

A methacryl ethyl-functionalized soluble polypyrrole: Synthesis, characterization, and potentiality in rapid fabrication of high-aspect-ratio pillar arrays

Guowei Lv^a, Shihu Zhang^a, Guolong Wang^a, Jinyou Shao^b, Hongmiao Tian^b, Demei Yu^{a,*}

^a Department of Chemistry, School of Science, State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, PR China

^b State Key Laboratory of Manufacturing Systems Engineering, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, PR China

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ABSTRACT

A methacryl ethyl-functionalized soluble polypyrrole was designed and prepared by chemical oxidative polymerization for rapid fabrication of high-aspect-ratio pillar arrays. The chemical structures of the pyrrole derivative and the corresponding polypyrrole were characterized by FTIR and ¹H NMR. The polypyrrole with a weight-average molecular weight (M_w) of 7376 exhibits good solubility in several organic solvents, favorable thin film-forming ability and two UV–Vis absorption peaks at 280 and 380 nm in tetrahydrofuran solution. The dilute chloroform solution of the polypyrrole is a Newtonian fluid with a low viscosity and shows a significant increase in the electrical conductivity with increasing the polypyrrole content. Moreover, an insulating photoresist can be transformed into a conductive photoresist by doping this polypyrrole. Electrowetting driven structure formation experiments have confirmed that the conductive photoresist can fulfill rapid fabrication of higher-aspect-ratio pillar arrays compared with the insulating photoresist.

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1. Introduction

Over the past few decades, high-aspect-ratio micro-/nanostructures have been widely used in various fundamental research and practical applications such as superhydrophobic surfaces, electronic devices, chemical sensors, micro-/nanofluidic systems and micro-/nanoelectromechanical systems (MEMS/NEMS) [1–7]. Conventional lithographic approaches, such as UV imprint lithography and hot embossing, are often the choice of the method for manufacturing these micro/nanostructures. However, such approaches typically need a comparatively large external force to press a patterned template mechanically against the substrate, possibly leading to poor geometrical integrity in the duplicated structure or even irreversible damage to the template and substrate [8]. Recently, a new patterning technique, electrowetting driven structure formation (EWSF), has been explored as a simple and economical way to fabricate high-aspect-ratio micro-/nanostructures [9–11]. More importantly, EWSF only needs a minimized external pressure to maintain the contact between the template and the thin polymeric film, thereby promising high integrity and throughput.

Commonly used polymers in EWSF are electrically insulating (typically with an electrical conductivity less than 10^{-8} S/cm) and suffer

from the low aspect ratio and slow replication dynamics [9]. Further explanation for the low performance of these insulating polymers is that the insulating polymer is not an equipotential body but permeated by the electric field, so that just a small reduction in the contact angle of electrowetting on dielectrics (EWOD) can be achieved. Therefore, a large radius of curvature and a small electrocapillary force at the concave polymer-air interface can be obtained in the microcavity of the template, resulting in a low-aspect-ratio micro-/nanostructure with a slow replication dynamics. In contrast to the insulating polymer, the conductive polymer allows a larger contact angle reduction of EWOD, thereby definitely promising higher aspect ratio and faster replication dynamics in EWSF [12–15].

Among the conductive polymers, polypyrrole has been considered as a key material for many potential applications such as electronic devices, electrodes, solid electrolytes for capacitors, electromagnetic shielding materials, sensors and actuators, because of its high electrical conductivity and good environmental stability [16–22]. However, both electrochemically and chemically synthesized polypyrroles are typically insoluble in organic solvents and infusible because of their strong intra- and intermolecular interactions, resulting in their poor thin film-forming ability. Several approaches have been developed to improve the solubility in organic solvents and, consequently, the processability of the polypyrrole, including side-chain-induced solubilization [23–27], counterion-induced solubilization [28–32], and colloid formation [33–35]. In particular, the side-chain-induced solubilization is a

* Corresponding author.

E-mail address: dmyu@mail.xjtu.edu.cn (D. Yu).

well-known approach. The introduction of simple and flexible substituents such as alkyl and alkoxy groups to the backbone of the polypyrrole markedly enhances the solubility in organic solvents and processability of the polypyrrole. Moreover, the introduction of functional substituents can further provide a wide range of other attributes [36–41]. However, these conductive polymers still suffer from the slow replication dynamics due to their relatively high melt viscosity. Thus, reducing the viscosities of these conductive polymers may be a promising way for rapid fabrication of high-aspect-ratio micro-/nanostructures via EWSF. One of the available routes is doping these conductive polymers into a low-viscosity insulating matrix, since the beneficial property of each component can be well integrated [42–44].

In this paper, a soluble polypyrrole, poly(*N*-(methacryl ethyl)pyrrole) (PMAEPy), was designed and prepared through introducing a long functional substituent to the backbone of polypyrrole. The chemical structure, molecular weight, solubility in organic solvents, thin film-forming ability, rheological properties and electrical conductivity of the dilute solution of PMAEPy were characterized. Moreover, a conductive photoresist was prepared by doping PMAEPy into a photocurable resin for rapid fabrication of higher-aspect-ratio pillar arrays via EWSF. In addition, a comparison between the insulating photoresist and the conductive photoresist was carried out concerning the structural aspect ratio and the replication dynamics of EWSF.

2. Experimental section

2.1. Materials

Pyrrole (99.5%, Zhejiang Taizhou Qingquan Medical & Chemical Co., Ltd.) was vacuum-distilled and stored in the absence of light before use. 18-crown-6, 2-bromoethanol, and methacryloyl chloride (98.0%) were purchased from Shanghai Darui Chemicals Co., Ltd. Potassium (analytical grade, 99%), iron (III) chloride (analytical grade), tetrahydrofuran, nitromethane, dichloromethane, ethanol, dimethylsulfoxide, dimethylformamide, chloroform, *n*-Butyl acetate, toluene, and isopropanol were purchased from Sinopharm Chemical Reagent Co. Ltd. The photocurable resin, bisphenol A (4) ethoxylated dimethacrylate (BPA4EODMA), was purchased from Guangzhou Deco Composite Technology. The photoinitiator, 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP), was purchased from Zibo Pioneer Import & Export Co. Ltd. Trimethoxy(1H,1H,2H,2H-heptadecafluorodecyl)silane (FAS) was purchased from SICONG chemical Reagent Co. Ltd. Indium tin oxide (ITO)-coated glass slides with a resistance of 8 Ω cm were used as transparent electrodes for the UV light transmittance. Polyimide (PI) films with a thickness of 25 μm were used as the electrode pair spacer.

2.2. Synthesis of soluble polypyrrole

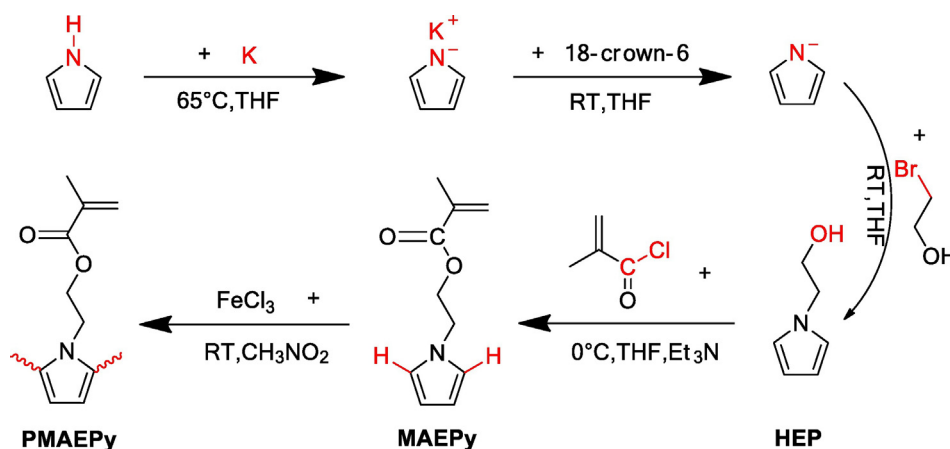
N-(2-hydroxyethyl)pyrrole (HEP), *N*-(methacryl ethyl)pyrrole (MAEPy) and poly(*N*-(methacryl ethyl)pyrrole) (PMAEPy) were synthesized according to the procedures shown in Scheme 1.

2.2.1. Synthesis of HEP

Pyrrolyl potassium salt (50 mmol) was added to a solution of 18-crown-6 (5 mmol) in dry tetrahydrofuran [45,46]. The mixture was stirred for 30 min under dry nitrogen. Then a solution of 2-bromoethanol (20 mmol) in dry tetrahydrofuran was slowly added into the mixture to permit heat elimination. Stirring was continued for 12 h at room temperature. After concentrating the solution in a rotary evaporator, the viscous solution was poured into 10-fold excess saturated aqueous solution of sodium sulfate with 1-fold dichloromethane. The solvents and pyrrole in the organic layer were eliminated under vacuum in an 80 °C water bath. Column chromatography using ethanol as eluent provided the pure *N*-(2-hydroxyethyl) pyrrole in 51% yield [47]. FTIR (KBr, cm⁻¹): 3600–3000 (s, OH), 3130, 3110 (w; =C–H), 2960, 2940 (w; —C–H), 1500, 1359, 1284 (m; pyrrole ring stretching vibration), 1068 (m), 980 (w), 727 (s; ring C–H bending vibrations); ¹H NMR (400 MHz, CDCl₃-d₁, δ, ppm): 6.728 (s, 2H_α, Py H), 6.207 (s, 2H_β, Py H), 4.020 (t, 2H, CH₂), 3.840 (t, 2H, CH₂), 1.881 (s, 1H, —OH).

2.2.2. Synthesis of MAEPy

HEP (50 mmol) and triethylamine (50 mmol) were dissolved in dry tetrahydrofuran at 0 °C. A solution of methacryloyl chloride (50 mmol) in dry tetrahydrofuran was added dropwise at 0 °C and the reaction mixture was stirred for 12 h at 0 °C. After concentrating the solution in a rotary evaporator, the viscous solution was poured into 10-fold excess saturated aqueous solution of sodium sulfate with 1-fold dichloromethane. The solvent in the organic phase was eliminated under vacuum in a 30 °C water bath. The residue was stirred in a ten times volume of a suspension of dichloromethane and aqueous 2 M NaOH overnight. The organic layer was dried over sodium sulfate and then the solvent in the organic layer was evaporated. Column chromatography using dichloromethane as eluent provided the pure MAEPy in 31% yield [48]. FTIR (KBr, cm⁻¹): 3130, 3110 (w; =C–H), 2960, 2940 (w; C–H), 1720 (s; C=O), 1637 (m; vinyl C=C), 1498, 1363, 1296 (m; pyrrole ring stretching vibration), 1161 (s; C–O), 1089, 1061 (m), 943 (w), 727 (s; ring C–H bending vibrations); ¹H NMR (400 MHz, CDCl₃-d₁, δ, ppm): 6.70 (s, 2H_α, Py H), 6.17 (s, 2H_β, Py H), 6.12 (s, 1H, C=CH₂), 5.60 (s, 1H, C=CH₂), 4.38 (t, 2H, CH₂), 4.18 (t, 2H, CH₂), 1.94 (s, 3H, CH₃).



Scheme 1. Synthesis of HEP, MAEPy and PMAEPy.

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