A Fatty Acid Derived Tetherable Initiator for Metal Oxide Surfaces

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ABSTRACT: A universal tetherable initiator, derived from fatty acids, for surface-initiated atom transfer radical polymerization (SI-ATRP) from metal oxide surfaces was prepared. A simple amidation between 2-bromoisobutyryl bromide (2BiB) and ω-aminolauric acid allowed preparation of 12-(2-bromoisobutyramido)dodecanoic acid (BiBADA). After minimal purification, BiBADA was used as a tetherable initiator for a broad range of metal oxide nanoparticles. The modified nanoparticles were grafted with methyl methacrylate (MMA) or *n*-butyl acrylate (BA) via supplementary activator and reducing agent (SARA) SI-ATRP with high

grafting density. Sub-10 nm Fe_3O_4 nanoparticles with intrinsically tethered initiator were also prepared using BiBADA as a surfactant template. Additional experiments demonstrated successful modification of aluminum foil surface with polymer brushes using BiBADA as a tetherable initiator.

INTRODUCTION

Polymer hybrid materials are materials that consist of polymeric and inorganic components blended on molecular or nanometer level.[1] Interest in polymer hybrid materials is driven by the opportunity to combine the processability and durability of polymeric materials with the mechanical, thermal, optoelectrical, and catalytic properties of the selected inorganic materials. This has rendered 'polymer hybrid materials' one of the most actively researched areas in the field of polymer materials. [2-6] One example are metal-oxide hybrid materials that have been proposed as candidate materials for applications ranging from medical diagnostics to energy storage. [6-9] Key to realize the opportunities of the 'hybrid material approach' is the availability of chemical processes that enable the tethering of polymers to inorganic components. While a range of methodologies for surface tethering have been described in the literature, the application of polymer grafting techniques remains a challenge. This is because the coupling of chains typically involves non-covalent coordination that is sensitive to minor differneces in surface chemical composition and charge. As a result, only few reliable and broadly applicable routines for preparation of well-defined polymer-metal oxide hybrid materials have been reported.

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Methods for surface modification with polymers are typically classified as "grafting-onto",[4, 10] "grafting-from",[10, 11] template,[10, 12] and "ligand-exchange" methods.[13, 14] In the "grafting-onto" method, the metal oxide surface reacts directly with a functional end-group on the polymer. This method is low-cost and straight-forward but grafting density is generally low. On the other, the metal oxide surface can be treated with a small molecule initiating group, and subsequently "grafted from" the functionalized surface to from polymer brushes. Polymer brushes with high density and well-controlled polymer brush architecture can be achieved. A star-shaped or molecular bottlebrush polymeric template can also be used as a nanoreactor for synthesis of a metal oxide nanoparticle with desired size and morphology within the designed template.[10] The other method, the "ligand-exchange" procedure uses pre-synthesized polymers, with a functional end-group, to exchange with small molecular ligands covering the metal oxide surface.

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Both the "grafting-onto" and "grafting-from" methods rely on generating an effective interaction between metal oxide surfaces and the anchoring group on the polymer chain ends or on tetherable initiators. Commonly used anchoring groups includes phosphonate,[9, 15] carboxylate,[15, 16] halo-/alkoxysilane,[17] amines,[13] catechol,[18, 19] and poly(ethylene oxide).[20] Among these anchoring groups, only phosphonate and alkoxysilane were commonly used as the anchoring group for a presynthesized tetherable initiator. The use of presynthesized tetherable initiators avoids the steric effect of the "grafting-onto" method as well as the two-step heterogeneous modification of the widely used polydopamine chemistry.[21] However, the precursors of these two types of initiators are expensive and are effective for a narrow selection of metal oxide surfaces. Furthermore, accessibly of phosphonates are restricted by the Chemical

Weapon Convention. [Reference] Therefore, a tetherable initiator that can be prepared at a reasonable cost and is universally suitable for a variety of metal oxide surfaces is lacking.

Previous research has demonstrated that carboxylate/carboxylic acid has the capability to anchor onto some metal oxide surfaces.[15] Indeed oleic acid is one of the most commonly used ligands for stabilization of metal and metal oxide nanoparticles.[22, 23] The micelle-like structure formed by the amphiphilic layer of oleic acid ensures miscibility in nonpolar solvents while holding firmly to the polar surface of the nanoparticle core. Hence, a novel tetherable initiator for surface initiated atom transfer radical polymerization (SI-ATRP) was designed based on the structure of oleic acid.

The development of reversible deactivation radical polymerization (RDRP) techniques in the past two decades has enabled preparation of polymeric materials with well-controlled molecular weights, molecular weight distributions, and various architectures.[24-26] Surface-initiated RDRP (SI-RDRP) techniques emerged from these developments as well as the concept of an ideal spatial control.[27, 28] SI-ATRP is the most broadly applied procedure among the SI-RDRP techniques, due to its accessible tetherable initiators, versatile monomer choices, and tolerance to varies reaction conditions and impurities.[29, 30] In recent years, the emergence of activator regenerated by electron transfer (ARGET) ATRP,[31] use of Cu (0) as supplemental activator and reducing agent (SARA) ATRP,[32, 33] initiator for continuous activator regeneration (ICAR) ATRP,[34] electrochemically-mediated ATRP (*e*ATRP),[35] photoATRP,[36-40] and metal-free ATRP[41-43] techniques provide a broad number procedures that can be optimally selected for different applications while minimizing the residual metal impurities in the final product.

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Herein we report development of a novel tetherable initiator for SI-ATRP. A one step amidation procedure, in which the commonly used monomer for Nylon-12, ω-aminolauric acid, was converted to 12-(2-bromoisobutyramido)dodecanoic acid (BiBADA). This novel initiator was demonstrated to be suitable for tethering to a large variety of metal oxide nanoparticles allowing initiation of polymerization from the functionalized surfaces (Scheme 1**a**). SARA ATRP was employed due to its facile setup and heterogeneous nature, which mitigated side-reactions between the reducing agent and the metal oxide nanoparticles.

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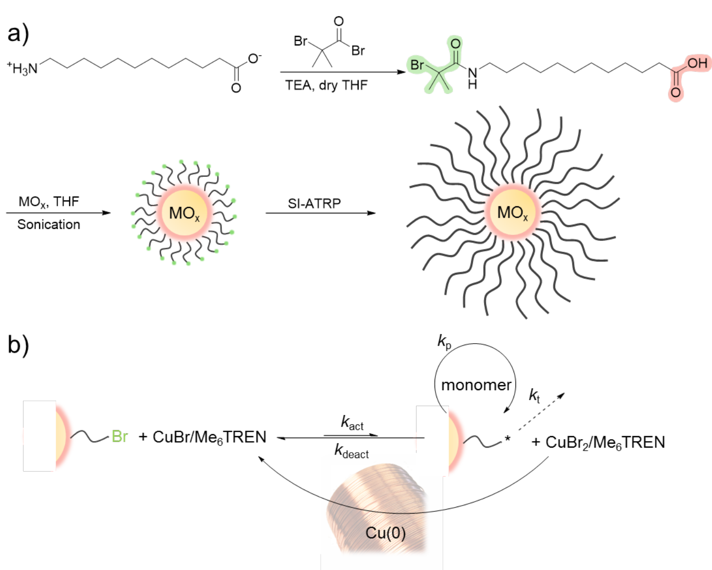
As the amino group in ω-aminolauric acid is highly accessible to multiple types of functionalization, this method is potentially a proof-of-concept for a versatile platform for surface modification of a broad spectrum of metal oxide nanoparticles.

Scheme 1. Preparation of polymer-grafted metal oxide nanoparticles



(a) Preparation of BiBADA and surface modification of metal oxide nanoparticles with polymer brushes. (b) The SARA ATRP equilibrium of surface-initiated polymerization from metal oxide nanoparticles.

RESULTS AND DISCUSSION

Synthesis of BiBADA and Surface Modification

The structure of the tetherable initiator, BiBADA, consists of three parts, a carboxylic acid anchoring group, an aliphatic chain of 11 CH_2 units, and a 2-bromoisobutyrate initiating group (Scheme 1**a**). It was synthesized in a one-step amidation reaction of *ω*-aminolauric acid with 2-bromoisobutyrate. The resulting product was purified simply by repeated washing with a dilute HCl solution. This facile procedure enabled scaled-up preparation of BiBADA.

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The modification of metal oxide nanoparticles with BiBADA was accomplished by simply dispersing the nanoparticles in THF at a concentration of 10 wt %. Five molecules of BiBADA were added per nm^2 of the nanoparticle surface. The modification was conducted in a sonication bath to ensure sufficient separation of nanoparticle aggregates and contact of the exposed surfaces with BiBADA. The stability of the THF nanoparticle dispersions was significantly improved after the surface modification. Then, the modified nanoparticles were washed three times with THF in a sonication-centrifuge (4000 G) cycle to remove the surplus BiBADA.

Surface-initiated Polymerization

The initiator-modified nanoparticles were then dispersed in a polymerization solution. A SARA ATRP reaction was conducted to graft poly(methyl methacrylate) (PMMA) or poly(*n*-butyl acrylate) (PBA) from the surface. To simplify the calculation, 1000 monomer molecules were added for each nm^2 of the nanoparticle surface. The only exception was the 200 nm barium titanate (BTO) particles as that ratio was not enough to disperse the particles in the monomer/anisole mixture due to its low specific surface area. The use of Cu(0) as supplemental activator and reducing agent (SARA) ATRP was chosen as the "grafting-from" procedure because of its facile setup and heterogeneous nature. As both the copper wire and the metal oxide nanoparticles were present as a solid phase, hence interaction between the reducing agent and particle surfaces were minimized. The reactions were allowed to proceed for 24 h to ensure a sufficient conversion of monomers. The inorganic cores were removed by acid etching to allow measurement of the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) analysis of the grafted polymers by size exclusion chromatography (SEC, see Table 1). The graft densities were calculated from the residual inorganic fraction remaining after thermogravimetric analysis (TGA). To measure the stability of the surface anchoring, the PMMA-grafted nanoparticles were subjected to three sonication-centrifuge cycles (**Scheme S1a**)

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and another TGA measurement was conducted after the treatment. The remaining weight percentage of the particle brushes, assuming no inorganic fraction loss, are listed in Table 1.

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Table 1. Summary of Polymer-Grafted Metal Oxide Nanoparticles pursued in this study[a]

Entry	**Particle**	**Size (nm)**	**Monomer**	M_n[b]	M_w/M_n[b]	σ (nm^{-2})[c]	D_h (nm)[d]	**Stability (%)**[e]
1	MgO	20	MMA	1.32×10^5	1.60	0.08	1600±200	53.6
2	α-Al_2O_3	30	MMA	2.37×10^5	2.10	0.06	501±4	52.4
3	α-Al_2O_3	30	BA	2.42×10^4	1.24	0.06	385±1	-
4	TiO_2	15	MMA	7.24×10^4	1.25	0.03	403±5	33.7
5	Co_3O_4	10-30	MMA	1.03×10^5	1.83	0.14	4800±100	78.9
6[f]	NiO	10-20	MMA	7.69×10^4	1.28	0.14	236±3	58.1
7	ZnO	18	MMA	8.77×10^4	1.33	0.17	282±1	46.4
8	Y_2O_3	10	MMA	1.66×10^5	1.72	0.24	650±10	24.5
9	ZrO_2	40	MMA	5.56×10^4	1.52	0.15	236±1	63.9
10	In_2O_3	20-70	MMA	1.40×10^5	1.49	0.20	377±9	87.2
11	ITO	20-70	MMA	1.23×10^5	1.92	0.11	396±3	60.9
12[f]	SnO_2	35-55	MMA	1.64×10^5	2.24	0.22	377±1	53.0
13	Sb_2O_3	80-200	MMA	3.66×10^5	1.93	0.14	870±20	74.3
14[g]	BTO	200	MMA	1.85×10^5	2.38	0.43	715±4	58.4
15[f]	La_2O_3	10-100	MMA	6.35×10^4	1.23	0.48	317±2	57.4
16	CeO_2	10	MMA	6.88×10^4	1.27	0.13	244±1	54.0
17	WO_3	60	MMA	2.36×10^5	1.98	0.28	762±5	76.4

[a] Typical reaction conditions: $[MO_x\text{-Br, assuming 1 Br/nm}^{-2}]_0/[M]_0/[CuBr_2]_0/[Me_6TREN]_0$ = 1/1000/0.2/0.5, 50 vol % anisole, 1.0 mm × 1 cm copper wire, room temperature. [b] Measured with SEC. [c] Calculated from Eq. S1. [d] Calculated from Eq. S2, assuming no inorganic content loss. [e] Z-averaged hydrodynamic diameter in THF measured by DLS. [f] Particles modified with neutralized BiBADA. [g] $[\text{BTO-Br, assuming 1 Br/nm}^{-2}]_0/[M]_0$ = 1/3000.

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This is the first report of successful SI-ATRP from the surfaces of some of the metal oxides. Other nanoparticles, such as α-Al_2O_3, were previously very challenging and surface grafting was accomplished only after a harsh activation reaction.[44] However with BiBADA as the surface functionalization reagent, no activation was needed to achieve an even higher graft density.

In order to graft polymers from certain metal oxide nanoparticles with relatively reactive surfaces, including NiO, SnO_2, and La_2O_3, an ammonium salt of BiBADA was used instead of BiBADA to functionalize the surfaces. Under these circumstances, the attached BiBADA molecules would not be washed away during the post-functionalization purification.

Besides, sufficient solvophobicity was found essential to successful surface modification. As a reference, amphiphilic colloidal silica nanoparticles were treated with BiBADA in a similar procedure. However, no initiating group were detected on the surface.

Characterization of Hybrid Nanoparticles

The molecular weight and dispersity of the detached PMMA brushes ranged from 10^4 to 10^5 and from 1.2 to 2.4, respectively. There are three major reasons for the relatively high dispersity, the first is that SARA ATRP of MMA is challenging due to fast activation[45] and 2-bromoisobutyramide initiating group may also limit the initiation efficiency of MMA owing to the penultimate unit effect.[46] Substitution of MMA with BA significantly improved the level of control over the polymerization while the reaction was much slower under the same polymerization conditions (Table 1 Entry 2 and **Table S1**). Second, the metal cations may leach into the reaction media and interact with the copper complexes. This was further demonstrated by the fact that no monomer conversion was observed in SI-ATRP from oxidative metal oxide nanoparticles, including CuO, Mn_2O_3, and MoO_3, and finally as the size and morphology distributions of the commercial nanoparticles samples were large (see **Supporting**

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Information), variation in surface curvature might broaden the molecular weight distribution.[47, 48]

The hydrodynamic size distributions of the hybrid nanoparticles in tetrahydrofuran (THF) were measured by dynamic light scattering (DLS, Table 1 and Figure 1**a**). It turned out that the polymer-grafted metal oxide nanoparticles inherited the broad size distributions from their inorganic cores, examples include Co_3O_4, Y_2O_3, and Sb_2O_3 (**Figure S6**, **Figure S9**, and **Figure S17**). Large aggregates were observed for MgO-*g*-PMMA in both DLS and TEM images (**Figure S1**), indicating that BiBADA is a non-ideal tetherable initiator for the alkali earth metal oxides. Shorter PBA brushes rendered the surface less hindered, which caused more aggregation in the TEM images. However, DLS indicated that solution dispersibility was still good.

To further understand the interaction between the carboxylate anchoring group and the metal oxide surfaces, the PMMA-grafted nanoparticles were dissolved in THF and processed through three sonication-centrifuge cycles (**Scheme S1a**). The TGA inorganic fractions were compared to the values before the treatment and calculated as the hybrid particle stability in Table 1. A significant amount of PMMA brushes were cleaved by sonication as indicated in **Scheme S1b**. Note that the chain cleavage process in densely tethered particles is expected to be irreversible because adjacent tethered chains are expected to relax and thus screen the particle surface. Therefore, a fraction of the grafted polymer brushes could be cleaved by sonication. This may facilitate characterization of the grafted polymer brushes and potentially applied to synthesis of polymer using particle templates.

One particular intriguing aspect of hybrid materials based on polymer-tethered particles is the possibility to fabricate 'one-component hybrid materials' by direct assembly of brush particles (i.e. without the need of a separate matrix polymer). To demonstrate this possibility, the

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Deleted: When the hybrid particles were treated with sonication, sufficient energy was provided for the reversible detachment of the carboxylate anchoring group from the metal oxide surface. Once a polymer chain left the surface, the neighboring polymer chains relaxed from a highly stretched configuration and blocked the pathway back to the surface. Consequently, the departed chain could not find a way back to the surface.

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Deleted: application of this novel technique mechanical (elastic) properties of films fabricated from ZrO_2-*g*-PMMA were evaluated using nanoindentation and compared to the respective linear polymer analogs (Figure 1b). Nanoindentation was performed by indentation using a Berkovich tip following analog procedures as reported previously [Schmitt paper]. Both the modulus (*E*) and hardness (*H*) of the ZrO_2-*g*-PMMA film were found to be more than twice as high as those of the linear reference material. Since the elastic modulus is a measure for the bonding strength between material constituents, these results provide direct evidence for the strong bonding between inorganic particle and polymeric tethers. The ability to assemble mechanically robust films by simple solution casting of ZrO_2 hybrid particles could provide new opportunities for the fabrication of, for example, optical materials.

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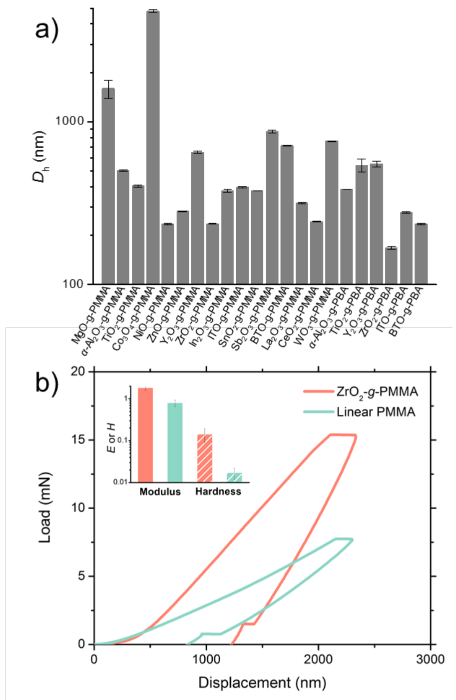

Figure 1. Characterization of polymer-grafted nanoparticles: (a) hydrodynamic size distributions of polymer-grafted metal oxide nanoparticles in THF measured by DLS; (b) characteristic load-displacement curves for ZrO_2-*g*-PMMA (rose) and its linear reference (aqua). Inset: corresponding moduli and hardness determined by nanoindentation.

One-pot Synthesis of Initiator-Modified Fe_3O_4

In addition to surface-modification of metal oxide nanoparticles, BiBADA was also used as micelle template for one-pot synthesis of magnetite nanoparticles (MNP) with immobilized ATRP initiators. The synthesis was derived from a known procedure.[6] BiBADA was added to an ammonium hydroxide solution to make a mixture of base and surfactant. Poly[oligo(ethylene glycol) methyl ether acrylate-480] (POEGA) was grafted from the surface after the *in situ* synthesis and surface modification of MNPs. Two reactions, lasting 24 h and 12 h, were performed resulting in preparation of two batches of samples, **OEG-MNP-1** and **OEG-MNP-2**, respectively.

The POEGA-grafted MNPs were readily dispersible in water. The magnetic relaxivities of the aqueous dispersion of the POEGA-grafted MNPs were measured at 37.0 °C under a 20 MHz (0.47 T) nuclear magnetic resonance (NMR) spectrometer,[50] and compared to Feraheme™, the only Food and Drug Administration (FDA) approved iron oxide nanoparticle for human use.[51, 52] The POEGA-grafted MNPs displayed similar longitudinal relaxivity (r_1), but over 5-fold higher transverse relaxivity (r_2). Thus, the relaxivity ratios (r_2/r_1) of both of the POEGA-grafted MNPs were significantly higher than the reference sample. It is known that the relaxivity ratio of an iron-based contrast agent increases rapidly with the increase of magnetic field strength[53] and much higher relaxivity ratios can be expected under a practical magnetic resonance imaging (MRI) conditions. Therefore, the POEGMA-grafted MNPs are expected to serve as a potential highly efficient contrast agent for T_2*-weighted MRI.

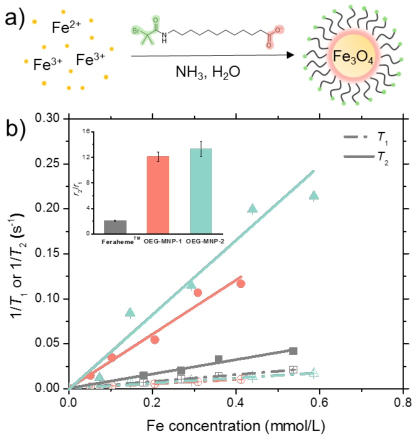

Figure 2. Synthesis of initiator-modified MNPs and magnetic relaxivity measurement of POEGMA-grafted MNPs. (a) One-pot synthesis of initiator-modified MNPs; (b) longitudinal (T_1, open dots) and transerve (T_2, solid dots) relaxation time measurements of aqueous dispersion of Feraheme™ (gray square), **OEG-MNP-1** (rose circle), **OEG-MNP-2** (aqua triangle) at various Fe concentrations and their corresponding linear fitting (solid and dashed lines), inset: corresponding relaxivity ratios.

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BiBADA as Initiator for Grafting from Metal Surfaces

BiBADA was also demonstrated to be an effective tetherable initiator for macroscopic metal surfaces. Due to the presence of a native oxide layer,[54] the surface chemistry of aluminum foils is similar to that of metal oxide nanoparticles, which promoted anchoring of BiBADA molecules. A simple and low-cost "paint-on" technique[55] was employed to graft polymer brushes from the surface of BiBADA modified aluminum foil (Figure 3a). The reaction was allowed to proceed for 3 h before the surface was rinsed extensively with water to remove detached polymer brushes.

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While there was no apparent change in surface hydrophilicity after BiBADA modification, the surface became much more hydrophilic after the growth of poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) brushes (Figure 3**b** and **c**). The untreated and treated aluminum foil was placed on a 55.0 °C hotplate. There was a small increase in water contact angle after heating. The reason for this lack of a steep change in contact angle was likely insufficient heat transfer through the glass slide attached to the back of the aluminum foil (**Figure S24**). A small decrease in water contact angle on the BiBADA-modified surface at elevated temperature was also observed, which could be expected as hydrogen bonding in water became less dominant.

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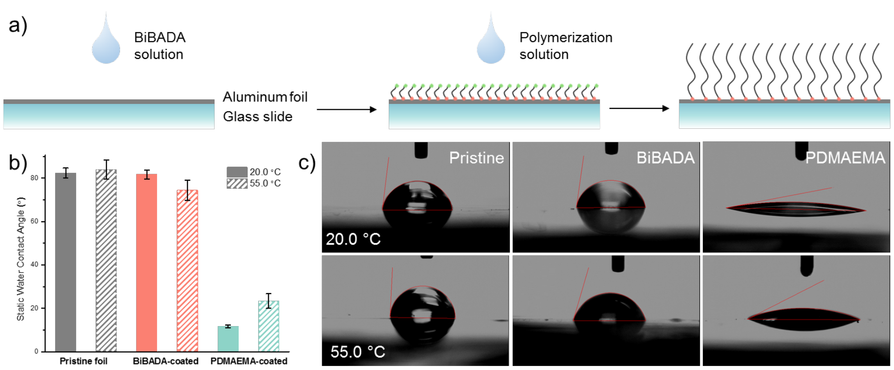

Figure 3. Painting PDMAEMA brushes from aluminum surface using BiBADA as a tetherable initiator. (a) The procedure for surface-modification of an aluminum foil with BiBADA and PDMAEMA brushes. Polymerization solution: [DMAEMA]$_0$/[CuCl$_2$]$_0$/[PMDETA]$_0$ = 500/1/1; 50 mmol/L NaCl, 200 mmol/L ascorbic acid; 80 vol % deionized water; 3 h. (b) Average static water contact angles of a pristine aluminum foil (gray), a BiBADA coated foil (rose), a PDMAEMA-coated foil (aqua) at 20.0 °C (solid) and on a 55.0 °C hotplate (shaded); (c) characteristic photos of 1.0 μL of water drops on untreated or treated aluminum foils.

CONCLUSION

A universal tetherable initiator, BiBADA, derived from fatty acids, was designed and synthesized. The simple amidation reaction, herein demonstrated, allows α-aminolauric acid to be a universal platform for surface functionalization of metal oxides and metals. Successful surface modification and surface-initiated polymerization from a broad library of metal oxide surfaces, including some previously tough or unreported surfaces, e.g., α-Al_2O_3 was demonstrated. Versatile applications were found for selected polymer-grafted metal oxide nanoparticles using BiBADA tetherable initiator. Facile "paint-on" polymerization from an oxidized metal surface was conducted using the BiBADA initiator. Therefore, BiBADA can be applied as a powerful platform for preparation of functional polymer nanocomposites and smart metal surfaces.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures; specifications of additional PBA-grafted metal oxide nanoparticles; cleavability test; hydrodynamic size distributions of polymer-grafted metal oxide nanoparticles; magnetization of BiBADA-modified MNPs; IR image of aluminum foil on a hotplate.

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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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