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New Polymethylene-based AB$_2$ Star Copolymers Synthesized via A Combination of Polyhomologation of Ylides and Atom Transfer Radical Polymerization

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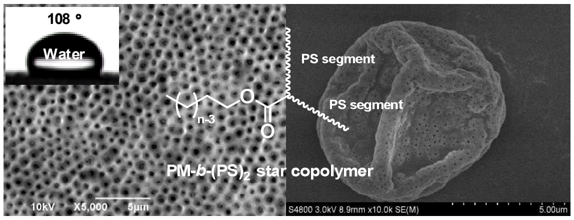

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RSC Advances

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

New Polymethylene-based AB_2 Star Copolymers Synthesized via A Combination of Polyhomologation of Ylides and Atom Transfer Radical Polymerization

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

New polymethylene-based AB_2 star polymers with well-defined architecture and various components were synthesized using a combination of polyhomologation of ylides and atomic transfer radical polymerization (ATRP). The chain structures of polymethylene-*b*-(polystyrene)$_2$ (PM-*b*-(PS)$_2$) and polymethylene-*b*-(poly(methyl methacrylate))$_2$ (PM-*b*-(PMMA)$_2$) were characterized through ^{1}H NMR, GPC and FT-IR. The porous films of such star copolymers were fabricated *via* static breath-figure (BF) process. The influence of polymer molecular weight, solution concentration and environmental temperature on the morphology of such block copolymer films was investigated. Porous surface of such film presents hydrophobic behaviour with static water-droplet contact angle of *ca.* 108 ° . The electrospinning of PM-*b*-(PS)$_2$ was performed using $CHCl_3$ as solvent and the wrinkle-like polymer particles with nanopores on their surface were obtained.

Introduction

Miktoarm star polymers, containing multiple arm species jointing at a central core, have attracted extensive research attention because of their unique self-assembly in bulk or solution and physicochemical properties.[1-5] With various functional groups or polymer segments, miktoarm star polymers find their potential applications in various areas, such as in catalysis,[6,7] biomedical systems,[7-13] nanoscopic imaging agents[14-16] and emulsion systems,[17,18] *etc*.

In past decades, the introduction of living anionic polymerization,[19] controlled/living radical polymerizations,[20-23] ring-opening polymerization,[24] and various coupling reactions[25-28] has generated a variety of novel miktoarm star polymers with well-defined architectures, compositions and properties.

Several strategies such as chlorosilane compounds based method,[29] iterative method,[5,30-33] “core-first” method,[34-41] “arm-first” method,[42-46] “in-out” method,[47-51] coupling method[52-60] and supramolecular reaction method,[61-64] *etc*. have been employed for the synthesis of miktoarm star polymers.

However, to date, there are only a few reports on the synthesis and application of mikto-, even homo-arm star polymer containing non-polar polyolefin segments such as polyethylethylene, ethylene-propylene random copolymer, polyisobutylene, polyethylene, isotactic polypropylene, polybutadiene and its hydrogenated polymers.[65-74] The incorporation of non-polar polyolefin segment into star polymer is expected to show unique self-assembly in solution or bulk and rheological properties. From the other piont of wiew, the poor adhesion and compatibility of non-polar polyolefin with other materials can be improved effectively by introducing various polar polymer segments and forming well-defined architectures.[75-79] Li and coworkers[65] have observed that multicompartment micelles can be formed in dilute aqueous solution of a ABC miktoarm star copolymer with a hydrophilic poly(ethylene oxide) and two hydrophobic but immiscible components (a polymeric hydrocarbon and a perfluorinated polyether). Saito and coworkers[67] reported a kind of multicompartment micelles from well-defined μ-[poly(ethylethylene)][poly(ethylene oxide)][poly(γ-methyl-ε-caprolactone)] miktoarm star terpolymers synthesized by a combination of two successful living anionic polymerizations and one controlled ring-opening polymerization. Polyethylene based A_2B_2 ((PE)$_2$-(PS)$_2$),[71] AB_2 (PE-*b*-(PEG)$_2$)[72] and AB_3 (PE-*b*-(PEG)$_3$)[72] miktoarm star copolymers were achieved *via* a facile strategy combining chain shuttling ethylene polymerization with click reaction and atomic transfer radical polymerization or just with click reaction. (PE)$_2$-(PS)$_2$ miktoarm star copolymer cound form spherical micells in cyclohexane with crystallized PE core and swollen PS shell. While, the amphiphilic PE-*b*-(PEG)$_2$ and PE-*b*-(PEG)$_3$ star copolymer can self-assemble to form platelate-like micelles in water. Recently, Liu and coworkers[74] reported a variety of (PE)$_n$-PDVB-(PS)$_m$ miktoarm star copolymers synthesized with star PEs as ATRP macroinitiators using “in-out” strategy. Therein, PE macroinitiators were generated *via* Pd-catalyzed coordinative living polymerization of ethylene.

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Recently, the readily design and construction of chain-end functionalized polymethylene which is polyolefin analogue, by polyhomologation of ylides[80,81] has contributed to several kinds of functionalized polyolefin copolymer with well-defined architectures and different compostions.[82-87]

Herein, we report on the synthesis of new well-defined polymethylene based miktoarm AB_2 star copolymers via a combination of polyhomologation of ylides and ATRP. Polymethylene based dual-macroinitiator was firstly achieved by the polyhomologation of sulfoxonium ylides followed by oxidation then the esterification with 2,2-dichloroacetyl chloride. Subsequently, the polymethylene-*b*-(polystyrene)$_2$ (PM-*b*-(PS)$_2$) and polymethylene-*b*-(poly(methyl methacrylate))$_2$ (PM-*b*-(PMMA)$_2$) star copolymers were syntheized *via* ATRP of styrene (St) and methyl methacrylate (MMA), respectively. The chain structures of such miktoarm star copolymers were characterized. The micellization behavior of PM-*b*-(PS)$_2$ star copolymer was preliminary studied. The porous films and particles of PM-*b*-(PS)$_2$ star copolymer were fabricated through a static breath-figure process[88-92] and an electrostatic method,[93-95] respectively.

Experimental

Materials

All manipulations involving air- and/or moisture sensitive compounds were carried out in an N_2-filled drybox or using Schlenk techniques. Trimethylsulfoxonium iodide (Acros, 98%), benzyltributylammonium chloride (Acros, 98%), Celite-545 (Acros), borane dimethyl sulfide (Acros, 1 M in CH_2Cl_2), phenolphthalein (Acros, 98.5%) trimethylamine N-oxide dehydrate (Acros, 98%) and 2,2-dichloroacetyl chloride (Acros, 98%) were used as received without further purification.

N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%), styrene, methylmethacrylate (Ling Feng company, Shanghai, 99%) were dried over calcium hydride, distilled under reduced pressure, passed through a neutral alumina column to remove stabilizer, and degassed with nitrogen prior to use.

Toluene and tetrahydrofuran (THF) were refluxed over sodium/benzophenone and distilled under N_2 before use. Triethylamine, chlorobenzene and 1,2-dichlorobenzene were refluxed over CaH_2 and distilled before use. Cu(I)Br (Acros, 99.9%) was stirred in glacial acetic acid overnight and filtered though a Buchner funnel then washed three times with ethanol and diethyl ether, dried in a vacuum overnight, and stored under nitrogen. All other chemicals were used as received.

Synthesis of polymethylene based dual-macronitiator PM-Cl$_2$

The hydroxyl terminated polymethylene (PM-OH) was prepared firstly via the polyhomologation of ylides followed by oxidation in a similar procedure described in our previous work[82]. PM-OH ($M_{n,GPC}$=700 g·mol^{-1}, M_w/M_n=1.20, $M_{n,{}^1H\ NMR}$ =1 000 g·mol^{-1}; 1.0 mmol of OH g^{-1} polymer according to ^{1}H NMR measurements).

In a typical procedure to synthesize PM-Cl$_2$, PM-OH (2.43 g; 2.43 mmol of OH groups) and dried toluene (60 mL) were added in a nitrogen-purged, 500 mL, round-bottom flask equipped with a stirring bar and a condenser and then stirred at 80 ^{o}C for 30 min. Dry pyridine (2.4 mL, 29.2 mmol) was introduced into such mixture via a syringe after it was cooled to room temperature. The flask was then put into an ice-water bath for 30 min. Subsequently, 2,2-dichloroacetyl chloride (2.3 mL, 24.3 mmol) pre-diluted in 10 mL of dry toluene was added dropwise for 30 min. The reaction mixture was stirred vigorously for 12 h at 80 and 95 ^{o}C, respectively. The final mixture was cooled to room temperature and poured into 1.0 L of acidic methanol (containing 30 mL of 1 M aqueous HCl). The resulting polymer was collected by filtration, washed successively with methanol (30 mL×2), 1 M aqueous HCl (10 mL×2) and methanol (30 mL×3), and dried at 40 °C overnight in vacuo, to give an off-white solid. PM-Cl$_2$(the one obtained at reaction temperature of 95 ^{o}C): $M_{n,GPC}$=900 g·mol^{-1}, M_w/M_n=1.12, 1.75 mmol of Cl g^{-1} polymer according to ^{1}H NMR measurement. ^{1}H NMR (500 MHz, 1,2-dichlorobenzene-d^4, 80 ^{o}C): δ=5.92 (s, H^e), 4.21 (m, $H^{d'}$), 1.55 (m, H^c), 1.50-1.00 (m, H^b), 0.95-0.94 (m, H^a).

Synthesis of polymethylene-*b*-(polystyrene)$_2$ (PM-*b*-(PS)$_2$) and polymethylene-*b*-(poly(methyl methacrylate))$_2$ (PM-*b*-(PMMA)$_2$) star copolymer

In a typical ATRP polymerization of styrene, PM-Cl$_2$ 0.50 g (0.88 mmol Cl) was added to a 50 mL Schlenk flask equipped with a stirring bar. This flask was then capped with a rubber septum and deoxygenated by degassing and backfilling nitrogen for three times. Then, CuBr (114 mg, 0.79 mmol) and PMDETA (0.35 mL, 1.58 mmol) were placed in another 20 mL Schlenk flask equipped with a stirring bar. This flask was capped with a rubber septum, purged with nitrogen for about 30 min, and charged with deoxygenated toluene (12 mL) and styrene (2.5 mL, 22 mmol) *via* syringes. The mixture was stirred at room temperature under a nitrogen atmosphere for about 30 min. The solution of this second flask was cannula-transferred (under a nitrogen atmosphere) to the first flask containing PM-Cl$_2$. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath preset at 95^{o}C for 20 h. The polymer was filtered, washed with methanol several times, dried overnight at 40 ^{o}C in vacuo and analyzed by GPC, ^{1}H NMR and FT-IR. ^{1}H NMR (500 MHz, 1,2-dichlorobenzene-d^4, 80 ^{o}C): δ=7.26-6.43 (m, H^{h+k}), 4.63-4.38 (m, H^j), 3.90-3.60 (m, $H^{d''}$), 2.32-1.42 (m, $H^{e'+c+i+f+g}$), 1.42-1.16 (m, H^b), 0.95-0.93 (m, H^a). FT-IR(KBr): max 3 082, 3 060, 3 025 (vs, phenyl); 1 732 (vs, C=O); 1 601, 1 583, 1 493, 1 452 (s, phenyl); 1 373 (vs, -$C(CH_3)_3$); 1 155 (s, -C(O)-O-C); 757, 698 (as, -CH-CH- on phenyl) cm^{-1}.

ATRP polymerizations of methyl methacrylate targeting PM-*b*-(PMMA)$_2$ star copolymers were carried out in a similar procedure described in the synthesis of PM-*b*-(PS)$_2$. The polymer solution was diluted in toluene, precipitated in the mixture of methanol/deionized water (3.5:1 v/v). The final polymers obtained after filtration and washing by such methanol/water solvent were dried dried overnight at 40 ^{o}C in vacuo and analyzed by GPC and ^{1}H NMR. ^{1}H NMR (500 MHz, 1,2-dichlorobenzene-d^4, 80 ^{o}C): δ=4.15 (m, $H^{d''}$), 3.70 (s, H^h), 2.32 (m, $H^{e'}$), 2.30-2.00 (m, H^{i+f}), 1.70-1.55 (m, H^{c+j}), 1.50-1.00 (m, H^{b+g}), 0.95-0.94 (m, H^a).

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Fabrication of PM-*b*-(PS)$_2$ porous films via a static breath-figure process

The fabrication of porous films of PM-*b*-(PS)$_2$ star copolymers was carried out at 22 ^{o}C and 12 ^{o}C respectively, in a static humid condition through casting polymer solution (12 and 17 mg·mL^{-1}) in carbon disulfide (CS$_2$) onto a clean glass substrate in a glass vessel with a cap. Saturated relative humidities (R. H.) of *ca.* 95% in the glass vessel were achieved by adding deionized water. After complete evaporation of solvent, the formed porous films were dried at room temperature.

Preparation of particles by electrostatic method

The PM-*b*-(PS$_5$)$_2$ with (M_n=19,200 g·mol^{-1}, M_w/M_n=1.19 (Entry 5, Table 1)) star copolymer was dissolved in CHCl$_3$ at the concentration of 2.5 wt-%. The electrical field was generated by a variable high voltage power supply (DW-P403-3ACDF). The pipet wastilted at approximately 5-10° from horizontal so that a small viscous drop was maintained at the capillary tip. The applied voltage was 11 kV and the distance between the spinneret and the grounded plate was 15 cm. All solutions are fed by NE-1000 syringe pumps at 2.0 mL·h^{-1}.

Polymers characterization

^{1}H NMR spectra of polymers were obtained on a Bruker AV 500 spectrometer (500 MHz) at 80^{o}C with 1,2-dichlorobenzene-*d$_4$* as the solvent. Molecular weights (M_w and M_n) and molecular weight distributions (M_w/M_n) of polymers were determined using GPC equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3, HR4, and HR5, 7.8×300 mm^2). GPC measurements of polymers were run at 35^{o}C using THF as eluent with a flow rate of 1.0 mL·min^{-1}. The data were calibrated with linear polystyrene standards. High-temperature GPC measurement: M_w, M_n and M_w/M_n of polymers were determined using a Waters Alliance GPC2000 equipped with three types of Styragel columns (Styragel HT5, Styragel HT4, and Styragel HT3) and a Waters 2410 differential refractive index detector relative to linear polyethylene standards. GPC analyses were performed at 135^{o}C using 1,2,4-trichlorobenzene as eluent at a flow rate of 0.92 mL·min^{-1}.

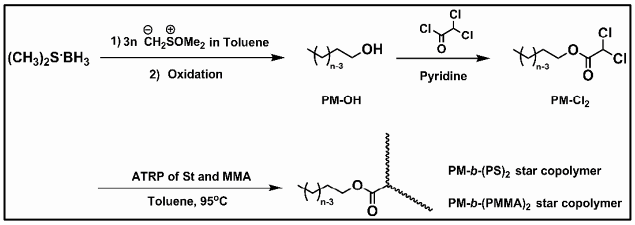
The solution of PM-*b*-(PS)$_2$ in CS$_2$ with concentration of 0.1 mg·mL^{-1} was prepared at room temperature. After standing for 24 h, the average sizes of the formed aggregates in such solution were determined by dynamic light scattering (DLS, ZS-90, Malvern Instruments).

The morphologies of PM-*b*-(PS)$_2$ porous films and particles were observed on SEMs (JSM 6390LV, JEOL, Japan and S4800, Hitachi, Japan) operated at 10 kV and 3.0 kV, respectively. The hydrophobicity of such porous films was characterized *via* static water-droplet contact angles which were determined with a Power each JL2000L (Shanghai Zhongchen Digital Technic Facilities Ltd. Co.) contact-angle goniometer. A 5 μL droplet of deionized water was placed on the surface of a film, and the static contact angle was measured 30 s later.

Results and Discussion

Synthesis of polymethylene-*b*-(polystyrene)$_2$ (PM-*b*-(PS)$_2$) and polymethylene-*b*-(poly(methyl methacrylate))$_2$ (PM-*b*-(PMMA)$_2$) star copolymer

The synthetic route of PM-*b*-(PS)$_2$ and PM-*b*-(PMMA)$_2$ star copolymers was illustrated in Scheme 1. Macroinitiator PM-Cl$_2$ was firstly synthesized by esterification of 2,2-dichloroacetyl chloride with hydroxyl terminated polymethylene (PM-OH) obtained *via* polyhomologation of ylides followed by oxidation. Then, the ATRP polymerizations of styrene and methyl methacrylate were carried out to achieve PM-*b*-(PS)$_2$ and PM-*b*-(PMMA)$_2$ star copolymers.



Scheme 1. Synthesis of PM-*b*-(PS)$_2$ and PM-*b*-(PMMA)$_2$ star copolymers

Excess amounts of 2,2-dichloroacetyl chloride and pyridine were confirmed to be important for preparing PM-Cl$_2$ efficiently. Meanwhile, in our case, the higher reaction temperature (95^{o}C) improved the conversion of PM-OH from 80% (at 80^{o}C) to nearly 100%. Figure 1 showed the ^{1}H NMR spectra of PM-OH (a), PM-Cl$_2$ (with 80% conversion) (b) and PM-Cl$_2$ (with 100% conversion) (c). Comparing with the ^{1}H NMR spectrum of PM-OH (Fig. 1(a)), two new peaks were present at δ=5.92 and 4.21 ppm (Fig.1(b)), respectively, confirming the formation of polymethylene 2,2-dichloroacetate (PM-Cl$_2$). In the case of incomplete conversion, the peak of methylene protons next to hydroxyl group in PM-OH was still remained (Fig.1 (b)). That peak can disappear completely (Fig. 1(c)) when the esterification was carried out at higher temperature of 95^{o}C.

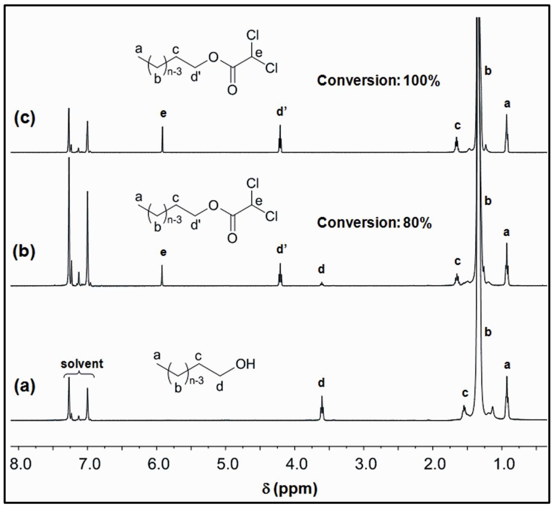


Fig. 1 ^{1}H NMR spectra of PM-OH and PM-Cl$_2$

Subsequently, styrene and MMA were polymerized in toluene using PM-Cl$_2$ as initiator with CuBr/PMDETA as a catalyst system, respectively, to achieve a series of PM-*b*-(PS)$_2$ and PM-

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b-(PMMA)$_2$ star copolymers. The results of such well-defined star copolymers were listed in Table 1. By varying polymerization conditions, the PM-*b*-(PS)$_2$ and PM-*b*-(PMMA)$_2$ star copolymers with narrow molecular weight distribution, different molecular weights and compositions can be succesfully achieved. The number average molecular weight (M_n) of PM-*b*-(PS)$_2$ can be well-controlled from 5,900 g·mol^{-1} to 19,200 g·mol^{-1} and the contents of PS segment increase from 84.7 wt-% to 95.3 wt% (Entries 1-5, Table 1). Two PM-*b*-(PMMA)$_2$ star copolymers with different PMMA contents of 90.0 wt-% and 93.2 wt-% (Entries 6 and 7, Table 1), respectively, were also obtained.

Table 1 Results of PM-*b*-(PS)$_2$ and PM-*b*-(PMMA)$_2$ star copolymers.

Entry	Polymers	M_n^{a} (g·mol^{-1})	M_w/M_n^{a}	$M_{n,theo}$^{b} (g·mol^{-1})	Content of PS or PMMA^c (wt%)
1^d	PM-*b*-(PS$_1$)$_2$	5900	1.16	5200	84.7
2^e	PM-*b*-(PS$_2$)$_2$	8300	1.15	7900	89.2
3^f	PM-*b*-(PS$_3$)$_2$	9200	1.08	8500	90.2
4^g	PM-*b*-(PS$_4$)$_2$	10300	1.18	9600	91.3
5^h	PM-*b*-(PS$_5$)$_2$	19200	1.19	17500	95.3
6^i	PM-*b*-(PMMA$_1$)$_2$	9000	1.25	7500	90.0
7^j	PM-*b*-(PMMA$_2$)$_2$	13300	1.30	12000	93.2

[a] Determined by GPC;
[b] Theoretical M_n calculated according to monomer conversion measured by gravimetric method;
[c] Calculated by M_n (GPC).
[d-j] Polymerization conditions: solvent=toluene (12.0 mL); temperature=95 °C; reaction time=20 h.
[d] $[St]_0/[PM\text{-}Cl_2]_0/[CuBr]_0/[PMDETA]_0=50:1:1.8:3.6$, $[St]_0=1.48$ mol·L^{-1}.
[e] $[St]_0/[PM\text{-}Cl_2]_0/[CuBr]_0/[PMDETA]_0=80:1:1.8:3.6$, $[St]_0=1.94$ mol·L^{-1}.
[f] $[St]_0/[PM\text{-}Cl_2]_0/[CuBr]_0/[PMDETA]_0=100:1:1.8:3.6$, $[St]_0=2.05$ mol·L^{-1}.
[g] $[St]_0/[PM\text{-}Cl_2]_0/[CuBr]_0/[PMDETA]_0=160:1:1.8:3.6$, $[St]_0=2.18$ mol·L^{-1}.
[h] $[St]_0/[PM\text{-}Cl_2]_0/[CuBr]_0/[PMDETA]_0=200:1:1.8:3.6$, $[St]_0=2.86$ mol·L^{-1}.
[i] $[MMA]_0/[PM\text{-}Cl_2]_0/[CuBr]_0/[PMDETA]_0=100:1: 1.8:3.6$, $[MMA]_0=1.74$ mol·L^{-1}
[j] $[MMA]_0/[PM\text{-}Cl_2]_0/[CuBr]_0/[PMDETA]_0=200:1: 1.8:3.6$, $[MMA]_0=2.91$ mol·L^{-1}.

GPC traces of PM-*b*-(PS)$_2$ star copolymers in Figure 2 (corresponding to Entries 1, 2 and 4 in Table 1) showed monomodal distributions without any tail in lower molecular weight region and any shoulder in higher molecular weight region, indicating the successful initiation of ATRP polymerization by PM-Cl$_2$.

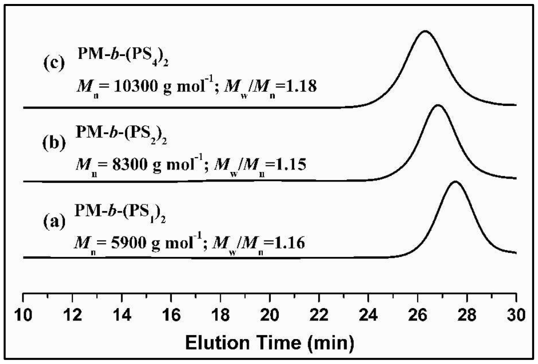

Fig. 2 GPC traces of PM-*b*-(PS)$_2$ star copolymers

The ^{1}H NMR spectrum of a representative PM-*b*-(PS)$_2$ star copolymer (Fig. 3(b)) revealed the presence of characteristic chemical shifts for PM and PS segment. Chemical shifts at δ=7.26-6.43, 4.63-4.38 and 2.30-1.42 ppm are assigned to protons of phenyl ring, methine protons next to the chloride atom at the chain end (-CH$_2$ (phenyl))-C*H*-Cl, peak j) and alkyl chain protons linked to the phenyl (–C*H*$_2$–C*H*–phenyl, peaks f, g, i and j), respectively. Moreover, the presence of polymethylene segment was confirmed by chemical shifts at δ=3.90-3.60, 1.42-1.16 and 0.95-0.93 ppm which are assigned to methylene proton next to oxygen atom (-C*H*$_2$-O-, peak d”), methylene protons of the polymethylene backbone ((-C*H*$_2$-)$_{n-3}$, peak b) and methyl protons in the chain end and branch of the PM segment (C*H*$_3$-CH$_2$- and –CH(C*H*$_3$)-, peak a) respectively. The peak e (δ=5.92) of proton next to two chloride atoms (-O(O)C-C*H*Cl$_2$) in PM-Cl$_2$ (Fig. 3(a)) disappeared completely in the ^{1}H NMR spectrum of PM-*b*-(PS)$_2$ (Fig. 3(b)). Being a similar chemical structure to PM-Cl$_2$, the poly(ε-caprolactone) based macroinitiator (PCL-Cl$_2$) with the same terminal group (-O(O)C-CHCl$_2$) was confirmed to form PCL based AB$_2$ star copolymer (PCL-*b*-(PS)$_2$) with two PS chains at each PCL precursor.[96] In general, GPC, ^{1}H NMR analysis and the similar character of PM-Cl$_2$ to that of PCL-Cl$_2$ for ATRP polymerization of styrene described above confirm the targeted structure of PM-*b*-(PS)$_2$ star copolymer.

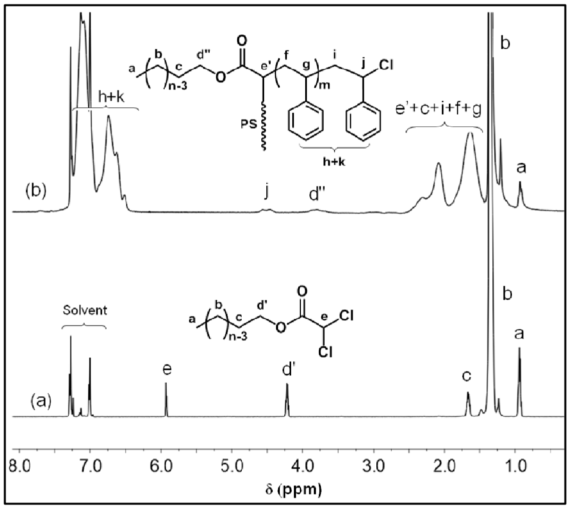

Fig. 3 ^{1}H NMR spectra of PM-Cl$_2$ (a) and PM-*b*-(PS)$_2$ star copolymer (b)

Figure 4 (b) showed the ^{1}H NMR spectrum of PM-*b*-(PMMA)$_2$ star copolymer. The succesful extention of the PMMA segment was indicated by the appearance of characteristic resonance peaks at δ=3.70, 2.30-2.00, 1.25-1.00 ppm (Fig. 4(b)) assigned to protons of repeat MMA units, respectively, and the absence of peak e assigned to proton next to two chloride atoms (-O(O)C-C*H*-Cl$_2$) in PM-Cl$_2$ (Fig. 4(a). GPC data (Entries 6 and 7, Table 1) also confirmed the extention of PMMA segment from PM-Cl$_2$.

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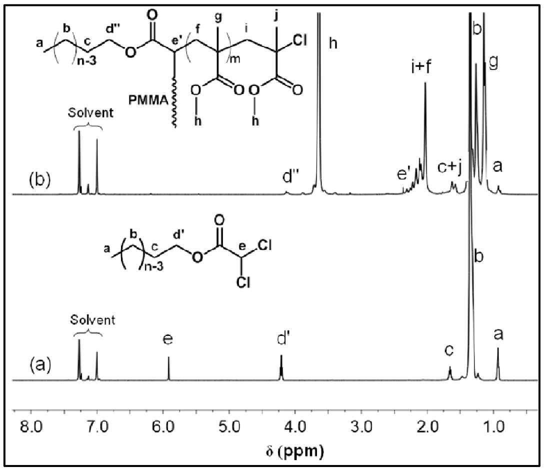

Fig. 4 ^{1}H NMR spectra of PM-Cl_2 (a) and PM-*b*-$(PMMA)_2$ star copolymer (b)

Solution behavior and morphology of PM-*b*-$(PS)_2$ star copolymer porous films and particles

The solution behavior of PM-*b*-$(PS)_2$ star copolymer was preliminarily studied at room temperature in CS_2 which is non-solvent for PM segment and good solvent for PS segment. As illustrated in Figure 5, PM-*b*-$(PS_2)_2$ (b) is well dissovled in CS_2 compared with pure CS_2 (a) when the concentration is as low as 4 mg·mL^{-1}. With the increase in star copolymer's concentration (c) and (d), a blue opalescence indicated the probable presence of micelles or aggregates.[82] To the PM-*b*-PS with the same PM segment, the solubility of copolymer increased when more PS segment is incorporated (as shown in Figure 5(e), 5(d) and 5(f), respectively). All the samples were dissolved in CS_2 at 50^{o}C, indicating the formation of PM-*b*-$(PS)_2$, because neither PM-Cl_2 nor PM-OH can be solved in CS_2 even at higher temperature. DLS data indicated that the average size of PM-*b*-$(PS)_2$ aggregates in diluted solution (0.1 mg·mL^{-1}) was about 90 nm. Further investigation on the micellization behavior of such star copolymer and its application will be performed in near future.

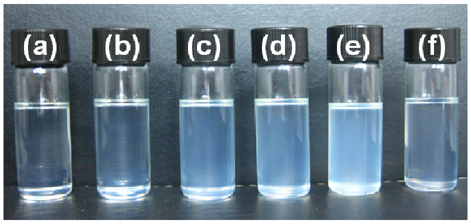

Fig. 5 Solution behavior of PM-*b*-$(PS)_2$ star copolymer in CS_2 at room termperature. (a) CS_2; (b) PM-*b*-$(PS_2)_2$: 4.0 mg·mL^{-1}; (c) PM-*b*-$(PS_2)_2$: 8.0 mg·mL^{-1}; (d) PM-*b*-$(PS_2)_2$: 17.0 mg·mL^{-1}; (e) PM-*b*-$(PS_1)_2$: 17.0 mg·mL^{-1}; (f) PM-*b*-$(PS_4)_2$: 17.0 mg·mL^{-1}

The porous films of PM-*b*-$(PS)_2$ copolymers were fabricated *via* a static breath-figure (BF) process. At first, water in a static humid environment (without air-flow) condensed onto the surface of the polymer solution in CS_2 due to significantly decreased temperature driven by rapid evaporation of solvent. Then, the water droplets arranged into a hexagonal array, sank into the polymer solution and were stabilized from coalescence by the precipitated PM-*b*-$(PS)_2$ at the water-solvent interface. Finally, the ordered porous film was formed after the totally evaporation of water droplets and CS_2 In this work, the influence of polymer molecular weight, solution concentration and enviromental temperature on the morphology of microporous films were investigated.

Porous films were fabricated by casting solution of PM-*b*-$(PS)_2$ star copolymers with different molecular weight in CS_2 (solution concentration=11.6 mg·mL^{-1}) onto clean glass substrate in a glass vessel with a cap at 22 ^{o}C and R. H. of 95%. SEM images of such porous films were shown in Fig. 6. The average pore size of PM-*b*-$(PS_1)_2$ (M_n=5,950 g·mol^{-1}. Entry 1 in Table 1) film is 1.64 μm (Fig.6(a)). While, a sharply decreased average pore size of 0.42 μm was observed in the case of PM-*b*-$(PS_4)_2$ (Entry 4 in Table 1) with higher M_n of 10,300 g·mol^{-1}. The decrease of copolymer's capability for stabilizing larger water droplets might be attributed to the smaller molar concentration of PM-*b*-$(PS_4)_2$ comparing with PM-*b*-$(PS_1)_2$ in the same weight concentration.

The hydrophobicity of porous PM-*b*-$(PS)_2$ film was characterized by determining static water-droplet contact angle on its surface. The porous PM-*b*-$(PS_4)_2$ film showed higher hydrophobicity (water-droplet contact angle=108°, Fig.6(b)) comparing with that of PM-*b*-$(PS_1)_2$ film (water-droplet contact angle=101°, Fig. 6(a)). The higher surface roughness of porous PM-*b*-$(PS_4)_2$ film, resulted by its smaller average pore size, might be the possible explanation for the above-mentioned phenomenon.

The environmental temperature of BF process also has an important influence on the morphology of porous films. In this work, a porous film with better regularity was formed at 22 ^{o}C (Fig. 6(c)) compared with that fabricated at 12 ^{o}C (Fig. 6(d)). The evaporation rate of CS_2 at 12 ^{o}C was slower than that at 22 ^{o}C. The condensed water droplets was slowly formed on the surface of solution and can't be stabilized efficiently by the slowly solidified copolymer's solution under slow evaporation of CS_2. So, the coalescence of some water droplets was formed and sank into copolymer's solution, resulting in the formation of porous film with irregular structures and larger pores (Fig. 6(d)) after the complete evaporation of water and CS_2.

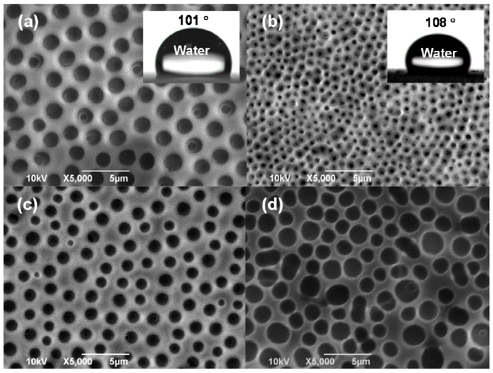

Fig.6 SEM images of PM-*b*-$(PS)_2$ star copolymers fabricated via a static BF procedure in CS_2 and R. H.=95%. (a) PM-*b*-$(PS_1)_2$: 11.6 mg·mL^{-1}, 22 $^{\circ}$C (inset: contact angle of water); (b) PM-*b*-$(PS_4)_2$: 11.6 mg·mL^{-1}, 22 $^{\circ}$C (inset: contact angle of water); (c) PM-*b*-$(PS_1)_2$: 16.6 mg·mL^{-1}, 22 $^{\circ}$C; (d) PM-*b*-$(PS_1)_2$: 16.6 mg·mL^{-1}, 12 $^{\circ}$C.

Electro-spinning/spraying are promising technologies to prepare fibers or paticles from polymer solutions or viscoelastic

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solutions based on high-voltage electrostatic repulsions. Recently, electrospun fibers or electrosprayed particles have emerged as exciting candidates for a wide range of applications in areas such as tissue engineering scaffolds, drug delivery materials and composite reinforcement, *etc.*[93-95]

In this work, PM-*b*-$(PS_5)_2$ solution in chloroform ($CHCl_3$) with concentration of 2.5 wt-% and the voltage of 11 kV were employed in the electrospinning process for the preliminary study. Figure 7 shows the morphologies of the electrosprayed PM-*b*-$(PS_5)_2$ particles with diameter of 16 μm (*ca.*). Interestingly, a wrinkle-like structure with nanopores (pore size= 100 nm (*ca.*)) on the surface was observed in the magnified SEM images (Fig.7(b) and 7(c)). The systematical study on the electrosprayed particles of PM-*b*-$(PS_5)_2$ star copolymer and the possible explanation for their special morphology was underwork.

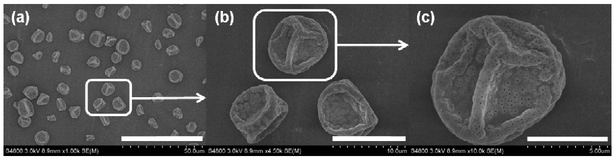

Fig.7 SEM images of PM-*b*-$(PS_5)_2$ electrosprayed particles using 2.5 wt-% $CHCl_3$ solution at voltage of 11 kV (Scale bar: (a) 50 μm; (b) 10 μm; (c) 5 μm).

Conclusions

By a strategy combining polyhomologation of ylides and ATRP, new well-defined polymethylene-based AB_2 star copolymers of PM-*b*-$(PS)_2$ (M_n=5 900-19 200 g·mol^{-1}, M_w/M_n=1.08-1.19) and PM-*b*-$(PMMA)_2$ (M_n=9 000-13 300 g·mol^{-1}, M_w/M_n=1.25-1.30) can be successfully synthesized for the first time. PM-*b*-$(PS)_2$ star copolymers can form micelles or aggregates in CS_2 which is solvent for PS segment and non-solvent for PM segment. Furthermore, they can be employed to fabricate hydrophobic (static water-droplet contact angle of *ca.* 108°) porous films with average pore sizes of 0.42-1.64 μm *via* a static breath-figure process by varying polymer molecular weight, solution concentration and environmental temperature. Interestingly, wrinkle-like PM-*b*-$(PS)_2$ particles (diameter of *ca.* 8 μm) with nanopores (pore size *ca.* 100 nm) on their surface can be achieved through electrospinning process. Further investigation on the formation of such particles is under way.

Acknowledgement

The authors greatly appreciate the financial support from the National Natural Science Foundation of China (No. 21074146, 21374130). Ping Lan thanks the financial supports from The Zhejiang Provincial Innovation Team of Science and Technology (No. 2012R10012-06) and The Science and Technology Program in Jiaxing City (No. 2012AY1024).

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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