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COMMUNICATION

Bioinspired Adhesive Polymer Coatings for Efficient and Versatile Corrosion Resistance

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Abstract

Anticorrosion ability of ultrathin coatings with bio-inspired organic polymers is demonstrated. We prepared a series of catechol-containing poly(alkyl methacrylate)s by free radical polymerization. These copolymers were spin-coated on various corrosion susceptible metal/alloy substrates of magnesium, aluminum, copper and iron without any harsh pretreatment. Several key factors like molecular structure, composition ratio and processing condition were wisely tailored to afford a transparent, firm and sub-micron polymer coating on those substrates. Corrosion resistance of the polymer-coated substrates was thoroughly investigated by immersion tests in salt-water and acidic solution, polarization test, and visual inspection. Formation of an anomalous dense layer of ca. 5 nm thickness adjacent to the metal surface and a remarkable effect of thermal treatment were clearly observed by neutron reflectivity measurement, leading to a highly protective ability against foreign molecules e.g. water or corrosive ions. Key molecular design for anticorrosive polymer coating was revealed to be a combination of strong and versatile binding ability of catechol units and defect free polymer layers formed on the metal substrates in the presence of hydrophobic alkyl chains.

Introduction

Structural metals/alloys are very useful and inevitable in our daily life and in numerous industrial applications. One major concern of using such materials is to maintain their structural or functional reliability and appearance from environmental pollutants or corrosive hazards. Therefore, several methods such as chromate passivation, electrochemical plating, anodizing, and coating/painting have been developed and used for a long-time.¹⁻⁴ Generally, in those cases a protection layer forms on the metal surface, which consists of several tens to hundreds of μm in thickness. On the other hand, during last few decades a tremendous effort has been made in all fields of science and technology to develop smart tools/devices with compact size, light-weight and sophisticated fabrication. Remarkably, these trends empowered a rapid advance in the field of nano-materials/technology and have led new innovations and applications with structural metals/alloys especially in the field of nano-medicine/robotics/mechatronics.⁵⁻⁸ In proportion to reduced backbone dimensions and weight, anticorrosion layer has to be more

sophisticated and thin, possibly below sub-micron size, with adequate performance. In this context, conventional anticorrosion techniques are limited by several disadvantages e.g. harsh pretreatment condition, high thickness, and sometimes complicated set-up/use of toxic hexavalent chromium.^{3,4,9,10} Therefore, it is the need of hour to develop ultrathin, versatile, ecofriendly and easy coating technique for state-of-the-art (nano)structural architectures.

In this report, we demonstrate a simple but efficient strategy for creating ultrathin protective coating for versatile and practically useful structural metal/alloy substrates. Considering environmental threat of Cr(VI), a substantial effort has been given to develop non-chromate based anticorrosive coating mainly based on phosphate or silicate.¹¹⁻¹⁵ Organic coatings have also attracted considerable attention owing to versatility, light-weight and easy process.¹⁶⁻¹⁸ For instance, heterocyclic organic compounds consisting of a π -system with O, N, or S heteroatoms like benzothiazole (BTAH) have been utilized for copper corrosion inhibition.¹⁸ It is noteworthy to mention that such organic coating exhibit high protection efficiency even at below sub-micron thickness. However, efficiency of such coating is highly dependent on combination of metal/alloy surface and anchoring moiety of the coating materials. Therefore, it is important to develop a universal design of such coatings, which shows high corrosion resistance for wide-range of substrates even with ultra-thin protection layer. Recently, computational study suggested that effective corrosion resistance of organic inhibitors generally attributes to the presence of strong metal binding component and intermolecular aggregation covering the metal surface. Thus, we envisioned that catechol group, which is common in adhesive foot proteins of several marine organisms,^{19,20} would be a suitable binding group to create a strong protection layer on a variety of metals/alloys from corrosive media. Dopamine and its derivatives, which are main contents of mussel proteins, have been reported to show good binding affinity towards metals, metal oxides, ceramics, or synthetic polymers.^{21,22} Such materials have been widely investigated as anchoring group to multi-functionalize surface of base materials,²³⁻³¹ adhesives,³²⁻³⁷ anti-bacterial,³⁸⁻⁴⁰ and some biological applications^{41,42}. However, to the best of our knowledge, the catechol-containing (macro)molecules have never been applied for anti-corrosion purpose on metals/alloys. In addition, polydopamine coating often gives a dark color to the base materials

and cost of dopamine unit is reasonably high, which may not be desirable for some practical large-scale applications. Within this context, we prepared a variety of poly(alkylmethacrylate)(PAMA)s with varying contents of catechol unit as a side chain (Figure 1). Here, we expected that catechol moiety acts as a universal binder to attach on versatile metal/alloy surfaces. PAMA counterparts assist in forming a stable protective layer by strong hydrophobic interactions among intra-/interchains. Moreover, this method may reduce overall cost significantly as majority of these polymers consist of cheap alkyl methacrylate units. As a model of highly corrosion susceptible structural materials, we chose magnesium (Mg), aluminum (Al), copper (Cu), and iron (Fe) metals/alloys. Corrosion resistance of ultrathin polymer coating on these substrates was examined by several methods such as immersion in aqueous 3.5% NaCl solution, electric polarization measurement and hydrogen evolution test under acidic condition along with visual inspection. In addition, effect of thermal treatment and detailed inhibition mechanism of the polymer coating against foreign molecule/ions was revealed by neutron reflectivity and grazing incident wide-angle X-ray diffraction (GI-WAXD) measurement.

Experimental section

General methods: All manipulations were carried out under argon atmosphere employing standard schlenk techniques. Alkyl methacrylates (methyl, hexyl, or dodecyl) were passed over activated basic alumina just before use to remove inhibitor. Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol. All other chemicals were purchased from commercial sources and used as received. ^1H and ^{13}C NMR spectra were measured for CDCl_3 or $\text{C}_2\text{D}_6\text{SO}$ (containing 1% TMS) solutions at 25 °C on JEOL JNM-ECX 300 spectrometer and the chemical shift are reported in ppm with respect to the reference SiMe_4 . Gel permeation chromatography (GPC) was performed on RI/Viscotek TDA 302 (Model 200) using THF as eluent and polystyrene as standards. FT-IR was measured for KBr pellet in a JASCO FT-IR 6100 instrument. Film thickness was studied by a DEKTAK 6M Stylus surface profiler. Water contact angle of coated surface was measured using Dropmaster 300 instrument. Scanning electron microscope (SEM) images of different substrates before and after acidic/salt-water immersion tests were studied by Hitachi SU4800/8000 instrument. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were studied using SII Seiko instruments TG/DTA 6200 and X-DSC 7000, respectively.

Polymer synthesis: Dopamine methacrylamide (DOMA) monomer (222 mg, 1 mmol) and AIBN (1 mol%) were mixed in a two-necked flask and back-filled twice with argon. Dehydrated DMF (8 mL/mmol of DOMA) and other monomer (x mmol) was added to the flask by a syringe and the solution was degassed by argon bubbling for 45 min. Polymerization was carried out at 75 °C for 24 h. The reaction mixture was cooled down to room temperature, dissolved in a small amount of dichloromethane, and precipitated in an excess of hexane (for 1A-D) or water (for 2 and 3). Crude polymer was reprecipitated in a similar way twice to remove any residual monomer by respective solvent combinations. Polymers were collected as white powders (1A-D and 2) or sticky tough materials (3) and finally dried under high vacuum at 45-50 °C for 12 h.

Thin-film formation and properties: Metal/alloy rods were cut into small plates of 2 mm thickness, embedded in epoxy resin except one top surface (for anti-corrosion study), and polished with SiC paper of successively finer surface from 600 to 1200 grit. Finally, those plates were ultrasonically cleaned successively with ethanol, deionized water, acetone, and alkaline solution containing NaOH (0.25 g L⁻¹), C₁₂H₂₅NaSO₄ (0.5 g L⁻¹), Na₂CO₃ (20 g L⁻¹) at 65 °C to remove organic impurities and dried under nitrogen flow.⁴³ A drop of approx. 100 μl polymer solution in THF was pipetted onto the substrate, uniformly spread over the whole area and then spun at 1000 rpm for 15 s and 2000 rpm for 10 s with 5 s slope in each case. Subsequent heating at 80 °C for 1 h in an air circulated oven lead to solvent evaporation and resulted in transparent polymer film strongly attached to the metal surface. For the test of coating adhesiveness, polymer and very small amount of Rhodamine B dye was dissolved in THF+MeOH (9:1) and drop-casted on glass plate. After keeping 15 mins in room temperature, glass slide was annealed at 80 °C for 1 h and cooled down to ambient condition. A commercially available scotch-tape was firmly attached on the coating and slowly peeled-out from the surface. This process was repeated several times using new tape each time. If polymer coating was not peeled out, coated substrate was further immersed in distilled water for 24 h and scotch-tape test was carried out again.

Anticorrosion tests: Mg alloy (AZ31) rod of 15 mm diameter was used for hydrogen evolution study. Metal plates were resin embedded except top side. Samples were immersed in an acidic buffer solution (1:1 mixture of 0.2 M Na₂HPO₄ and 0.1 M citric acid) of ~ pH 5 for specified time at room temperature. A simple set-

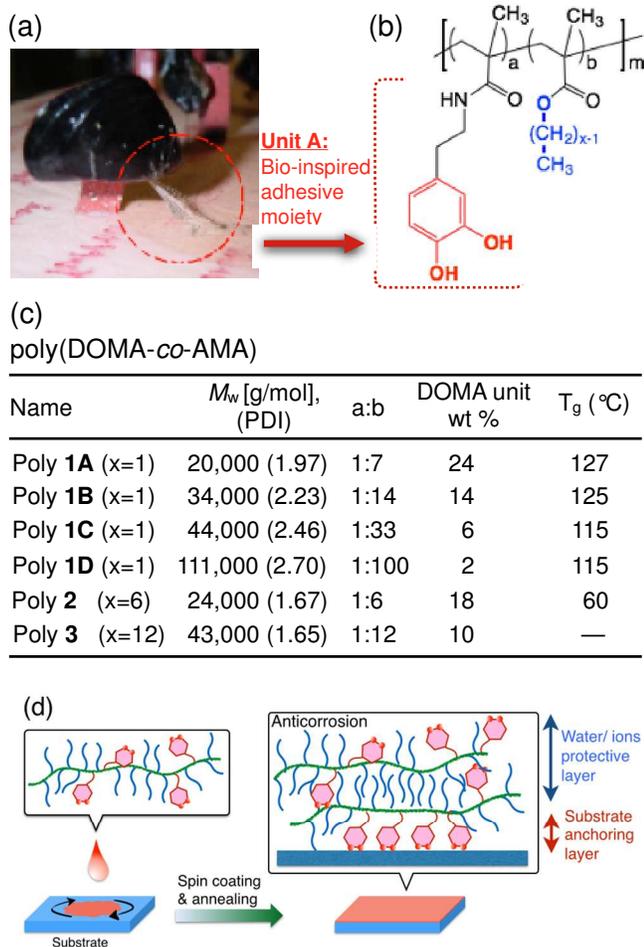


Fig. 1 (a) Photograph of a blue mussel and its adhesive byssus, which contains mainly catechol and amine (dopamine) units. (b) Chemical structure of poly(dopamine methacrylamide-co-alkyl methacrylate), poly(DOMA-co-AMA). (c) Various combinations, compositions, and gel permeation chromatography (GPC) data of poly 1-3. (d) Schematic illustration of preparing ultrathin polymer coating and possible pathway of forming stable protecting layer on metal/alloy substrates.

up for this experiment has been shown in Figure S14. Salt-water immersion test was studied for all samples in 3.5 wt.% NaCl aq. solution at room temperature. Al (99%, Nilaco Corp.), Cu (99.9%, Nilaco Corp.), Fe (3N5 purity, ESPI), and Mg (AZ31) were used in our study. Metal plates were cut into small plates and cleaned according to the procedure mentioned earlier. Anti-corrosion study by electrochemical method was done using ALS-CHI 660A electrochemical set up having four electrodes combinations. Coated/uncoated Mg substrates were used as working electrode, standard calomel electrode as reference electrode, platinum wire as counter electrode and sense (Figure S17). Before final measurement, all samples were immersed in 3.5 wt.% NaCl solution for 1 h. Open circuit potential was monitored for 10 min for each case to reach an electrochemical steady state. Finally, cathodic current and anodic current were measured independently at a scan rate of 1 mV/s.

Neutron reflectivity and GI-WAXD measurement: Films were prepared from a THF solution on a Silicon block by a spin-coating method. The film was annealed under vacuum at 363 K for 12 h. Prior to the measurements in deuterated water, the film was aged in water for 2 h, which was apparently enough to cause a structural change in the film. The density profiles of the film in air and in contact with the water were examined by NR measurements using horizontal-type neutron reflectometer SOFIA at a materials and life science experimental facility, J-PARC.^{44,45} The grazing incidence wide-angle X-ray diffraction (GI-WAXD) experiments in out-of-plane geometry were carried out with a Rigaku Smartlab using CuK α radiation. GI-WAXD data were collected with the angular interval between steps 0.08° and a scan speed of 0.5° per min.

Results and discussion

Catechol-containing copolymers were synthesized by free radical polymerization of dopamine methacrylamide (DOMA) and alkyl methacrylates (AMA) with varying equivalent ratio of monomers. DOMA was made according to a reported method²⁸ and copolymerized with alkyl (methyl, hexyl, or dodecyl) methacrylate using 1 mol% azobisisobutyronitrile (AIBN) in dimethylformamide (DMF) at 75 °C for 24 h (Scheme S1 & S2). Several copolymers of different combination and composition ratio were prepared in high yields and well characterized by ¹H NMR (Figure S2-S7), FT-IR (Figure 3a), and gel permeation chromatography (GPC) (Figure 1c). The composition of the catechol unit in the obtained copolymers was estimated to be around 25-2.0 wt.% from ¹H NMR depending on the feed ratio of monomers. GPC measurement showed that the weight-average molecular weight (M_w) and polydispersity (PDI) were in the range of 2.0-11.1x10⁴ and 1.7-2.7 respectively (Figure 1c). All these copolymers were well soluble in common organic solvents like tetrahydrofuran (THF), chloroform, dimethylformamide, or dimethylsulfoxide. Thermal stability and properties of these polymers were studied by TGA and DSC. All these polymers were thermally stable at least below ca. 270 °C when overall DOMA unit

Fig. 2 (a) Comparison of TGA curves among different polymers poly **1A-D** (black), poly **2** (red) and poly **3** (blue). Heating rate was 10 °C/min. (b) DSC thermograms (second heating cycle) of poly **1A-D** (black), poly **2** (red).

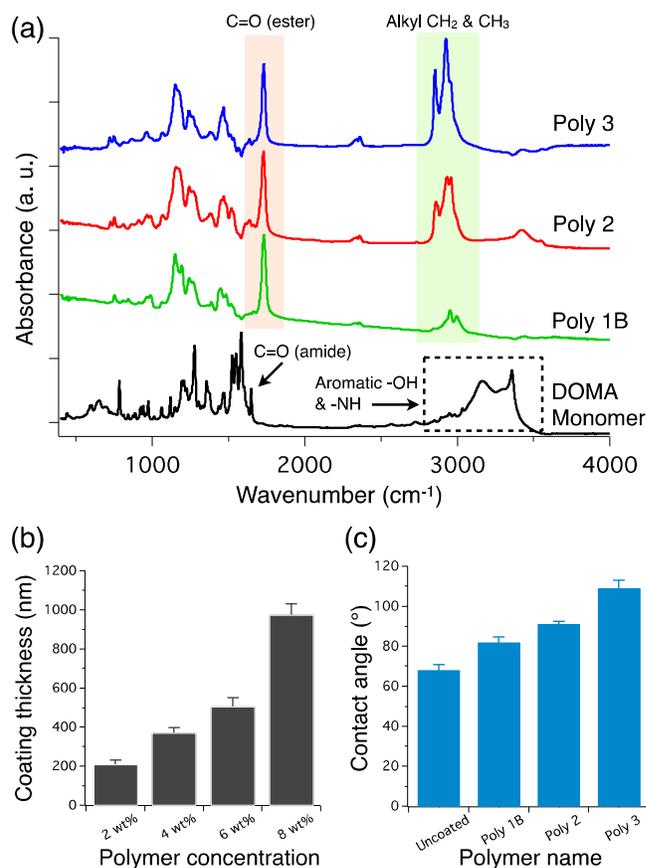
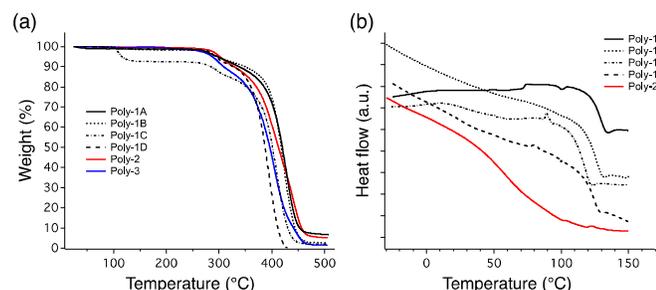


Fig. 3 (a) FT-IR spectra comparison of dopamine methacrylamide (DOMA) monomer and different polymers in KBr pellet. (b) Relation between polymer concentration and thin-film thickness measured by surface profiler. (c) Static water contact angle comparison of different polymer coated metal substrates at 298 K.



was >10 wt.% in the polymer. However, significant weight loss or early decomposition was observed when DOMA unit was below this level (Figure 2a). Therefore, DOMA unit is very important for enhanced thermal stability and this could be crucial for high-temperature practical applications. DSC thermograms of poly **1-3** have been shown in figure 2b and glass-transition temperature (T_g) were estimated from the second heating cycle. T_g of poly **1A-D**, and **2** were close to 120 and 60 °C, respectively. Poly **3** does not have a narrow or distinct T_g under recorded condition (-70 to 150 °C). It is immediately noticeable that T_g decreased significantly with increasing alkyl chain length, which is common for these kind of polymers.^{46,47} For making thin-film, THF solution of poly **1-3** were subjected to spin coating on various substrates followed by annealing at 80 °C for 1 h. Thickness of the polymer coating was evaluated to be in the range of 0.3-1.0 μ m, and could be easily controlled by changing concentration (wt.%) of the polymer solution (Figure 3b). Static water contact angle (θ) was measured to understand the behavior of metal/alloy surface and thin-film nature after polymer coating. Hydrophobicity of the polymer films was significantly increased with increasing alkyl side chain length, which is consistent with the normal trend of hydrophobic nature among saturated alkyl chains (Figure 3c, S12).

At first, we studied stability and protecting ability of the polymer coating under corrosive acidic medium. In this case, we chose commercially available magnesium alloy (AZ31) as a substrate since Mg is very aggressive among practically useful structural metals.⁴⁸

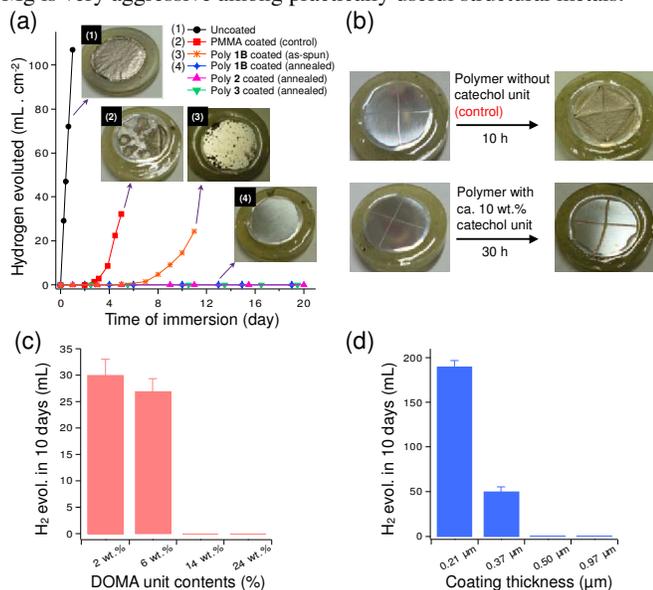


Fig. 4 (a) Hydrogen evolution plots of uncoated, PMMA coated, and poly 1-3 coated Mg alloy (AZ31) plate in acidic buffer of pH 5. Inset pictures are mentioned Mg alloy samples after H₂ evolution test. (b) Photographs of cross-cut test of PMMA coated and poly 1B coated Mg alloy plates in acidic buffer of pH 5 at room temperature. Metal plates were 15 mm in diameter, resin embedded except the top side and spin-coated with 8 wt.% polymer solution. Effect of (c) DOMA unit contents (wt.%) in the polymer, and (d) thin-film thickness under hydrogen evolution test.

It generates hydrogen (H₂) gas violently under acidic condition and therefore the degree of corrosion can be quantitatively estimated by this method. To evaluate optimum condition such as chemical structure/composition or film thickness for highly efficient anticorrosion property, different polymers were screened by the amount of H₂ evolved from polymer-coated substrates. H₂ evolution rate of polymer coated and uncoated samples after immersion in an acidic buffer of pH 5 for several days have been shown in Figure 4a. Poly(methyl methacrylate)(PMMA) coated and uncoated bare substrates were used as references. PMMA coated sample was not damaged under acidic condition for first 2-3 days of immersion but this film swelled, eventually peeled out from the metal surface and 5-6 % weight loss of the substrate immediately occurred after 4-5 days (Figure 4a). In contrast, incorporation of small amount of catechol units into the PAMAs significantly prevented swelling and thus improved anticorrosion ability. Indeed, poly 1-3 coated samples exhibited excellent protection ability against corrosive medium. H₂ evolution and weight loss were negligible even after immersion for 20 days. Surprisingly, these copolymers can prevent penetration of the foreign molecules even after making intentional cross-cut on the coating with tip of a knife. As shown in Figure 4b, cross-marked PMMA coated film completely peeled out from the metal surface after few hours of immersion in the acidic buffer. In contrast, corrosion happened only in the scratched area for poly 1-3 with ca. > 10 wt.% of catechol content. These phenomena clearly suggest that our polymers make a firm adhesive layer on the metal surface, which can prevent attack from corrosive ions very efficiently. In addition, we examined dependence of coating thickness and critical overall contents of catechol moiety using poly 1A-D. When overall catechol

contents exceeded ca. 10 wt.%, H₂ evolution was completely suppressed, whereas polymers with a composition ratio below this critical value showed good protection ability for initial 2-3 days but could not maintain for longer period of time. Moreover, film thickness above ca. 0.5 μm was crucial in longer durability and anticorrosion ability (Figure 4c-d). It is noteworthy to mention that thermal treatment after spin-coating of the polymer solution was found to have significant role for long durability and protection ability. As shown in Figure 4a, polymer film without thermal treatment (as-spun) slowly damage after 7-8 days of immersion and tiny holes formed on the coating by penetration of corrosive protons to the metal surface. Unlike the PMMA film, this case corrosion did not spread over the entire region except some tiny holes, which were not observed for annealed samples. To further clarify this phenomenon, we performed neutron reflectivity and grazing incident wide-angle X-ray diffraction (GI-WAXD), which have been discussed in the later section along with a detailed anticorrosion mechanism.

We further investigated electrochemical corrosion behavior of poly 1-3 coated substrates by polarization tests in NaCl solution at room temperature. Although we could not observe any significant effect of alkyl chain counterpart of the polymers by H₂ evolution test, this method remarkably revealed the importance of alkyl side chain length along with catechol units. All samples were immersed in the aqueous 3.5 wt.% NaCl solution for 1 h and the open-circuit potential was monitored for 10 minutes until the potential reached an almost steady state. Subsequently, the potential was swept cathodically and anodically at a scan rate of 1 mV s⁻¹. Generally, the lower current density of the coated substrate than that of uncoated substrate indicates better corrosion resistance.^{1,49} As shown in Figure 5, corrosion current density (*i*_{corr}) of uncoated Mg alloy (AZ31) was observed to be 50.2 μA cm⁻². On the other hand, *i*_{corr} of polymer-coated samples 1B, 2 and 3 were estimated to be 11.3×10⁻², 17.1×10⁻⁵, and 39.1×10⁻⁴ μA cm⁻², respectively. It is immediately noticeable from both cathodic and anodic polarization curves that alkyl chain length of copolymer has a significant role in protecting substrate from corrosive media. Evidently, hexyl group (poly 2) is the best side chain among these alkyl side chains as current density of poly 2 coated sample was lowest in the observed potential range (Figure 5a, black line). In addition, anodic current curves of poly 1B/3 have shown irregular/sudden change, indicating formation of tiny pitting on the coating from the beginning of electric polarization or after a certain potential (Figure 5b, green & blue line). Surprisingly, smooth current density curve was observed for poly 2 in the entire potential range, which implies coating was not subjected to any kind of defects under observed electrochemical circumstance (Figure 5b, black line). As discussed in the earlier section, thermal treatment after coating is very important for better protection and this was further verified under electrochemical condition. As-spun film of poly 2 exhibited more current density in both cathodic and anodic sweep (Figure 5, black dashed line) than annealed sample, which

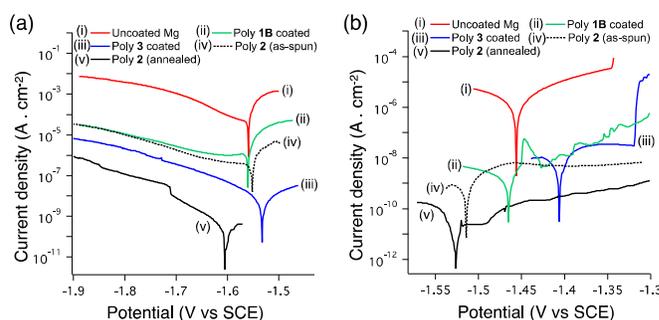


Fig. 5 (a) Cathodic, and (b) anodic polarization curves of uncoated/polymer coated Mg alloy (AZ31) substrate after 1 h immersion in 3.5 wt.% aqueous NaCl solution at 298 K (scan rate 1 mV/s).

suggests significant improvement of the protecting ability of polymer coating from corrosive ions after thermal treatment. Certainly, these results demonstrate that thermally treated catechol containing hexyl methacrylate polymer film (poly **2**) is most suitable among other alkyl side chains for protecting metal/alloy substrates from corrosive media. Therefore, poly **2** was employed in all cases for further studies.

Our simple molecular design of combining catechol unit and hydrophobic alkyl side chain revealed to be an effective strategy for the protection of highly corrosion vulnerable Mg substrate. To further explore versatility of these polymers toward other corrosion susceptible metals/alloys of Al, Cu and Fe, we performed salt-water immersion test. To evaluate anti-corrosion ability, half of the circular metal plates were coated with poly **2** and the other half remained as uncoated surface. Then, those metal specimens were immersed in 3.5 wt.% NaCl aqueous solution at room temperature for 48-240 hours. Figure 6a shows apparent feature of various samples before and after immersion in the salt water at room temperature. In all cases, the uncoated area was completely or partially corroded while the coated area remained unaffected under exactly the same condition. Most surprisingly, polymer film did not swelled along the boundary area and corrosion did not invade towards the coated region. Along with visual inspection of different substrates before and after acidic/salt-water immersion test, scanning electron microscope (SEM) was also studied to confirm metal/alloy surface integrity and polymer coating stability (Figure 7, S16). Here, it is noteworthy to mention about two important features of these coating materials. First, the polymer film was completely transparent and therefore does not affect the appearance of the base materials. As shown in figure 6b and S8, thin-film of poly **2** made on glass/quartz plate was completely transparent to human eye and this was further confirmed by the absence of absorption peak in the visible range (400-700 nm). In addition, color of this film remained unchanged for several months under ambient condition, which indicates catechol unit does not degrade or crosslink by aerobic oxidation which produce brown/pink color in solution phase. Besides functional efficiency, adhesiveness or mechanical stability of a coating is very important for long-term

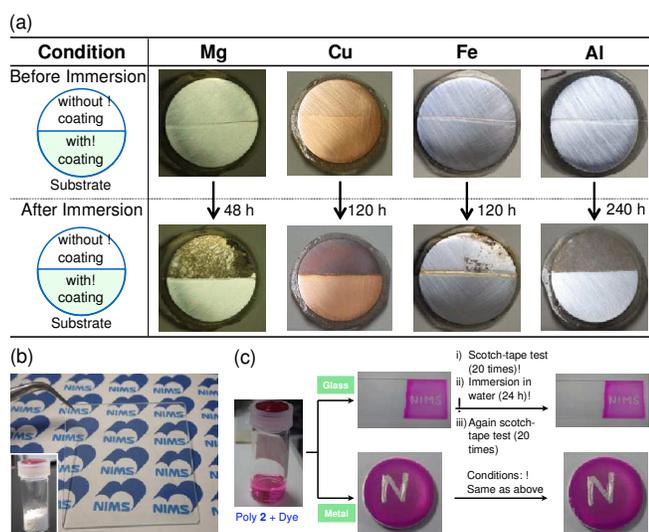


Fig. 6 (a) Visual appearance of half-circle coated various substrates before and after immersion in salt water for specified time in hours. Plates were 15 mm in

diameter and resin embedded except on the top side. (b) Polymer film on a glass substrate showing complete transparency of the coating. Inset picture in left is white powder of poly **2**. (c) Photographs of simple scotch-tape test of poly **2** coated glass/metal substrate. Very small amount of Rhodamine B dye was used to confirm the presence of polymer. For details see supporting information.

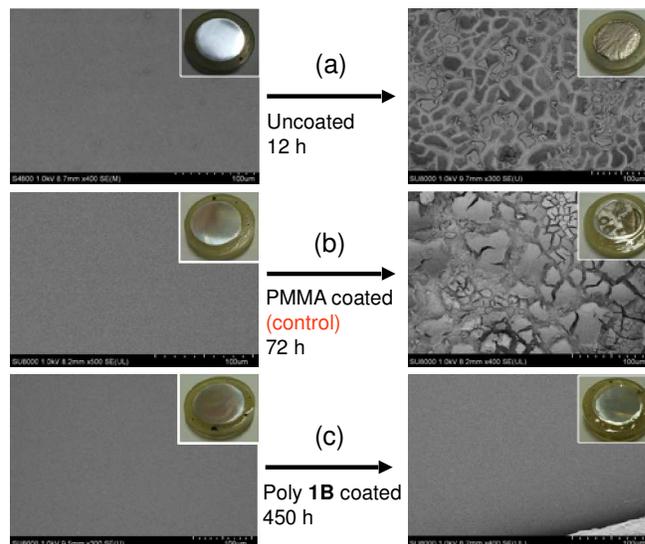


Fig. 7 SEM images of (a) uncoated, (b) PMMA coated, and (c) poly **1B** coated Mg substrates before and after hydrogen evolution test at 298 K. Inset images are respective resin embedded samples.

protection. Therefore, we did a simple scotch-tape test to demonstrate adhesive efficiency of our polymer coatings on glass/metal substrates. This test was also carried out for PMMA coated substrates as a reference, very small amount of dye was mixed with polymer and coated surface was scratched to understand stability of the coating easily by visual inspection. As shown in figure 6c and S9-11, poly **2** coating was not peeled out/damaged after several attachments, peeling out of scotch-tape, and immersion in distilled water for 24 h followed by repeated scotch-tape test. In contrast, polymer coating without catechol units (PMMA coated) was totally damaged just after few scotch-tape test (Figure S9). Generally, coating materials expose to normal water of pH~7 under ambient conditions but there could be contact with acidic/basic solution under exceptional cases during external applications. Thus, we checked thin-film stability under different pH (11, 9, 3, and 1) conditions by comparison of static water contact angle (θ) and visual inspection. In general, contact angle of a coated substrate changes greatly if acidic/basic solution partially or completely damage the top surface. Therefore, comparison of contact angle after different immersion period gives direct information about the thin-film stability. We investigated thin-film stability of poly **2** on glass plates under wide-range of pH and data have been shown in figure S13. There was a small decrease of θ (~8°) after immediate immersion in all cases but remained stable for longer immersion period. This indicates that although there was insignificant change of coating surface just after immersion in solution phase, but it is completely stable under harsh pH environment for at least 36 hours. Thus, after thorough investigation we conclude that a very firm, transparent, and stable protective layer was formed on the substrate with association of strong binding of catechol units and hydrophobic hexyl side chains. Further investigation about weatherability and stability of this coating method against other external hazards like UV radiation, toxic gases, soils, and microbes are in progress.

To further investigate the detailed anticorrosion mechanism, especially the effect of thermal treatment and accessibility of foreign molecules through polymer coating, we performed neutron reflectivity and GI-WAXD measurement. First, we performed GI-WAXD measurements of poly **1B**, **2**, and **3** before and after annealing. We did not observe any significant difference in the

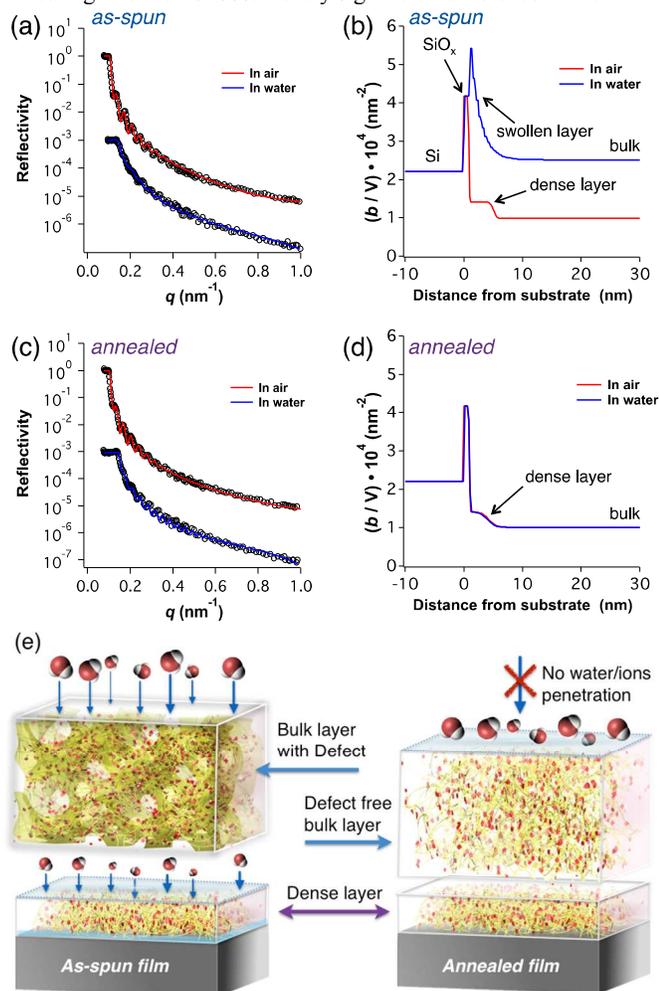


Fig. 8 Neutron reflectivity for (a) as-spun and (c) annealed films in air and water. Open symbols depict experimental data, and solid lines represent the reflectivity calculated on the basis of the scattering length density (b/V) profiles shown in (b, d). For clarity, the values in panel (a, c) are offset from one another. (e) Schematic illustration of difference between as-spun and annealed film determined by neutron reflectivity measurement.

packing or crystallinity of the polymer chain among different samples (Figure S18). This outcome clearly indicates that polymer packing does not generally affect the barrier ability against foreign molecules. Consequently, we performed neutron reflectivity measurement to get more insight into the inhibition mechanism of the polymer coating. Figure 8a and 8c show the reflectivity curves as a function of the scattering vector ($q = (4\pi/\lambda)\sin\theta$, where λ and θ are the wave length and the incident angles of the neutron beams, respectively) for as-spun and annealed poly **2** films under air and deuterated water (D_2O). For clarity, the data set for the film in D_2O is offset by three orders of magnitude. The open symbols denote the experimental data, and the solid curves were fit curves calculated from the scattering length density (b/V) profiles in Figure 8b and 8d. To realize the role of thermal treatment and importance of catechol

units for high anticorrosion efficiency, only interfacial regions are shown. Since the solid curves in Figure 8a and 8c are in good agreement with the experimental data, it is most likely that the model (b/V) profiles drawn in Figure 8b and 8d would reflect the density profiles of the films. The (b/V) values for silicon (Si), native oxide layer (SiO_x) and D_2O used in these calculations were 2.21×10^{-4} , 4.18×10^{-4} , and $6.62 \times 10^{-4} \text{ nm}^{-2}$, respectively. In the both cases of as-spun and annealed coating, when measured under air, the (b/V) values were constant over the entire region of the film thickness with ca. 150 nm, except for the interface with the Si substrate. This indicates that a slightly dense layer formed with ca. 5 nm in thickness adjacent to the substrate, although density of the upper region was identical to the polymer bulk. Since this phenomenon was not observed for spin-coated PMMA film,⁵⁰ it is more likely that catechol moiety stimulated anchoring of the polymer chains to the substrate and resulted in slightly dense layer at the interface. In the case of measurement under water for non-annealed film, the (b/V) value was drastically changed (Figure 8b). The magnitude was slightly higher than that in air, and drastically increased at the substrate interface. This indicates that the adsorbed D_2O molecules (with high (b/V) value) reached the substrate and enriched it. Similar behavior has been reported for PMMA spin-coated film, in which tiny channels were generated during solvent evaporation, and the thin film was swelled by penetrated water within several hours.⁵⁰ Surprisingly, annealing process overcame this shortcoming and significantly improved the barrier ability against foreign molecules. Thus in the case of annealed film, D_2O could not penetrate the substrate even after 2 hours of immersion in D_2O , which is a duration enough to be swollen by the water molecules (Figure 8d).⁵¹ These results suggest that annealing promotes to close tiny channels and make polymer chain arrangements more uniform, which leads to the prevention of foreign molecules. Therefore, we conclude that a combination of formation of a ca. 5nm dense layer adjacent to the substrate and thermally cured sub-micron layer above this dense layer completely protect from foreign molecules and exhibited high anticorrosion property (Figure 8e).

Conclusions

Inspired by an underwater bio-adhesion, we have developed a simple and practical coating method for anti-corrosion of versatile metal/alloys. Our strategy to develop new type of anticorrosive polymer was simply introducing a small amount of catechol group, having versatile binding ability, to the conventional poly(alkyl methacrylate)(PAMA)s. To achieve adequate anticorrosion performance, we thoroughly tailored molecular structure, composition ratio and processing conditions. We observed that spin-coated copolymers enabled formation of a dense nanolayer adjacent to the metal surface, which normally does not occur with conventional PAMAs. This happened by strong binding affinity of the catechol unit towards metal/alloy substrates, resulting in a spontaneous condensation of the polymer chains at the metal interface. Additionally, annealing process was found to be essential to show better protecting ability against corrosive molecules, due to the formation of defect free coating. Although catechol unit containing polymers were reported earlier for functionalizing versatile metal surfaces, it was never considered as a potential unit for the protection of base materials. In this era of nanoscience/technology, commercialization of a wide-range of nano-devices is inevitable in the near future. Protection of structural integrity of such fine architectural materials becomes more apparent from the viewpoints of reliability, durability and economy. As far as we are concerned, these issues have not been seriously addressed in recent times. Along with conventional bulk metal/alloy, our coating strategy can strongly support realization of delicate fabrication of

(nano)structural architecture and practical applications of such smart devices in nano-medicine/ robotics/ mechatronics and so on. Moreover, highly efficient protective coatings can be obtained by simply introducing small amount of catechol group into the conventional poly(alkyl methacrylate). This concept can especially open a new direction for converting affordable conventional polymers into highly valuable, environment friendly, economic, and multi-purpose polymer coatings.

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