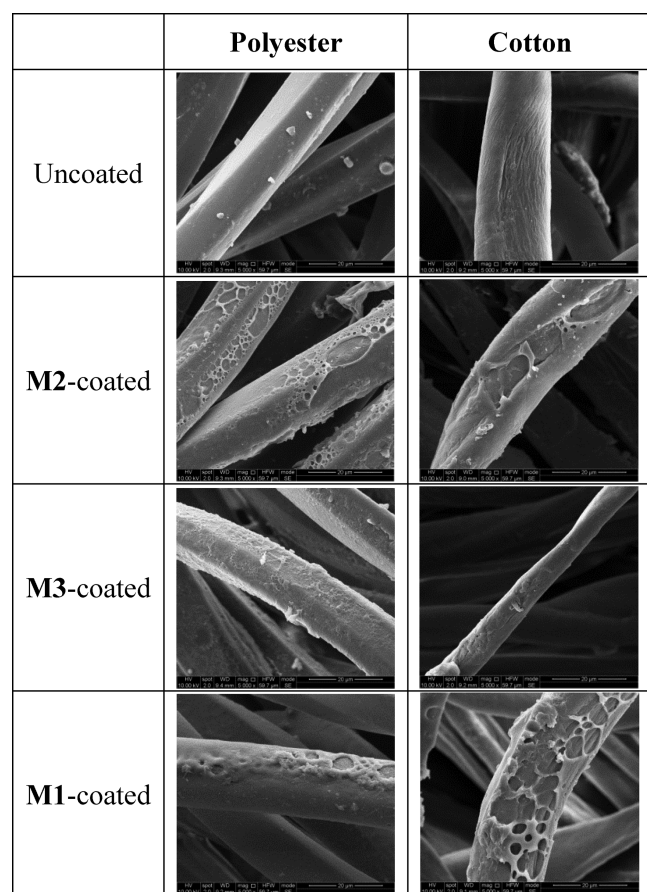


Figure 2. SEM images of uncoated and coated cotton and polyester weaves. Coatings were prepared from 1% solutions of the respective polymers in *n*-hexane. The presence of a thin coating layer is evidenced by edges and other layer irregularities, absent in images of the uncoated fibers.

In order to rank the efficacy of the coating materials, we measured the CAs on coated polyester prepared from solutions of **M1** (C17), **M2** (C6), and **M3** (C11) in different concentrations (0.1%, 0.5%, and 1% w/v) in chloroform (Figure 3a). Here, the effect of the alkyl chain length is very clear because dilute solutions are unable to efficiently coat the polyester textile in the experimental conditions, as evidenced by the fact that, for **M2** and **M3** at 0.1% w/v, water droplets were rapidly absorbed by the textile. At 0.5% w/v, **M2**, bearing the shortest alkyl chain, yields a CA of around 30° below the plateau value. On the other hand, even dilute solutions of **M1** afforded near-optimal CAs. In order to qualitatively assess the robustness of optimal hydrophobic coatings, water droplets on top of a horizontal **M1**-coated piece of woven polyester were monitored for 10 min after vertical placement on the substrate. The hydrophobic layer was able to effectively hold the droplet, preventing both loss of the CA and change of shape. Indeed, no collapse of the droplet or significant wetting of the fabric was observed throughout, with the droplet losing about 30% of its volume by evaporation (Figure 3b).

The performance of these materials on real substrates was further tested on the cotton weave of a lab coat, which because of its high intrinsic hydrophilicity, surface area, and absorption capability provided a more stringent test for the hydrophobization capacity of catechol-based polymers than polyester. In this case, the effect of the alkyl chain length was more

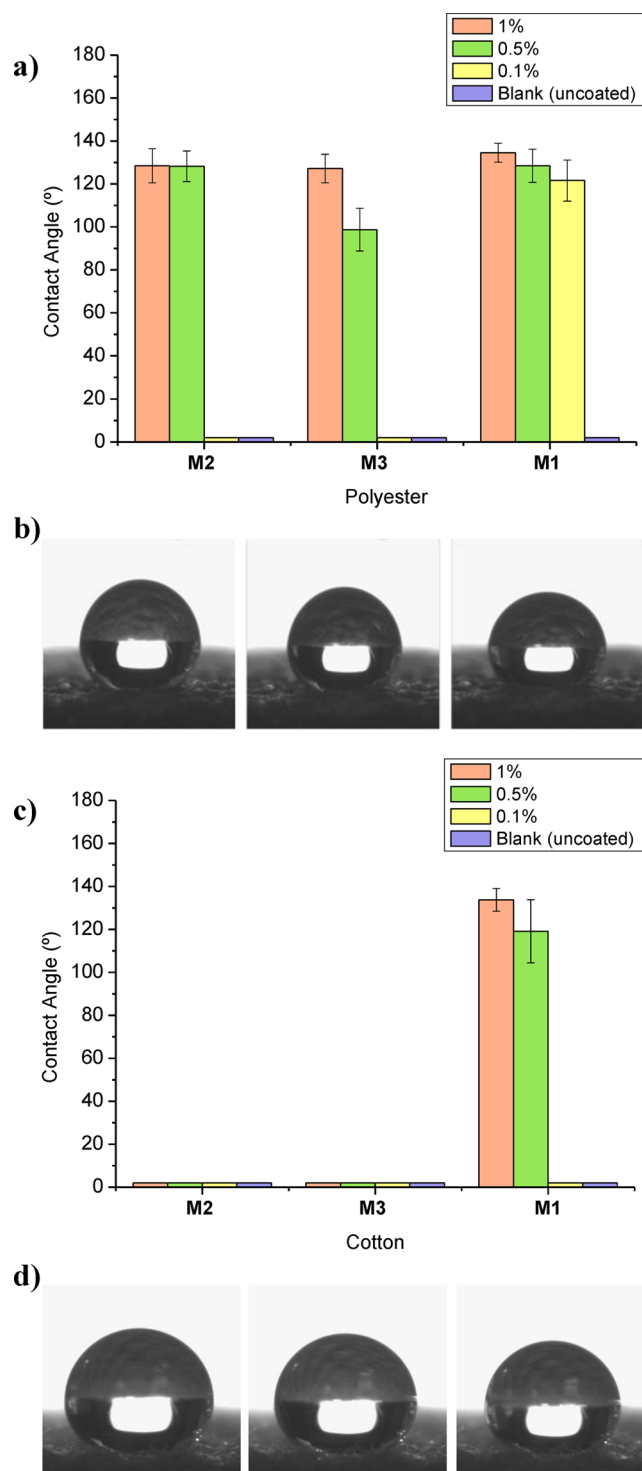


Figure 3. (a) Effect of the solution concentration used for dip-coating on the efficacy of coating materials **M2**–**M1** on polyester (a) and cotton (c). Zero values for the CA indicate fast collapse (<10 s) of the water droplet due to absorption in the textile. Robustness of **M1** coatings on polyester (b) and cotton (d) prepared from 1% w/v chloroform solutions: evolution of the water droplets after 1, 5, and 10 min (left to right).

evident because neither **M2** (C6) nor **M3** (C11) was able to provide water-repellency (>1 min) that would last enough for us to take meaningful CA measurements. As far as **M1** is concerned, very dilute coating solutions (0.1%) were not effective, but even a 0.5% w/v solution already afforded

reasonably good CA values, around 120° (Figure 3c). For optimal coatings prepared from 1% w/v solutions, CA values consistently reached above 140° , thanks to the weave roughness. Finally, **M1** coatings on cotton also passed the robustness test by keeping the fabric dry for at least 10 min, with no apparent loss on the CA value. As observed for polyester-coated surfaces, the absence of noticeable absorption in the fabric would indicate that the observed volume loss is due to slow evaporation of the liquid (Figure 3d).

In order to assess the effect of the double alkyl chain substitution, comparative CA measurements were taken on substrates coated with **M4**, derived from catechol **4** and bearing two C17 substituents. On glass, **M4** showed a moderate 15% higher CA (102°) than those of polymers derived from single-substituted monomers (**M1**–**M3**). On a polyester textile coated according to the ex situ immersion procedure mentioned above, **M4** afforded a CA value of 135° , essentially identical with that of **M1**, indicating that this is probably the maximum (optimal) CA achievable with this family of catechol-based hydrophobic coatings on the polyester fabric used. SEM images of **M4**-coated polyester fibers are similar to those already shown for the other materials, where the presence of a coating layer is clearly observed (see the Supporting Information, Figure S3). On cotton, nevertheless, slightly lower CA values were recorded for **M4**, probably hinting at a lower polymerization degree, leading to a lesser robustness of this coating. In view of the comparative results of **M1** and **M4** and the performance of single-functionalized **M1** on cotton, it seems clear that double-long alkyl chain substitution on these catechol-based materials does not provide a significant improvement on their hydrophobic performance, whereas chain lengths of at least C17 proved critical in order to achieve satisfactory water-repellency.

To complete characterization of the coating properties, a series of experiments were carried out to assess the resistance of polymer **M1** against chemical aging conditions. First, we tested the in situ resistance of cotton samples (ca. $2\text{ cm} \times 2\text{ cm}$) previously coated from 1% w/v solutions of **M1** in chloroform, as outlined above. For this, triplicate samples were subsequently kept at room temperature in aqueous 1 M HCl, 1 M NaOH, and 3% w/v hydrogen peroxide, respectively, for 24 h with magnetic stirring. Test samples were then rinsed with $3 \times 100\text{ mL}$ of distilled water and dried at room temperature. After their respective treatments, samples aged in either aqueous acidic or oxidizing media afforded CAs statistically indistinguishable from those of unaged blanks, whereas those aged in basic conditions showed rapid absorption of water droplets (Figure 4a).

It should be noted that in the latter case the cut edges of the cotton weave were visibly ragged after the experiment, as opposed to the other aged samples, which showed no visible wear. We thus ran a second round of experiments in order to study the intrinsic resistance of the polymeric material, i.e., chemically aged prior to coating. In this case, aliquots of 100 mg of polymer **M1**, as obtained from the synthetic procedure outlined previously, were directly suspended in 30 mL of aqueous 1 M HCl, 1 M NaOH, and 3% w/v hydrogen peroxide, respectively, for 24 h with magnetic stirring. Each suspension was then extracted with $2 \times 20\text{ mL}$ of CHCl_3 and washed with $2 \times 20\text{ mL}$ of water, after which 90 mg of dry aged polymer were isolated from the organic phase and dissolved in 9 mL of chloroform in order to coat cotton samples according to the above-mentioned procedure.

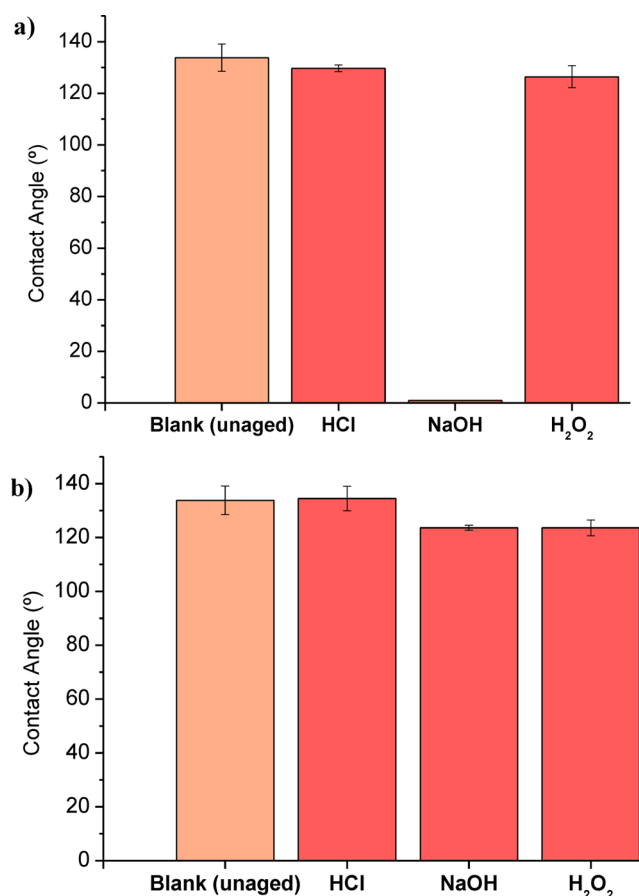


Figure 4. Chemical resistance of **M1** coatings on cotton against acidic (1 M HCl), basic (1 M NaOH), and oxidizing (3% w/v H₂O₂) aqueous media: (a) hydrophobicity of samples coated with **M1** and subsequently treated in the aging media; (b) hydrophobicity of samples coated with previously aged polymer **M1**.

In all cases, the CA values of water droplets measured on samples coated with aged polymer were essentially identical with those of blank samples, i.e., coated with unaged polymer (Figure 4b). Although it could not be ascertained whether a very small amount of polymer had been solubilized in the aqueous phase as a result of any of the aging treatments and subsequently resisted extraction in the organic phase, we conclude that the polymer did not suffer significant degradation in any of the tested media/conditions. In view of these results, the complete loss of hydrophobicity of coated cotton samples after aging in aqueous 1 M NaOH is more likely attributable to the degradation of the textile weave.

3.4. Oil Absorption and Phase Separation Tests.

Because of its superior water-repellency performance, **M1** was used as the coating material for the assessment of the surface-modifying properties of this family of catechol-based coatings by means of oil-absorbance tests, as well as two simple oil/water separation experiments simulating the removal of oily pollutants from aqueous phases. In addition to cotton and polyester textiles as common-use materials, filter paper was also studied as a fibrous, absorbent nontextile model substrate.

Oil Absorption Capacities of Treated Absorbents. At first glance, the three materials show notable differences in morphology that are expected to determine their respective liquid absorption capacities (see the Supporting Information, Figure S4). Both cotton and polyester are woven materials

made of bundles of single fibers with diameters of ca. 20 μm , but cotton's weave is thicker and less porous than that of polyester, which exhibits a relatively regular pore system. As opposed to textiles, filter paper appears as an unstructured material, where cellulose fibers are randomly oriented and loosely entangled/bound.

Because of their absorbent nature and medium-to-high polarity, all three untreated substrates are inherently capable of retaining varying amounts of oil, as well as water. Indeed, all three uncoated materials are stained by both oil and water droplets placed on their surface even in very short times (1–3 s), as expected. In these regard, thus, untreated substrates act as indiscriminating absorbents. On the other hand, all treated substrates showed intrinsic water repellency (i.e., no water absorption), as evidenced by their buoyancy in water, alongside significantly enhanced oil absorption. As far as net capacity (c) is concerned,⁴⁹ comparative tests were carried out using *n*-tetradecane (TDC) and pure olive oil as nonvolatile model pollutants. For this purpose, coated samples of known dry weight were soaked in test oils for 10 min, taken out, allowed to drain for 30 min, and reweighed. Compared to untreated substrates, the oil absorption capacities roughly doubled in all cases, showing values between 100% and 180% (w/w), depending on both the material and oil phase tested (Table 2).

Table 2. Percentual Weight Absorption Capacities (%) of M1-Coated and Uncoated (in Parentheses) Absorbent Substrates for Liquid Tests

absorbent substrate	water	oil	
		TDC	olive oil
cotton	repellent (85 \pm 9)	146 \pm 7 (67 \pm 5)	164 \pm 6 (81 \pm 4)
polyester	repellent (92 \pm 9)	101 \pm 9 (46 \pm 4)	179 \pm 7 (89 \pm 7)
filter paper	repellent (140 \pm 13)	86 \pm 3 (50 \pm 7)	97 \pm 5 (61 \pm 3)

Although differences in the absorption capacities between substrates may be largely attributed to significant variations in the parameters such as the porosity, surface area, and regularity of the microstructure of the absorbents,⁵⁰ as well as the viscosity/smearing ability of the oil test liquids, these results demonstrate that the surface properties of household absorbent materials with differing morphologies can be very effectively tampered with the *ex situ* procedures described. This allows their intrinsic absorbent qualities to be turned around, without recourse to specific micropatterning designs or chemical modification. Interestingly, the oil absorbent capacity of treated cotton versus TDC (146%) turned out to be similar to that of the same substrate versus olive oil (164%) and strikingly superior to the native water absorbent capacity of the untreated weave (85%). This is quite remarkable because TDC has a low viscosity (2–3 cP), comparable to that of water (1 cP), and does not appreciably smear treated substrates, in contrast to olive oil (viscosity ca. 80 cP; see Figure 5 for differential smearing effects).

The robustness of the hydrophobic coatings was further assessed by repeated cleaning and reuse cycles. The absorbed oil could be completely removed by rinsing oil-soaked substrates in an organic solvent such as ethanol or acetone, taken out, and then dried. Clean, treated substrates were then subject to five consecutive absorption/removal experiments,

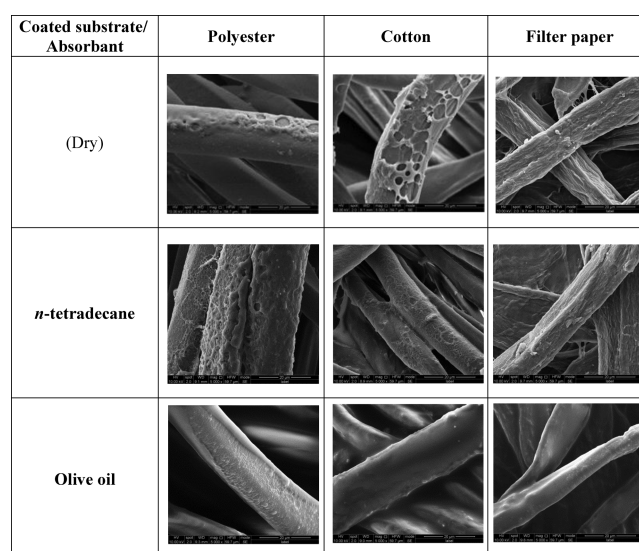


Figure 5. From left to right, SEM images of polyester, cotton, and filter paper fibers after absorption of TDC (top) and olive oil (bottom). After draining of excess oil, no obvious smearing is observed for TDC, as opposed to olive oil.

after which the net adsorption capacities did not deteriorate, nor did the substrate dry weights after reuse deviate significantly from their respective weights before use (Figure 6). The CAs of the reused coated materials after five cycles were shown to be comparable to their corresponding initial values (see the Supporting Information, Table S1).

Removal of Oil Contaminants from Water. The absorption capacity values determined for M1-coated substrates were used to simulate oil pollutant removal using these materials. With this aim, a ca. 2.5 \times 2.5 cm² coated sample of known weight of a given substrate was put in contact for 10–15 s with a water/oil bath containing a quantity of oil equal to the corresponding saturation value of the substrate. The sample was then taken out of the mixture and weighed using the same protocol as that described above (Figure 7a–e) after excess oil was drained. In these conditions, ca. 90–95% of the initial oil weight could be removed by absorption onto the coated substrate. As above, an appropriate solvent could be used to rinse the oil from the absorbent material, which could then be further reused.

Finally, the water repellence of M1-coated cotton weaves was used for phase separation by filtration of a water/oil mixture. Because of the lipophilic and absorbent nature of treated surfaces, oils quickly soaked them and, after oil saturation, permeated through, while water was retained on the top (Figure 7f).

4. CONCLUSIONS

In summary, a new general strategy for the synthesis of functional catechols has been applied to the preparation and systematic study of the performance of a family of robust hydrophobic coatings. These compounds were obtained by polymerization of catechol derivatives differing in the length and number of alkylic side chains, by means of an oxidative mechanism reminiscent of that reported for PDA and eumelanin, but advantageous in two counts. First, because the oxidative polymerization reaction makes use of an already functionalized catechol and an exogenous source of nitrogen (ammonia) in the presence of air, it affords functional PDA-like materials bearing a maximized-by-design content of the

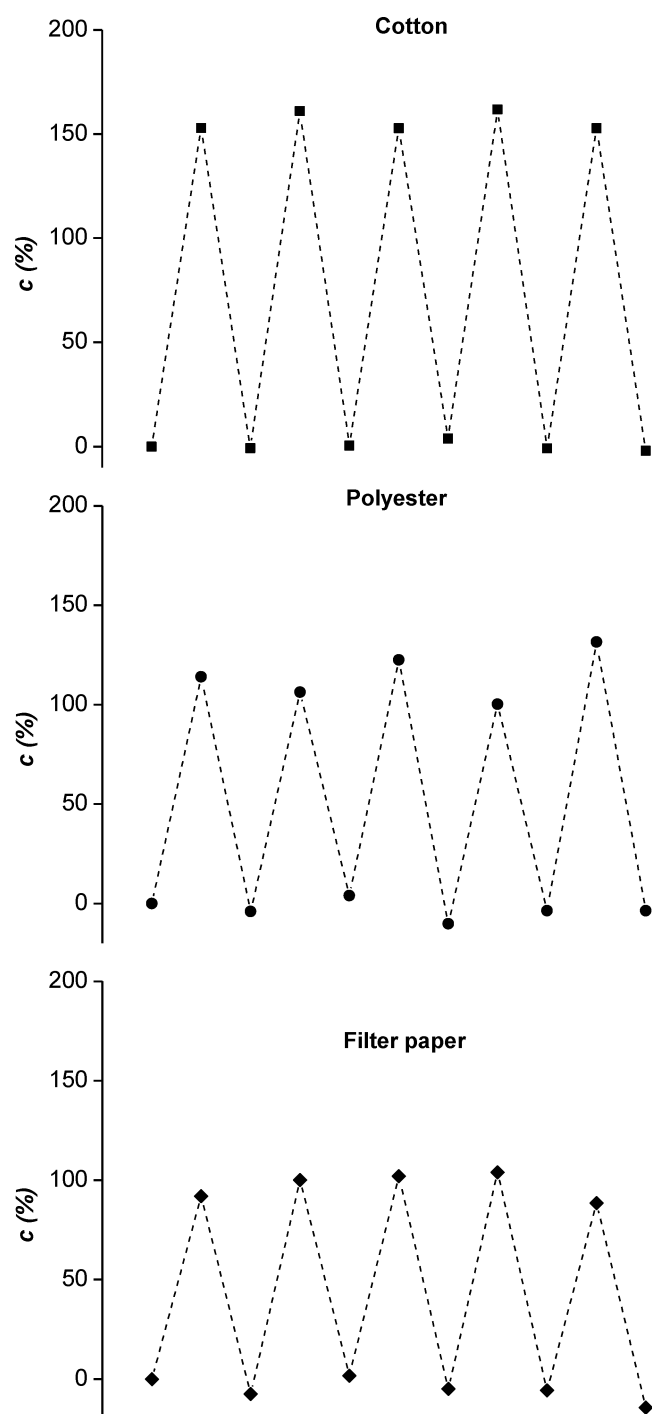


Figure 6. Recyclability of M1-coated fibrous substrates (cotton, polyester, and filter paper) assessed by the net oil absorption capacity, c . Five TDC absorption/cleaning cycles were carried out (immersion, 10 min; draining, 30 min; rinsing in ethanol, 30 min). Clean substrates were dried under vacuum at 30 °C for 1 h before reweighing.

functional side chain. Second, in contrast to eumelanin, PDA and their Michael-addition reaction derivatives, these materials proved to be soluble in certain common organic solvents and thus amenable to very fast, simple *ex situ* treatments, which may be conveniently optimized in terms of coating conditions and are capable of affording ultrathin coatings on different substrates.

As a proof-of-concept of the viability of this procedure and the robustness of the water-repellent character of the polymeric

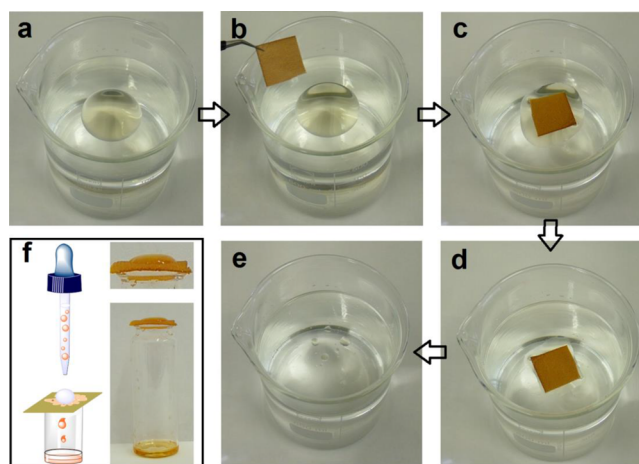


Figure 7. Selective oil removal: (a) TDC/water mixture; (b–e) soaking of a M1-coated cotton sample. (f) Schematic representation of an oil/water phase separation by filtration over a hydrophobically coated substrate fiber (right); picture after filtration using a M1-coated cotton sample, with the water phase retained on the top (left). A small amount of dye was added to the oil phase to help with visualization of the oil/water interface.

materials, the CAs of coated samples of polyester and cotton weaves were measured and their evolution with time was followed. Long alkyl chains of at least C17 were necessary in both cases to ensure effective water repellency, as attested by CA measurements. On the other hand, double substitution on the monomer proved redundant with regard to water repellency, in comparison with the C17 monosubstituted catechol derivative. As far as the optimal coating conditions are concerned, the most effective coatings were prepared by immersion of substrates for 1 min in 0.5–1% chloroform solutions; higher concentrations or immersion times were not necessary to prepare fully effective water-repellent coatings even on highly hydrophilic cotton, showing no noticeable wetting or even loss of CA for at least 10 min. These coatings showed effectiveness in the transformation of water-absorbent polyester and cotton weaves, as well as filter paper, into reusable water-repellent, oil-absorbent substrates, capable of retaining roughly twice their weight of model hydrophobic compounds (TDC and olive oil), as well as of separating water/oil mixtures by simple filtration.

■ ASSOCIATED CONTENT

📄 Supporting Information

Further details on the chemical characterization of the polymeric materials prepared and the morphological and functional properties of the resulting coatings. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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📄 Notes

The authors declare no competing financial interest.

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