



Well-defined monocarboxyl-terminated polystyrene with low molecular weight: A candidate for the fabrication of highly ordered microporous films and microspheres *via* a static breath-figure process

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ABSTRACT

Aiming at the fabrication of highly ordered microporous films, a series of well-defined monocarboxyl-terminated polystyrenes (PS–COOH) with low molecular weight (PS_{13K}–COOH: $M_n = 13 \text{ kg mol}^{-1}$, $M_w/M_n = 1.04$; PS_{10K}–COOH: $M_n = 10 \text{ kg mol}^{-1}$, $M_w/M_n = 1.05$; PS_{4.4K}–COOH: $M_n = 4.4 \text{ kg mol}^{-1}$, $M_w/M_n = 1.05$ and PS_{2.1K}–COOH: $M_n = 2.1 \text{ kg mol}^{-1}$, $M_w/M_n = 1.08$) were synthesized firstly *via* reversible addition-fragmentation chain transfer (RAFT) polymerization using *S*-1-dodecyl-*S'*-(α , α' -dimethyl- α'' -acetic acid) trithiocarbonate as chain transfer agent. Then, a facile static breath-figure (BF) process was employed to fabricate microporous films of PS–COOHs. The influencing factors on the morphology of such microporous films, such as relative humidity, temperature, solvent, polymer concentration and molecular weight of polymer were investigated. Highly ordered microporous film with average pore size of 1.33 μm and better regularity was fabricated through a static BF process using PS_{10K}–COOH solution in CS₂ (40 mg mL⁻¹) at 22 °C in relative humidity of 95%. It was noteworthy that highly ordered microporous film (the average pore sizes from 0.77 μm to 0.83 μm) can be successfully fabricated using PS–COOH with very low M_n of 2.1 kg mol⁻¹ for the first time. Moreover, microsphere pattern of PS–COOH with the average diameters from 0.85 μm to 5.40 μm was formed when replacing water with methanol as environmental vapor in the chamber for the static BF process.

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1. Introduction

The micropatterned materials with well-defined pore size and large surface area have attracted increasing attention, owing to their potential applications in the fields of

light-emitting diodes [1,2], templates [3–5], cell culture scaffolds [6,7], fluorinated super-hydrophobic surfaces [8,9], biocatalytic films [10,11], carbon nanotube [12] and polymeric microsieves [13,14]. The breath-figure (BF) process [15–20] is a highly reliable methodology to fabricate microporous films, which not only adjust their morphology and pore size (varying from hundreds of nanometers to several micrometers in diameter), but also construct highly ordered two- or three-dimensional micropatterned films. However, in order to obtain highly ordered microporous

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films *via* BF process, many influencing factors such as polymer's chemical structure and component, molecular weight of polymer, solvent, polymer concentration, relative humidity, temperature, airflow velocity, substrate are needed to be chosen and optimized [18–24].

Among a variety of polymers, polystyrene (PS) based materials such as homopolymer [3,10,21,25–32], block copolymers [20,33–42], star and comb-like polymers [43–46], organic–inorganic hybrid materials [47–51], and metal nanoparticles [12,52–54] were good candidates for fabricating highly ordered microporous materials and widely employed. Compared with other architectures, linear PS homopolymers with/without terminal polar group was more readily achieved only by one step polymerization or a simple combination of polymerization or transformation reaction. Thus such polymers were employed to obtain highly ordered microporous films *via* BF process and still attracted a few attention in recent years [3,21,25–32]. Although there were different results obtained in different BF systems, proper molecular weight of non-polar PS homopolymer was generally considered to play an important role in the fabrication of well-controlled microporous films [21,30]. In one work of Han's group [21], PS with very high M_w (1970 kg mol⁻¹) leads to highly viscous polymer solution and water droplets cannot sink into the solution, resulting in few porous structures in polymer film. While, for a PS with small M_w of 29.3 kg mol⁻¹, the solution with lower viscosity cannot prevent coalescence between condensed water droplets, resulting the formation of disordered pores. Only by using PS with proper M_w of 223.2 kg mol⁻¹, highly ordered microporous films can be successfully fabricated. Otherwise polystyrene homopolymer with hydrophilic terminal groups such as carboxyl and hydroxyl group are generally believed to be good candidates to fabricate highly ordered microporous films by BF process [3,32]. The molecular weight of such terminal functionalized PS was considered to be one of the most important influencing factors in such processes. The monocarboxyl-terminated polystyrene (PS–COOH) with M_w of 50 kg mol⁻¹ and dicarboxyl-terminated polystyrene with M_w of 200 kg mol⁻¹ were successfully used to fabricate the large area films with uniform pores, respectively [26–29]. Especially, He et al. [28] showed how to facily adjust the solution concentration, relative humidity and temperature in the system, simultaneously, to control the morphology and pore size. Nevertheless, when using PS–COOH with lower M_n of 30 kg mol⁻¹ and 22 kg mol⁻¹, the ordered structure of pores was destroyed or no highly ordered structure organization in a long-range distance was formed [30,31]. In all cases, the M_w or M_n and the polar end group of PS–COOH are associated with the tune of an appropriate viscosity and surface energy. Higher terminal carboxyl group content of PS–COOH with lower molecular weight could be more conducive to obtain a well-organized microporous structure on the film surface.

Herein, four well-defined PS–COOH polymers with low molecular weight (M_n = 13–2.1 kg mol⁻¹, PDI = 1.04–1.08) were synthesized by RAFT polymerization using a chain transfer agent containing a –COOH group. Then, they were fabricated to highly ordered microporous films using a facile static BF process [12,14,16,20,37–42,55–60]. The

influencing factors on the film morphology were systematically investigated. Interestingly, microsphere pattern was formed when replacing water with methanol as environmental vapor in the chamber for static BF process.

2. Experimental

2.1. Materials

All manipulations involving air- and/or moisture sensitive compounds were carried out using Schlenk techniques. *S*-1-dodecyl-*S'*-(α , α' -dimethyl- α'' -acetic acid) trithiocarbonate (DDAT) was synthesized according to the reported method [61]. Styrene (St) was dried over calcium hydride, distilled under reduced pressure, passed through a neutral alumina column to remove stabilizer, and degassed with argon prior to use. Analytical grade carbon disulfide (CS₂), chloroform (CHCl₃), dichloromethane (CH₂Cl₂), toluene and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Other chemicals were used as received without further purification unless stated otherwise.

2.2. Synthesis of PS–COOH homo-polymers

The carboxyl-terminated trithiocarbonate (DDAT) as chain transfer agent was prepared according to a similar procedure reported in the previously published literature [61]. In a typical RAFT polymerization of styrene, DDAT (1.0 g, 2.8 mmol) was added to a 25 mL dry Schlenk flask equipped with a magnetic stirring bar. This flask was then capped with a rubber septum and deoxygenated by degassing–backfilling with argon for three times. Then, the other 25 mL dry Schlenk flask equipped with a magnetic stirring bar was capped with a rubber septum, purged with argon for about 30 min, and charged with styrene (St) (6.5 mL, 55 mmol) *via* syringe. The solution was bubbled with argon for about 30 min to deoxygenate and then was cannula-transferred to the first flask containing DDAT chain transfer agent. The mixture was degassed with three freeze–pump–thaw cycles followed by heating the flask in an oil bath preset at 140 °C under an argon atmosphere. The polymerization was stopped after 6 h *via* cooling with a liquid nitrogen bath. The reaction mixture was dissolved in 10 mL toluene and precipitated by pouring the solution into a large excess of cold methanol under magnetic stirring. The PS–COOH homopolymer was filtered, washed with methanol several times, dried overnight at 40 °C *in vacuo* to give a pure pale yellow solid in 94% yield and analyzed by GPC and ¹H NMR. PS_{2.1K}–COOH: M_n = 2.1 kg mol⁻¹, M_w/M_n = 1.08. ¹H NMR (CDCl₃): δ (ppm) = 7.30–6.30 (*m*, H^h), 5.03–4.60 (*b*, H^c), 3.39–3.16 (*m*, H^c), 2.50–1.33 (*m*, H^{b+f+i+j}), 1.33–1.12 (*s*, H^d), 1.02–0.82 (*t*, H^a). FT-IR (KBr): max 3082, 3059, 3025 (*vs* phenyl); 2923 (*s*, –CH₃); 2850 (*s*, –CH₂–); 1743 (*vs* C=O); 1601, 1583, 1492, 1452 (*s*, phenyl); 1068 (*s*, C=S); 841 (*s*, C–S); 756, 697 (*as*, –CH–CH– on phenyl) cm⁻¹. Other polymers were also prepared in a similar procedure (PS_{13K}–COOH: M_n = 13 kg mol⁻¹, M_w/M_n = 1.04; PS_{10K}–COOH: M_n = 10 kg mol⁻¹, M_w/M_n = 1.05; PS_{4.4K}–COOH: M_n = 4.4 kg mol⁻¹, M_w/M_n = 1.05).

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