

A Facile and Environment-friendly Method for Fabrication of Polymer Brush^{*}

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Abstract A novel environment-friendly system is proposed to fabricate polymer brush, which has the advantages including non-toxic and inexpensive initiator (eosin Y), visible-light exposure ($\lambda = 515$ nm), water medium and ambient environment. The experimental results from UV-Vis spectroscopy, AFM-based single molecule force spectroscopy (SMFS) and other measurements indicate that a polymer brush with a living nature is fabricated *via* free radical polymerization. This polymer brush may find applications in coatings, bio-interfaces and so forth.

Keywords Polymer brush; Green chemistry; Free radical polymerization; Living polymerization

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-017-1934-5>.

INTRODUCTION

The synthesis of polymer brushes *via* surface-initiated polymerization (SIP) has attracted broad interest because it is an effective strategy to fabricate functionalized surfaces^[1–4]. The versatility of synthetic routes allows the facile fabrication of polymer brushes that are useful in smart materials^[5, 6], functionalized coatings^[7], bio-functional interfaces and *etc*^[8]. However, anhydrous and oxygen-free conditions are often required in the preparation of polymer brushes. Besides, the catalysts used in former studies are often toxic and expensive^[9].

To address such problems^[10–12], some research groups have made progress in fabricating polymer brushes by an environment-friendly way^[13–15] with the advantages of visible-light exposure^[16], low-toxic catalysts^[17], ambient environment^[18], water medium and so forth^[19, 20]. The visible-light-induced reactions catalyzed by metallic and organic photoredox reagents (such as ruthenium^[21, 22], iridium^[23] and eosin Y (EY))^[24, 25] are considered as a valuable and green method for the polymer synthesis with high efficiency^[26]. In the photoredox catalyzed visible-light-induced polymerization, light may be absorbed by a photo-initiator for transferring energy to the surrounding reactive agents, then generate carbon radicals or ions to initiate monomer addition^[27]. Organic dyes (*i.e.*, EY) are favored in this field for their superiorities of initiating efficiency, biocompatibility and low cost^[28] over metal complexes, such as ruthenium and iridium that are expensive and potentially toxic^[29]. Due to the marvelous properties, EY has been widely used in cell staining^[30], hydrogel preparation^[31, 32] and *etc*^[33–35].

^{*} This work was financially supported by the National Natural Science Foundation of China (No. 21222401) and the Sichuan Youth Science & Technology Foundation (No. 2017JQ0009).

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Received December 12, 2016; Revised January 12, 2017; Accepted January 14, 2017

doi: 10.1007/s10118-017-1934-5

Furthermore, as a photoredox catalyst, it could generate phenol radicals, which might further be coupled into cross-linked structures under mild condition^[36, 37].

Although considerable progresses have been made in the last decade, a facile and more environment-friendly method in fabricating polymer brush is still desirable. Herein, we report the fabrication of polymer brush by using 2-(4-methoxy-3-methylphenyl)ethylamine (MOE) as a monomer, non-toxic and inexpensive EY as an initiator *via* visible-light exposure at ambient environment in water medium. Interestingly, the polymer brush can be grafted from surface *via* free radical polymerization with a “living” character.

EXPERIMENTAL

Materials

2-(4-Methoxy-3-methylphenyl)ethylamine (MOE) is purchased from J&K Scientific Co., Ltd. (3-Aminopropyl)-trimethoxysilane (APTES) and cysteamine are purchased from Sigma-Aldrich. Eosin Y (EY) is purchased from Accela ChemBio Co., Ltd. Deionized (DI) water ($> 15 \text{ M}\Omega\cdot\text{cm}$) is used as the solvent for the reaction and rinse. Other chemicals are analytically pure agents and utilized without further treatment.

Substrates Preparation

The quartz slides are firstly immersed in the hot piranha solution (a mixture solvent of 98% H_2SO_4 and 30% H_2O_2 at the ratio of 7:3, *V:V*) for 30 min. After extensive rinsing by DI water, the quartz slides are immersed in the APTES solution ($2 \text{ mmol}\cdot\text{L}^{-1}$, CH_2Cl_2 solution) at room temperature for 4 h. During the silanization, containers are sealed and placed in a dark box. The quartz slides are then rinsed in an ultrasonic bath with CH_2Cl_2 , ethanol and DI water for 5 min, respectively. The silanized quartz substrates are dried by air flow for further use. The gold-coated slides are immersed in an ethanol solution of cysteamine ($26 \text{ mmol}\cdot\text{L}^{-1}$) at room temperature for 20 min. Then, the amino-modified gold-coated slides (hereafter referred as Au-substrate) are soaked in ethanol for 20 min. The samples are rinsed with ethanol and DI water for several times, respectively. After that, the slides are dried by air flow for further use.

Visible-light-induced SIP via Free Radical Polymerization

MOE and EY are dissolved in 10 mL of DI water to reach a concentration of $5 \text{ mmol}\cdot\text{L}^{-1}$ and $0.15 \mu\text{mol}\cdot\text{L}^{-1}$, respectively. The amino-group modified substrate is immersed in the solution. After stirring over 30 s, the system is exposed to green light (LED with an emission of $\lambda = 515 \text{ nm}$, Model: MR16, TKS Co.) at a distance of 5 cm. It has been reported that a primary amine group will form a covalent bond with α -carbon of phenol radicals catalyzed by a photoredox initiator^[38]. In this work, a covalent bond will be formed between the α -carbon of benzene ring adjacent to the methoxyl group and the primary amine group from another MOE or the amino group modified surface, attributing to the fact that methoxyl group is similar to hydroxyl group in the activation of benzene ring^[39]. After irradiation for a certain period of time, polymer brushes from monomer MOE (PMOE) are grafted from the substrate. Then, the polymer grafted substrate is immersed in DI water for 20 min to remove physisorbed substance. The scheme of the above procedure is shown in Fig. 1.

UV-Vis Spectra Measurements

The quartz substrate after visible-light-induced SIP process is measured by UV-Vis spectroscopy (Lambda 35, Perkin-Elmer). After the LED irradiation for a certain period of time, the light is switched off and the UV-Vis absorbance of sample substrates is recorded.

Static Contact Angle (CA) Measurements

Water contact angles are measured using a constant volume drop of DI water ($5 \mu\text{L}$) and recorded by a drop shape analysis system (DSA 100, Kruss) at room temperature. More than 8 measurements are carried out for each sample. The averaged values are presented finally.

Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) Measurements

The FTIR (Nicolet 5700 spectrometer) and XPS (Kratos SAM 800 spectrometer) analysis are carried out to

verify the structures and surface elements of Au-substrates bearing polymer brush. The sample substrates are rinsed by ethanol to remove the physisorbed substance before measurements.

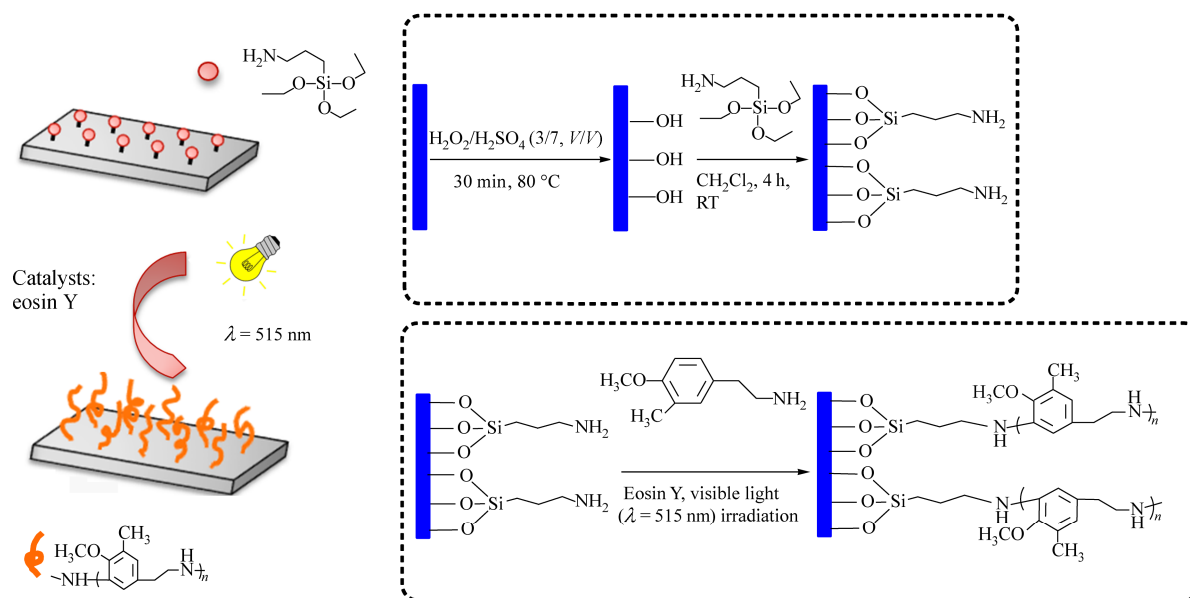


Fig. 1 The scheme of visible-light-induced SIP reaction from MOE

Ellipsometry Measurements

The thickness of the polymer brush on the Au-substrates is measured by a Mueller Matrix Ellipsometer (Wuhan Eoptics Technology Co., Ltd.)^[40, 41].

AFM-based Single Molecule Force Spectroscopy (SMFS) Measurements & AFM Imaging

SMFS and AFM imaging are performed on a commercial AFM (Nanowizard II, JPK instruments AG) with a V-shaped Si₃N₄ AFM cantilever (Bruker Corp., CA). Force-extension (F-E) curves are achieved from the AFM manipulation under force measurement mode. The AFM tip is controlled to pick up and stretch the polymer brush grafted from the substrate in DI water environment at room temperature (20 sites for a sample substrate, and over 200 times for each site). The spring constant of the cantilever is determined by the thermo excitation method, which is in the range of 40 pN·nm⁻¹ to 50 pN·nm⁻¹. The stretching velocity applied in this study is 2.0 μm·s⁻¹. The F-E curves are analyzed by Igor Pro 6.0 with custom procedures. AFM images are obtained under contact mode. The instrumentation details of SMFS can be found elsewhere^[42–45].

RESULTS AND DISCUSSION

The Possible Mechanism for SIP via Free Radical Polymerization

The mechanism for SIP *via* free radical polymerization is shown in Fig. 2. In the initial stage, irradiation of EY can generate the excited state EY*, and a single electron transfers (SET) from MOE to EY*, resulting in the formation of MOE radical and EY radical. The latter then transfers an electron to oxygen (O₂) in the solution to regenerate EY. As for MOE radical, a covalent bond is formed between the α-carbon of benzene ring adjacent to the methoxyl group and the primary amine group from another MOE or the NH₂-modified substrate^[34, 38, 39]. By repeating this process, a linear polymer brush is grafted from surface *via* free radical polymerization. The H radicals would be consumed by O₂ *via* a redox process.

UV-Vis Spectra of the Samples

UV-Vis spectroscopy is used to monitor SIP catalyzed by EY under visible-light irradiation. A marked absorption at 199 nm (*A*₁₉₉) is observed, which increases as the irradiation time extends (Fig. 3). When

irradiation time is over 1 h, new peaks at 233 and 287 nm (similar to the characteristic peaks of MOE, Fig. S1 in supporting information, SI) are observed. The increase of UV absorbance may be caused by the free radical polymerization of MOE from surface or physisorption. The possibility of physisorption is excluded by a control experiment (see SI for details, Fig. S2a). Furthermore, to investigate the influential factors for the formation of polymer brush, a series of control experiments are performed (detailed in SI, Fig. S2). It can be validated that the polymer brush is grafted from the surface only when all the three conditions are satisfied, *i.e.*, visible-light irradiation, monomer and the catalyst, EY (see Table 1).

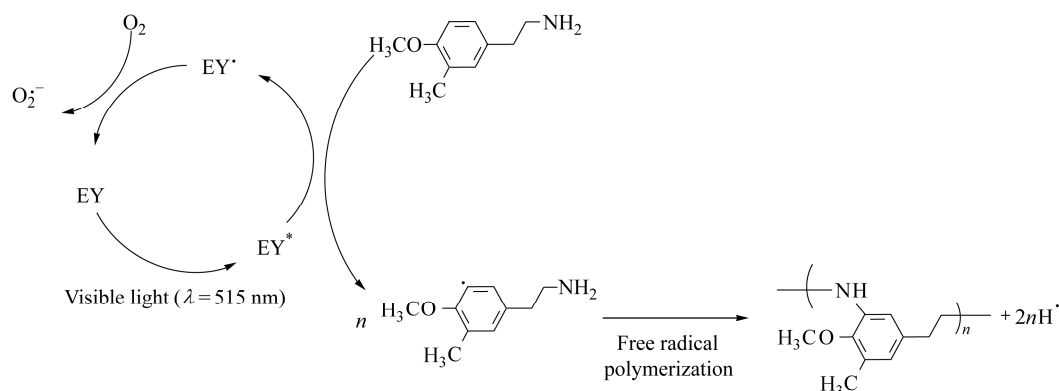


Fig. 2 Mechanism of free radical polymerization of MOE catalyzed by EY via photoredox process

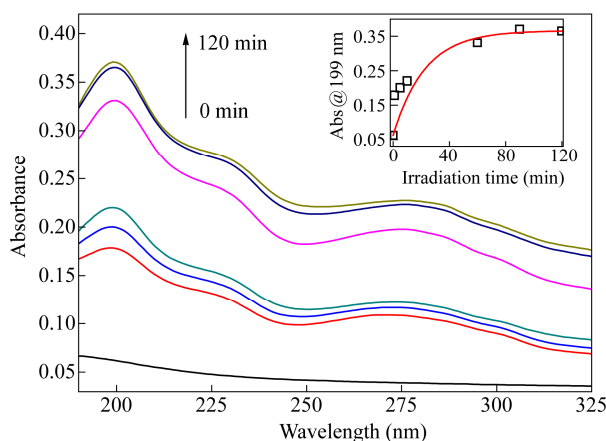


Fig. 3 UV-Vis spectra of the samples after SIP reaction with increasing irradiation time of visible-light. The inset shows the absorbance at 199 nm versus irradiation time (0, 1, 5, 10, 60, 90 and 120 min).

Table 1 Influential factors in the formation of visible-light-induced SIP of MOE (detailed in SI)

Entry	Light ^a	Monomer ^b	Catalyst ^c	ΔA_{199} ^d (%)
1	+	+	–	9.9
2	–	+	+	9.4
3	+	+	+	192.1

^a The experiments are performed at room temperature under green LED light ($\lambda_{\text{max}} = 515$ nm); ^b MOE concentration: 5 mmol·L^{−1}; ^c EY concentration: 0.15 μmol·L^{−1}; ^d ΔA_{199} (%) is calculated by the following equation: $\Delta A_{199} (\%) = (A_t - A_0)/A_0$ (A_t represents the absorbance after immersion in DI water for 20 min after reaction, A_0 represents the absorbance of initial substrate).

Morphology and Wettability of the Samples

In order to confirm the formation of polymer brush, morphological changes of the sample substrate before and after irradiation for different time are analyzed by AFM imaging^[46–48] (Figs. 4a–4c). It can be found that the

roughness (R_a) of sample surface increases from 0.4 nm to 1.5 nm and to 2.2 nm after irradiation for 1 and 5 min, respectively. As for the wettability, the water contact angle of the starting substrate is $46.2^\circ \pm 1.3^\circ$, which then increases to $62.3^\circ \pm 1.8^\circ$ and to $80.0^\circ \pm 1.3^\circ$ after 1 and 5 min irradiation, respectively (Fig. 4d). The change of wettability is associated to the fact that the repeating unit of polymer brush is more hydrophobic than the amino group on the initial substrate (Fig. 1). By ellipsometry, the thickness of the polymer brush with SIP reaction for 30 min is measured to be (5.01 ± 0.13) nm.

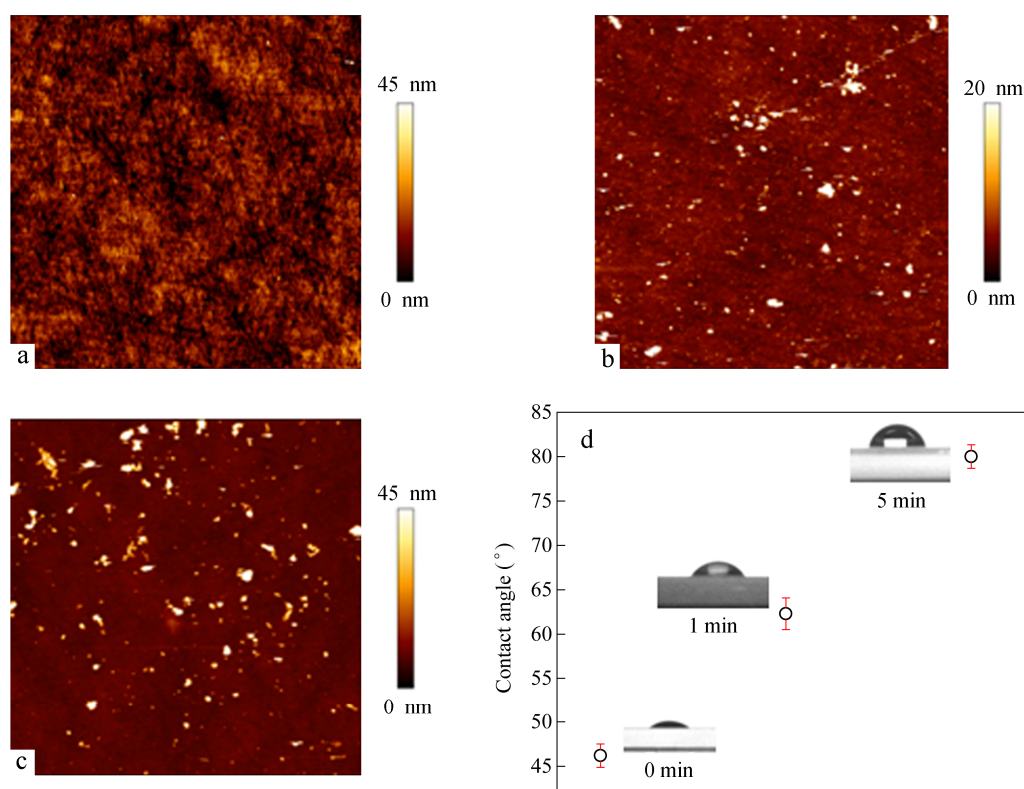


Fig. 4 AFM morphological images ($10\ \mu\text{m} \times 10\ \mu\text{m}$) of (a) initial amino-substrate, (b) after SIP reaction for 1 min and (c) 5 min; (d) Contact angles of initial substrate, with SIP reaction for 1 and 5 min, respectively

FTIR and XPS Study

In order to study the change of surface structure and chemical elements of the polymer-grafted surface, FTIR and XPS measurements are applied to analyze the surface of Au-substrate before and after SIP for 1 h. For the initial surface, the stretching vibrations around 3500 and $1600\ \text{cm}^{-1}$ belong to the amino group (black curves in Figs. 5a and 5b). However, the polymer grafted sample has a new peak at $1100\ \text{cm}^{-1}$ (grey curve in Fig. 5b), suggesting the formation of secondary amine group. N 1s XPS spectra (Fig. 5d) show a new peak at $401.2\ \text{eV}$, which is assigned to the secondary amine group. Furthermore, new FTIR peaks (Fig. 5a) attributed to the isolated C—H vibration of benzene ring ($1500\ \text{cm}^{-1}$) and methoxyl ($1200\ \text{cm}^{-1}$) are in accordance with the XPS results (Fig. S3 in SI) of carbon atoms of benzene ring ($284.8\ \text{eV}$, C 1s) and methoxyl ($286.1\ \text{eV}$, C 1s and $532.8\ \text{eV}$, O 1s) from PMOE. Therefore, both FTIR and XPS analyses confirm the formation of secondary amine group and other characteristic groups from the repeating unit of the polymer brush on the surface.

SMFS Confirms the Linear Structure of Polymer Brush

The above results have confirmed the formation of polymer brush catalyzed by EY under visible-light irradiation. To validate that a linear polymer is grafted from the surface, SMFS is used to study the substrates after SIP^[42–45, 49]. Due to the polydisperse nature of the polymer and the random position where the AFM tip

picks, the apparent contour lengths of the stretched polymer chains vary^[50, 51]. The typical F-E curves of polymer chains with different contour lengths are presented in Fig. 6(a). To compare F-E curves of different contour lengths, the F-E curves are normalized by their extensions corresponding to the same force (e.g., 300 pN).

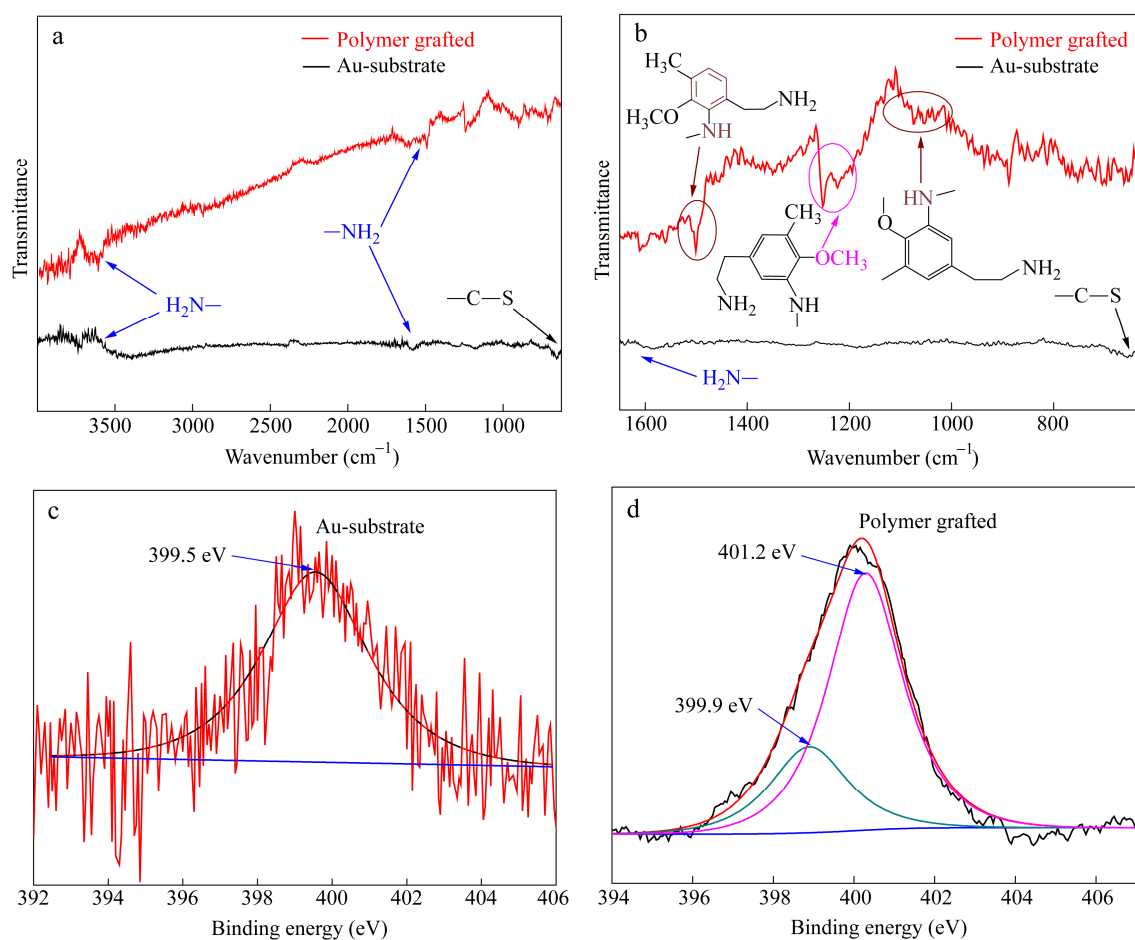


Fig. 5 (a) FTIR spectra of initial Au-substrate (black curve) and after SIP reaction for 1 h (grey curve); (b) The partial FTIR spectra of (a) from 600 cm⁻¹ to 1650 cm⁻¹; N 1s XPS spectra of (c) initial Au-substrate and (d) after SIP for 1 h

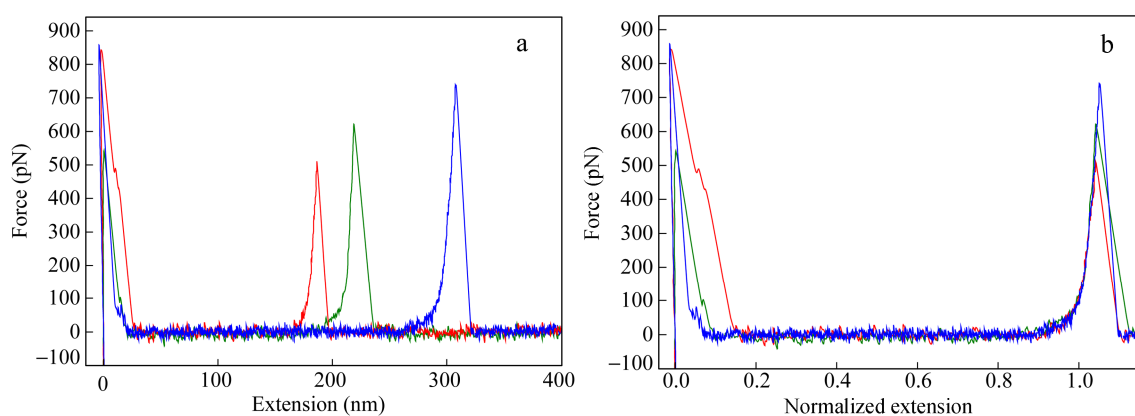


Fig. 6 (a) Typical F-E curves of surface grafted linear polymer after SIP reaction for 5 min and (b) the normalized F-E curves of surface grafted linear polymer

The superposition of the normalized F-E curves (Fig. 6b) indicates that the polymer chains of different contour lengths have identical elastic modulus, which implies that the linear polymer chains have the same repeating unit^[52, 53]. Furthermore, the initial amino modified quartz slide is used as the control sample in the force measurements. In this case, only blank F-E curves can be obtained during the measurements (Fig. S4 in SI), indicating that there are no polymers on the initial substrate.

UV-Vis Spectra and SMFS Confirm the Feature of Living Polymerization

As mentioned in the above sections, the sample after SIP shows an increase of A_{199} when irradiation time extends (Fig. 7). It is interesting to check whether this SIP reaction has a living feature. The criterion for the living polymerization is: If only new monomer is introduced into the system, the polymer chain grows continuously and the molecular weight increases linearly as the reaction time extends until the monomer conversion to 100%^[54–56].

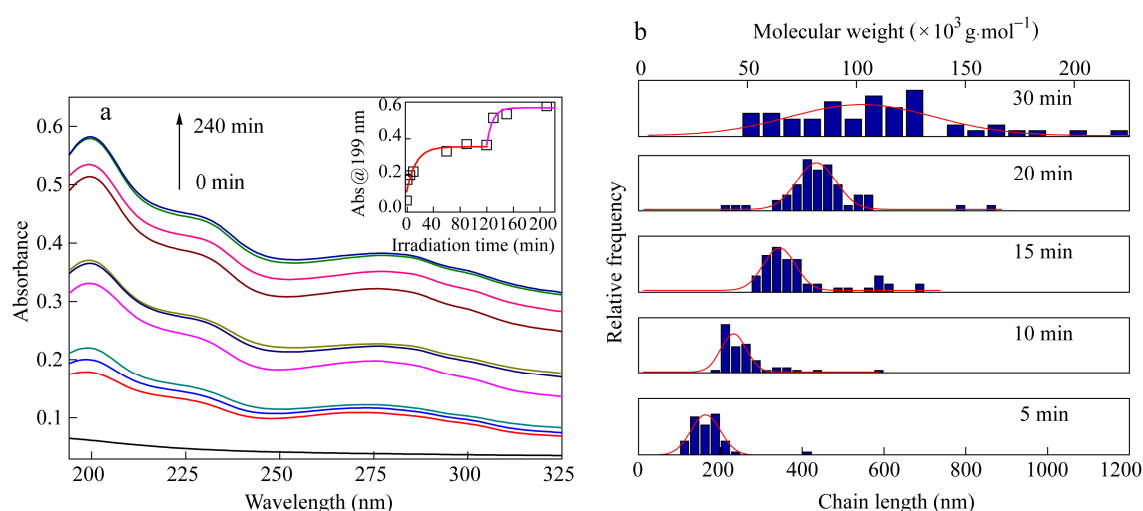


Fig. 7 (a) UV-Vis spectra of “living” free radical polymerization of MOE *via* SIP reaction (The inset shows A_{199} versus irradiation time.); (b) Statistical histograms of apparent polymer contour lengths (from SMFS) and molecular weight after SIP reaction for different time

To verify this, UV-Vis spectra and SMFS measurements are performed to monitor the polymerization with the catalysis of EY under visible-light irradiation. After continuous irradiation for over 2 h, the UV absorbance does not increase any more (Fig. 7a). It indicates that the conversion of monomer reaches ~100%. Then, we add the monomer (5 mmol·L⁻¹) into the mixed solution and expose the system to visible light for a certain of time. Interestingly, we find that the UV absorbance continuously increases until the added monomer is completely consumed (Fig. 7a). This phenomenon matches well with the criterion of living polymerization.

Besides, SMFS measurement has also been used to study the “living” radical polymerization of SIP (detailed in SI). Apparent contour lengths of the F-E curves obtained on the identical substrate with various irradiation time are analyzed statistically (Fig. 7b). The most probable chain contour lengths from Gaussian fit are 163, 233, 342, 437 and 537 nm after irradiation for 5, 10, 15, 20 and 30 min, respectively. From Fig. 2, the length of the repeating unit of polymer brush is estimated as 0.59 nm. The apparent molecular weight (MW) can be calculated from the apparent contour length (L) by the Eq. (1):

$$\text{MW} = L \text{ (nm)} \times 163.2 \text{ (g} \cdot \text{mol}^{-1}) / 0.59 \text{ (nm)} \quad (1)$$

where 163.2 g·mol⁻¹ is the molecular weight of the repeating unit (Fig. 2). Then, the corresponding apparent MW is calculated. As shown in Fig. 7(b), the most probable MW from Gaussian fit after different reaction time are 30.5×10^3 , 43.8×10^3 , 64.2×10^3 , 82.0×10^3 and 100.8×10^3 g·mol⁻¹, respectively. It is observed that as the

reaction time increases, the MW of polymer brush increases quasi-linearly as well (Fig. S5 in SI). Furthermore, the thicknesses of polymer brush after different SIP reaction time are measured by ellipsometry. The results show that the thickness of the polymer brush also increases quasi-linearly (Fig. S6 in SI). These results meet the criterion of “living” radical polymerization. The phenomena are in consistent with the results of UV-Vis measurement that the SIP reaction in the current study shows a living nature.

CONCLUSIONS

In summary, we have proposed a novel system to fabricate polymer brush in an environment-friendly way. By using the non-toxic initiator of EY, upon visible-light ($\lambda = 515$ nm) exposure, polymer brush from the monomer (MOE) can be developed on the surface. Furthermore, the whole SIP reaction is performed in water medium under room temperature and ambient environment. The results obtained from the surface characterizations including UV-Vis spectroscopy, FTIR, XPS, SMFS and other measurements indicate that linear polymer brushes with a “living” nature have been fabricated *via* free radical polymerization, which may find useful applications in environment-friendly coatings, bio-interfaces and so forth.

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