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ARTICLE

Synthesis of Polystyrene with Cyclic, Ionized, Neutralized End Groups and the Self-Assemblies Templated by Breath Figures

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Polymers with functional end groups were synthesized via atom transfer radical polymerization (ATRP) using a novel cyclic lactone initiator, which can be readily converted into ionized and neutralized groups by hydrolysis and acidification processes, respectively. Results from Fourier transform infrared (FTIR) and ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy indicate that the cyclic lactone end group can be fully converted into sodium carboxylate in alkaline solution whereas the acidification process induces both neutralization and esterification. Gel permeation chromatography (GPC) curves reveal intramolecular esterification instead of intermolecular esterification during the acidification process. The polymers with various end groups that show different hydrophilicity were then utilized to fabricate honeycomb-patterned porous films by the breath figure method. Polystyrene with ionized or neutralized end group forms highly ordered self-assembled films in an easy and reproducible way whereas that with a less hydrophilic lactone end group generates irregular films. Moreover, polystyrene with an ionized end group that is the most hydrophilic results in porous films with a multilayered structure and much smaller surface pore size (it decreases to ~610 nm from 1.8 μm for films prepared from the neutralized polymer). In addition, we found that the end-functionalized polystyrene with a very low molecular weight (~2960 g/mol) is able to form highly ordered honeycomb films. It is speculated that the ionized end group endows polystyrene with high interfacial activity, leading to the unique surface morphologies. This is evidenced by the results of water contact angles on film surfaces with a pincushion structure through removing the top surface layer. The proposed approach to well-controlled end-functionalized polymers is useful in the fabrication of self-assemblies with adjustable morphologies.

Introduction

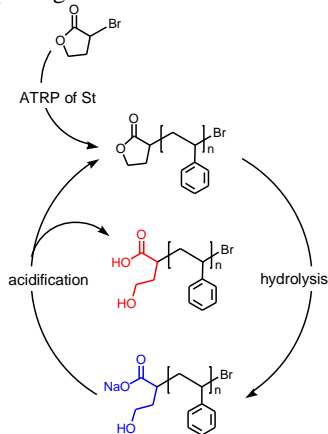
Polymer with functional end groups has received considerable attention because a well-designed end group can endow the polymer with improved or distinctive properties. Such polymers have found a great variety of applications in, for example, enhancing the efficiency of solar cells,¹⁻³ introducing stimuli-responsibility,⁴⁻⁶ acting as precursors for bioconjugates,^{7, 8} and driving self-assembly.⁹⁻¹¹ For instance, Kim et al. found that high-efficiency polymer solar cells with a fill factor of 0.69 can be obtained by altering the end group of poly(3-hexylthiophene) from hydrophilic to hydrophobic.² The high efficiency was attributed to the improved transport channel. The behaviors of stimuli-responsive polymers can also be modulated through introducing only one functional group on the polymer chain-end. Harada, Theato and coworkers concluded that the conformation of polymers end-capped with azobenzene, a photoactive group with superior reversible photoisomerization, can be controlled by temperature or light.^{5, 6}

Various studies have been focused on the end-group effect on the self-assembly of polymers. Yu et al. discovered that the aqueous solution of poly(lactic acid-co-glycolic acid)-*block*-poly(ethylene glycol)-*block*-poly(lactic acid-co-glycolic acid), PLGA-*b*-PEG-*b*-PLGA, transfers from a sol state to a reversible sol-gel transition as a function of temperature when end-capped with acetate or propionate group; however, the butyrate end-functionalized polymer forms precipitates.⁹ Qiao et al. revealed that the pore diameter, pore shape, and regularity of films prepared from polymers with different end groups were of significant difference. They changed the end group from acetonide to hydroxyl, which was then modified with pentadecafluorooctanoyl chloride.¹¹ Recently, Billon et al. synthesized a polymer with one chain end ionic group by nitroxide-mediated polymerization and prepared honeycomb structured films that are very regular.¹² They investigated in detail the effects of substrates, polymer concentration, and wet thickness on the pore size and surface morphologies. All of the above-mentioned examples demonstrate that the introduction of

a subtle end group onto the polymer chain end may result in greatly different self-assemblies.

Up to now, a large number of methods have been demonstrated to be able to prepare end-functionalized polymers, including atom transfer radical polymerization (ATRP),¹³ reversible addition–fragmentation chain transfer (RAFT),¹⁴ nitroxide mediated polymerizations (NMP),¹⁵ ring-opening polymerization (ROP)¹⁶, and anionic polymerization.¹⁷ ATRP is one of the commonly used techniques to synthesize functional polymers, especially polymers with series of end-functionalized groups. Polymer with a well-defined structure is conducive to explore the end group effect. There are three main strategies for preparing series of end-functionalized linear polymers by an ATRP method. The first one is using a series of functional initiators.^{18, 19} However, it needs to be very careful to obtain polymers with the same polymerization degree from every initiator in order to compare with each other. The second method is post-functionalization of the halogen at the end of the polymers or macro-initiators, which can be easily transformed to functional groups via well-established organic procedures, such as nucleophilic substitution or radical addition reaction.^{20–22} The third one is based on a post-functionable initiator.^{23, 24} In the latter two methods, a series of end-functionalized polymers can be obtained based on the exactly same main polymer chain so that the end group effect on the properties and behaviors of the polymers can be explored precisely. Previously, we synthesized polystyrene (PS) terminated with hydroxyl groups through reacting PS–Br with a series of hydramines by nucleophilic substitution.²⁵ The introduced hydrophilic end groups show great influence on the film morphologies. However, some of the polymers have insufficient conversion of end groups (~60%) if the hydramines have larger steric hindrance and weaker nucleophilicity.

In this work, linear PS with a cyclic, ionized or neutralized end group was synthesized on the basis of a post-functionable ATRP initiator, α -bromo- γ -butyrolactone. This hydrolysable cyclic initiator can be easily converted into ionized and neutralized states by hydrolysis and acidification, respectively (Scheme 1). The polymers were characterized in detail. Interestingly, the three states, cyclic, ionized, and neutralized, corresponding to low, high, and medium hydrophilicity, respectively, lead to different self-assembly behaviors of the polymers. This facile and straightforward strategy provides a novel approach to polymers with controlled functional end groups and is useful in fabricating functional films with adjustable morphologies.



Scheme 1. Synthetic route of end-functionalized polystyrene based on a post-functionable ATRP initiator, α -bromo- γ -butyrolactone.

Experimental

Materials

N,N,N,N',N' -Pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled from calcium hydride and stored at room temperature in a desiccator. Styrene (St) was obtained from Sinopharm Chemical Reagent Co. and distilled under reduced pressure before use. Initiator, α -bromo- γ -butyrolactone (**I**, 97%, Aldrich), was used without further purification. Copper (I) bromide (CuBr) was stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol under an argon blanket. The compound was dried under reduced pressure at 60 °C overnight. Deuterated chloroform (CDCl₃, 99.9%) was purchased from Sigma. Poly(ethylene terephthalate) (PET) film was kindly provided by Hangzhou Tape Factory and cleaned with acetone for 2 h before use. Water used in all experiments was deionized. All other chemicals were analytical grade and used as received.

Synthesis of PS with a Cyclic End Group, PS–cyl by ATRP

The procedure used for synthesizing linear PS with five membered lactone end group, PS–cyl is as follows. ATRP of styrene was performed with a ratio of St/I/PMDETA/CuBr = 320/4/2/1. A 250 mL Schlenk flask was added with α -bromo- γ -butyrolactone (6.525 mmol, 603 μ L), PMDETA (3.263 mmol, 675 μ L), and St (0.522 mol, 60 mL) under a nitrogen atmosphere. The solution was degassed by three freeze–pump–thaw cycles. Then CuBr (1.631 mmol, 234.9 mg) was added, and another three freeze–pump–thaw cycles were performed. The polymerization was allowed to proceed at a preheated 110 °C oil bath. After that, the flask was quenched in liquid nitrogen to stop the polymerization. Then, the reaction mixture was dissolved with a small amount of tetrahydrofuran (THF), precipitated in methanol, and repeated three times. The obtained product was dried in a vacuum overnight. The details of the resultant PS–Br are summarized in **Table 1**. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.26–6.2 (5H, C₆H₅), 4.25–4.05 (2H, –CH₂–O–), 2.2–1.2 (3H, CH₂CH), 1 (3H, CH₃). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 179.9 (1C, C=O), 145.5 (1C, aromatic C), 130.5–125.5 (5C, aromatic C), 48.2–38.8 (2C, CH₂CH). IR: ν (cm⁻¹) 1777, 1600, 1494, 1449.

Table 1 Results of linear polystyrene prepared via ATRP

Entry ^a	Time (min)	Conv. ^b (%)	$M_{n,th}$ ^c	$M_{n,GPC}$ ^d	PDI ^d
1	90	41.3	3440	2960	1.08
2	105	57.1	4760	4440	1.07
3	130	80.7	6720	5950	1.08

^aReaction conditions: [St]₀/[I]₀/[CuBr]₀/[PMDETA]₀ = 320/4/1/2, polymerization at 110 °C. ^bCalculated by the gravimetric method. Conv. (%) = W_p/W_{St} , where W_p and W_{St} are weights of the resultant polymer and styrene in feed, respectively. ^cTheoretical number-average molecular weight, $M_{n,th}$, was calculated according to $M_{n,th} = [St] \times M_{St} \times \text{conv.}/[I] + M_I$. ^dGPC using differential refractive index detection vs. linear polystyrene standards.

Synthesis of PS with an Ionized End Group, PS-ion, via Hydrolysis of PS-cyl

In a typical hydrolysis reaction, 600 mg of PS-cyl in 20 mL of THF and 2 g of NaOH (50 mmol) in water (4 mL) were added into a 250 mL round-bottomed flask. The mixture was refluxed for 24 h and then precipitated in methanol. The precipitation procedure was performed three times. The obtained product was dried in a vacuum oven overnight to achieve the final product. Please note that PS-ion has a hydroxyl end group (-OH) in addition to the ionized carboxyl (-COONa). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.26–6.2 (5H, C₆H₅), 3.8–3.7 (2H, -CH₂-O-), 2.2–1.2 (3H, CH₂CH), 1 (3H, CH₃). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 185.2 (1C, C=O), 145.5 (1C, aromatic C), 130.5–125.5 (5C, aromatic C), 48.2–38.8 (2C, CH₂CH). IR: ν (cm⁻¹) 1600, 1565, 1494, 1449, 1408.

Synthesis of PS with a Neutralized End Group, PS-neu, via Acidification of PS-ion

The procedure of acidification was performed as follows. PS-ion (200 mg) was dissolved in 11 mL of THF/methanol mixture (10/1, v/v) in a 50 mL round-bottomed flask. Then, 2 mL of hydrochloric acid was added, and the reaction proceeded at ambient temperature for 1 h. The raw product was precipitated in methanol, repeated three times, and then dried in a vacuum oven overnight to achieve the final product. Please note that PS-neu has a hydroxyl end group (-OH) in addition to the neutralized carboxyl (-COOH). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.26–6.2 (5H, C₆H₅), 4.25–4.05 and 3.8–3.7 (2H, -CH₂-O-), 2.2–1.2 (3H, CH₂CH), 1 (3H, CH₃). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 179.9 (1C, C=O), 145.5 (1C, aromatic C), 130.5–125.5 (5C, aromatic C), 48.2–38.8 (2C, CH₂CH). IR: ν (cm⁻¹) 1777, 1600, 1494, 1449.

Formation of Self-assembled Honeycomb Films via the Breath Figure Method

The polymers were dissolved in carbon disulfide at a concentration of 10 mg/mL. An aliquot of 50 μL for each polymer solution was drop-cast onto a PET substrate placed under a 2 L/min humid airflow (25 °C and ~80% RH). Owing to the condensation of water vapor on the solution surface during the evaporation of carbon disulfide, the transparent solution turned turbid rapidly. After solidification, the film was dried at room temperature.²⁶

Instruments and Measurements

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker (Advance DMX500) NMR instrument with tetramethylsilane (TMS) as the internal standard and CDCl₃ as the solvent at room temperature. Considering the extremely weak signal of carbonyl group on the polymer chain end in ¹³C NMR, the concentration of PS was increased to 300 mg/mL to enhance the intensity of the signals under optimized experimental parameters: relaxation time is 3 s, scan times is 3000 for PS-cyl and PS-neu, and 8000 for PS-ion.

Fourier transform infrared (FTIR) spectra were collected on a Nicolet FTIR/Nexus 470 spectrometer. Thirty-two scans were taken for each spectrum at a nominal resolution of 1 cm⁻¹.

Molecular weight and molecular weight distribution were measured by a PL 220 gel permeation chromatography (GPC) instrument at 25 °C, which was equipped with a Waters 510

HPLC pump, three Waters Ultrastaygel columns (500, 103, and 105 Å), and a Waters 410 DRI detector. THF was used as the eluent at a flow rate of 1.0 mL/min. The calibration of the molecular weights was based on PS standards.

A field emission scanning electron microscope (FESEM, Sirion-100, FEI) was used to observe the surface morphology of films after being sputtered with gold using an ion sputter JFC-1100. The porosity of the honeycomb films was determined using Image-Pro Plus via measuring the pore area and polymer area.

Water contact angles were measured on the honeycomb films by a Drop-Meter A-200 contact angle system (MAIST Vision Inspection & Measurement Ltd. Co.) at room temperature. The average values calculated from at least five parallel measurements are reported.

Results and discussion

Synthesis and Characterization of Chain-End Functionalized PS

The ATRP of styrene was carried out under bulk condition using α-bromo-γ-butyrolactone as a hydrolysable cyclic initiator and PMDETA as the ligand in conjunction with CuBr at 110 °C. The results are summarized in **Table 1**. It can be seen that the molecular weights measured by GPC are close to the theoretical values calculated on the basis of monomer conversion, and the polymers have narrow molecular weight distributions (PDI < 1.1) even when the monomer conversion reaches as high as 80%. The GPC traces (**Fig. 1**) are unimodal and symmetrical, which further indicate that α-bromo-γ-butyrolactone is a suitable initiator for the ATRP of styrene, although, as far as we know, this initiator was not ever reported before.

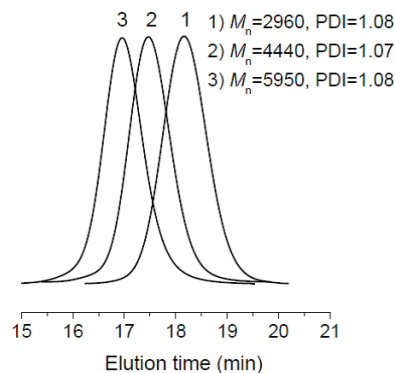


Fig. 1 GPC curves of linear polystyrene (PS-cyl) with different molecular weights.

PS with an ionized end group, PS-ion, can be successfully obtained by hydrolyzing PS-cyl with NaOH in THF under reflux. And, PS with a neutralized end group, PS-neu, was prepared by reacting PS-ion with hydrochloric acid at ambient temperature. These polymers were characterized by FTIR (**Fig. 2**), ¹³C NMR (**Fig. 3**), and ¹H NMR (**Fig. 4**). For example, the absorption band at 1777 cm⁻¹ due to the carbonyl in the lactone end group (**Fig. 2A**) disappears completely after hydrolysis (**Fig. 2B**). Meanwhile, shoulder peaks arising from sodium carboxylate, which are overlapped with peaks from vibrations of PS main chain, are clearly observed at 1565 cm⁻¹ and 1408 cm⁻¹, indicating the successful hydrolysis of the cyclic end group. Further verification of the hydrolysis process was

established by ^{13}C NMR and ^1H NMR. The ^{13}C NMR spectra reveal characteristic chemical shifts of carbonyl in lactone group and sodium carboxylate at 179.9 ppm (**Fig. 3A**) and 185.2 ppm (**Fig. 3B**), respectively. Notably, the ^1H NMR spectra strongly confirm the successful hydrolysis reaction. Before hydrolysis, the characteristic peak of the methylene proton next to the oxygen atom ($-\text{CH}_2-\text{O}-$, peak c) in the lactone end group is located at 4.25–4.05 ppm (**Fig. 4A**), which completely disappears after hydrolysis and is replaced by a new peak at 3.8–3.7 ppm (**Fig. 4B**). The detailed characteristic peaks are summarized in the Experimental section. All of these data suggest that the hydrolysis process is successfully carried out under the alkaline condition. It should be noted that this alkaline condition does not affect the bromide at the opposite chain end, which is consistent with the results reported by Summers et al.²⁷

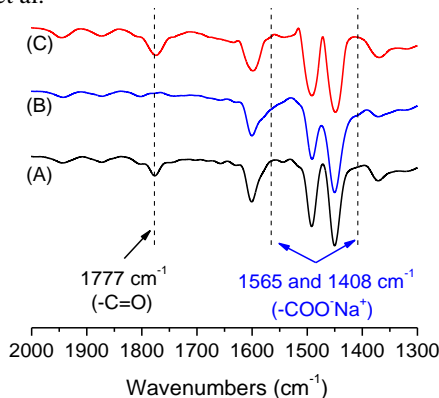


Fig. 2 FTIR spectra of (A) PS-cyl, (B) PS-ion, and (C) PS-neu.

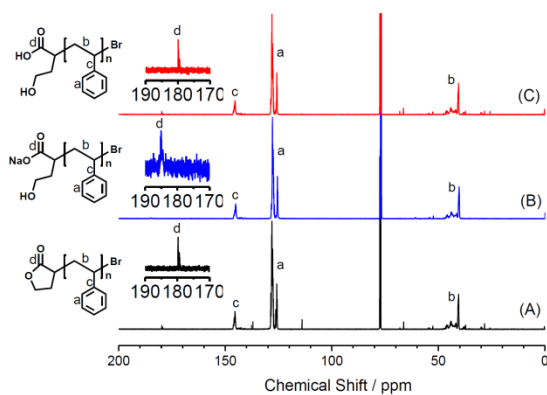


Fig. 3 ^{13}C NMR spectra of (A) PS-cyl, (B) PS-ion, and (C) PS-neu.

We found that it is rather complicated in the acidification process. As shown in **Fig. 2C**, the characteristic absorption peak of the carbonyl group appears again in the FTIR spectrum at 1777 cm^{-1} , and the shoulder peaks arising from sodium carboxylate at 1565 cm^{-1} and 1408 cm^{-1} disappear. Results of ^{13}C NMR confirm successful acidification because the signal of the ionized carbonyl group $-\text{COONa}$ at 185.2 ppm (**Fig. 3B**) returns to 179.9 ppm (**Fig. 3C**). Based on these results, we are sure that the ionized end group $-\text{COONa}$ has been fully converted. However, both of the characteristic peaks of the methylene protons in the five membered ring and opened ring can be observed from the ^1H NMR spectrum (**Fig. 4C**), which implies that under the acidic condition the acidification reaction is accompanied by an esterification process. As we all know

that an esterification reaction can be reversible; therefore, it is reasonable that the resultant product after acidification is a mixture of five membered ring lactone and neutralized opened ring containing a carboxyl group and a hydroxyl group.

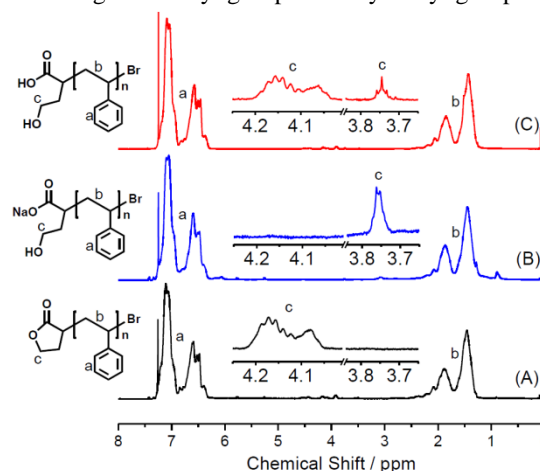


Fig. 4 ^1H NMR spectra of (A) PS-cyl, (B) PS-ion, and (C) PS-neu.

Moreover, the esterification process can take place in two routes, i.e., intermolecular and intramolecular esterification. The results of FTIR and NMR cannot answer which reaction is the prevailing one. It can be speculated that almost only intramolecular esterification occurs in our case because it is a reaction at the end group of macromolecules. The results of GPC support this hypothesis (**Fig. 5**). It can be seen that PS-neu exhibits monomodal distribution without any distinct shoulder peaks, which means no remarkable intermolecular esterification.

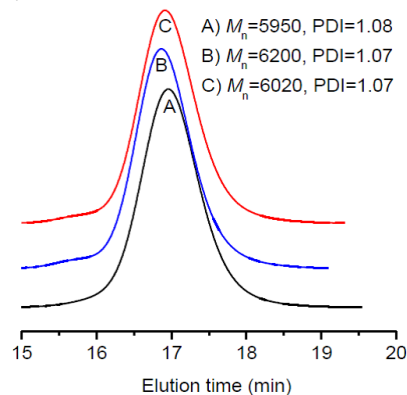


Fig. 5 GPC curves of (A) PS-cyl, (B) PS-ion, and (C) PS-neu.

In conclusion, we synthesized PS end-capped with a cyclic lactone group (PS-cyl) or that with an ionized sodium carboxylate and a hydroxyl (PS-ion). The neutralized polymer (PS-neu) is a mixture of five membered ring lactone and neutralized opened ring, the latter of which is more hydrophilic. Our previous results demonstrated that 40 wt.% hydrophilic polymer in blends is more than enough to exert influence over film morphologies.²⁵ Therefore, the self-assembly of these three polymers was compared.

Formation of Honeycomb-Patterned Porous Films via the Self-assembly of Breath Figures

Ordered honeycomb structured films can be prepared in a simple bottom-up process via the breath figure technique,

which takes advantage of the condensation of water droplets on a cold surface.^{28, 29} Thanks to the cost efficiency and simple operation of the breath figure method, the resultant ordered films have shown a wide range of potential applications in fields of catalysis,^{30, 31} microcontainers,^{32, 33} photoelectronics,³⁴⁻³⁶ sensors,³⁷ superhydrophobic surfaces,³⁸⁻⁴⁰ biomaterials⁴¹⁻⁴³ and separation membranes.⁴⁴⁻⁴⁶ For most of these applications, it is very important to control the pore size of the honeycomb films. Changing parameters such as polymer concentration can adjust pore size but only on a very small scale.⁴⁷ The structure of polymer have been demonstrated to be able to show a significant influence on the morphologies of the films.⁴⁸ Earlier study by Han et al. reveals that linear PS without any hydrophilic end group is able to form ordered honeycomb films only under very specific conditions, correlated with polymer molecular weight, solvent, relative humidity, and so on.⁴⁹ On the other hand, if a polymer is too hydrophilic, the corresponding casting conditions should also be fine-tuned to generate ordered honeycomb films.⁴⁸ In our previous work, we found that the introduction of a very short hydrophilic PHEMA block or a special hydrophilic end group leads to films with much smaller pore size; however, the pores are not ordered.^{25, 50}

Fig. 6 shows the external surfaces and cross-section morphologies of honeycomb films prepared from PS having different end groups. In our case, PS-cyl is able to form honeycomb films that are not very ordered (**Fig. 6A**). However, highly ordered honeycomb films can be obtained by transferring the cyclic end group to ionized or neutralized end group. It has been widely reported that PS with carboxyl end group is able to form ordered honeycomb films by the breath figure method.^{29, 51-53} It is worth pointing out that the PS-neu film (**Fig. 6C**) is actually prepared from a mixture of PS with a lactone end group and that with a neutralized end group. The ordered structure suggests that it is not necessary to use 100% carboxyl end-functionalized polystyrene, and a certain amount of hydrophilic end groups are enough to stabilize the water droplets. This result is consistent with our previous results of blend systems.²⁵

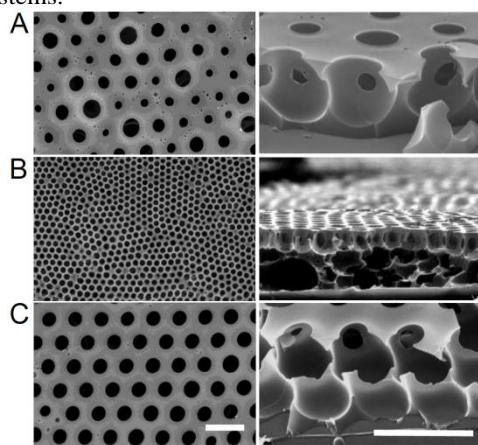


Fig. 6 Top-down (left panel) and cross-section (right panel) SEM images of honeycomb films prepared from 10 mg/mL solutions of (A) PS-cyl, (B) PS-ion, and (C) PS-neu. The scale bars are 5 μm .

In addition, it has been reported that linear PS with high molecular weight is easier to achieve ordered films than low molecular weight PS.⁴⁸ Srinivasarao and Bolognesi found that PS-neu ($M_n = 50,000$ and $100,000$ g/mol) can form ordered arrangements.^{29, 51} In this work, it is interesting that ordered

films can be prepared from end-functionalized PS with a molecular weight as low as 2960 g/mol.

The end groups show remarkable influence on the pore diameter of the films. The film prepared from PS-neu (**Fig. 6C**) has a surface pore diameter of about 1.8 μm . However, the pore diameter of the film prepared from PS-ion decreases to about 610 nm (**Fig. 6B**). From the cross-sectional views, PS-ion leads to a multilayered structure, unlike the monolayered structure from PS-cyl or PS-neu. Two reasons are responsible for the unique structure from PS-ion. On the one hand, Eisenberg and coworkers confirmed that end-ionized polymers can form star-like micelles in organic solvents as a result of nonsolubility of the ionic end group.⁵⁴ In the breath figure technique, star polymer with higher segment density than linear polymer is in favor of forming a solid polymer layer at the water/solution interface to stabilize the condensed water droplets.⁵⁵ On the other hand, the sodium carboxylate end group is much more hydrophilic than carboxyl or lactone group and hence shows much higher interfacial activity. Therefore, from the point view of thermodynamics, it is able to stabilize much larger interfacial area, resulting in smaller pores. This hypothesis is well supported by the following water contact angle results.

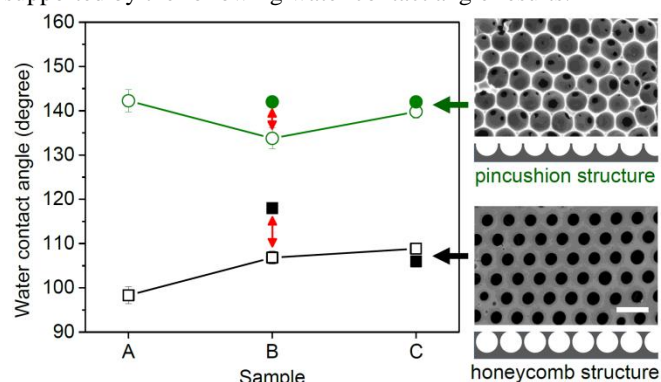


Fig. 7 Water contact angles on honeycomb (square) and pincushion structured (circle) films prepared from (A) PS-cyl, (B) PS-ion, and (C) PS-neu. Hollow: experimental; filled: calculated.

As shown in **Fig. 7**, honeycomb structured films prepared from PS-cyl, PS-ion, and PS-neu have water contact angles of 98°, 107°, and 109°, respectively. The top layer of the films was then removed by an adhesive tape to expose the pincushion structure. Only the bottom layer remains for multilayered films. As expected, the films with pincushion structure show obviously higher water contact angles, which are 142°, 134°, and 140°, respectively. It is well known that theoretical water contact angles can be estimated according to Cassie and Baxter's law:

$$\cos\theta_{\text{cal}} = (1-f_{\text{pore}}) \times \cos\theta_{\text{polymer}} + f_{\text{pore}} \times \cos\theta_{\text{pore}}$$

where θ_{cal} is the calculated apparent contact angle, f_{pore} is the area fraction of pores on the surface, θ_{polymer} is the contact angle of a polymer in the form of a thin and smooth film, and θ_{pore} is the contact angle of the pore, which is 180° in Cassie state.⁵⁶

Taking ordered PS-ion and PS-neu films (**Fig. 6B** and **C**) as an example, f_{pore} was measured as ~0.48 and ~0.27 using software Image-Pro Plus, respectively; and θ_{PS} is assumed to be 90°. Consequently, θ_{cal} of PS-ion and PS-neu films are ~118° and ~106°, respectively. After peeling off the top layer, both PS-ion and PS-neu pincushion structured films have an increased f_{pore} of ~0.79, and hence the θ_{cal} is ~142°. It is clear that, for PS-neu films before and after peeling off the top layer,

the experimental values (109° and 140°) are close to the calculated results (106° and 142°). On contrast, the experimental values of PS-ion films (107° and 134°) are lower than those theoretically calculated (118° and 142°). In addition, as these pincushion structured films have similar f_{pore} values, the contact angles should be almost the same. However, the water contact angle of PS-ion (134°) is smaller than those of PS-cyl (142°) and PS-neu (140°) films. Moreover, when a polymer with a long poly(acrylic acid) block was used, the difference in surface water contact angles of the neutralized and ionized samples can be as large as 30°⁵⁷ which is much larger than that induced by only one end group. It is speculated that the highly hydrophilic sodium carboxylate can effectively segregate at the water/solution interface, i.e., the pore wall, decreasing the water contact angles. This interfacial activity largely determines the pore diameter and structures. It should be noted that such interfacial segregation is the same in either the bottom layer or top layer for the multilayered films. In fact, the segregate behavior of hydrophilic moieties is consistent with our previously reported results.^{37,43}

Conclusions

Polystyrenes with cyclic, ionized and neutralized end groups were synthesized by post-functionalization of a lactone initiator on the polymer chain end. The cyclic lactone end group can be fully converted into sodium carboxylate in alkaline solution whereas the acidification process leads to both neutralization and esterification. These polymers were then utilized to fabricate honeycomb films by the breath figure method. It is concluded that polystyrene with hydrophilic end group is much easier to form ordered honeycomb films. Moreover, polystyrene with an ionized end group, PS-ion, exhibits multilayered structure and much smaller pore size than that with a neutralized end group, PS-neu. It is attributed to both its larger segment density induced by the formation of star-like micelles and its higher interfacial activity at the interface of solution/water droplets. We demonstrated that this simple approach to well-controlled end-functionalized polymers is useful in the formation of self-assemblies with adjustable morphologies such as honeycomb-patterned films.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Original SEM images of Fig. 6]. See DOI: 10.1039/c000000x/

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Graphic Abstract

Synthesis of Polystyrene with Cyclic, Ionized, Neutralized End Groups and the Self-Assemblies Templated by Breath Figures

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Polymers with functional end groups are synthesized using a cyclic lactone ATRP initiator for honeycomb-patterned porous films by the breath figure method.

