

Patterning on Nonplanar Substrates: Flexible Honeycomb Films from a Range of Self-assembling Star Copolymers

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The effect of glass transition temperature, T_g , on the self-assembly of “honeycomb” microstructures on nonplanar substrates was probed by the synthesis of a library of core cross-linked star polymers with different arm compositions. Star polymers based on poly(dimethyl siloxane), poly(ethyl acrylate), poly(methyl acrylate), poly(*tert*-butyl acrylate), and poly(methyl methacrylate) were synthesized by the “arm first” strategy using atom-transfer radical polymerization. Reaction conditions were optimized, and a series of high molecular weight star polymers were prepared in high yield. The glass transition temperature of the star polymers ranged from -123 to 100 °C which allowed the suitability for the formation of porous honeycomb-like films via the “breath figure” technique on nonplanar surfaces to be investigated. All star compositions successfully formed ordered films on flat surfaces. However, only star polymer compositions with a T_g below 48 °C could form homogeneous honeycomb coatings on the surface of nonplanar substrates.

Introduction

The patterning of polymeric thin films on flat substrates is a widely used and critically important technique in many industrial processes.¹ However, the conformal formation of highly ordered patterned films on nonplanar substrates is significantly less developed, even though these systems may pave the way for a new class of materials and microstructures. These films could be utilized in specialized separation and high technological applications, for example, biosensors,² membranes,³ tissue engineering,^{4,5} microreactors,⁶ photonic band gap,⁷ and optoelectronic devices.⁸

In the past, ordered porous materials have been made through assembled templates including colloidal particles,⁹ emulsion latex particles,¹⁰ rodlike polymers,¹¹ and block copolymer lithography.¹² The bulk materials are normally cross-linkable inorganic entities so that the organic templates can be removed by subsequent decomposition. However, traditional limitations of these procedures exist: these films are difficult to grow on curved surfaces.¹³ In fact, for many practical applications, films need to be prepared on substrates with cylindrical, spherical, or concave

surfaces and the development of strategies for the fabrication of porous films on curved surfaces will further expand the applicability of these ordered porous films.

The facile preparation of porous materials on nonplanar substrates, however, is not a trivial exercise.¹⁴ Usually, the strategy involves the formation of a porous material and its transfer onto a curved substrate. Recently, we reported the first example of the preparation of porous honeycomb-like films that could contour to the surface of nonplanar TEM grids.¹⁵ We adapted a simple and cheap technique, which utilizes water droplets as a template for a precipitating polymer, known as the “breath figure” (BF) technique. It was reported as early as 1911 that water droplets condense on surfaces in a hexagonal array.^{16,17} In 1994, Francois and co-workers reported a method which utilizes these water droplets to form a self-assembled highly ordered honeycomb film, by casting a polymer solution from a volatile solvent under a flow of humid air.¹⁸ In this process, water droplets condense as microspheres (breath figures) from the humid environment onto the polymer solution surface, initiated by the rapid evaporation of the solvent. These water droplets self-assemble into an ordered hexagonal pitch, induced in part, by convection currents. The polymer then precipitates around these ordered templates, stabilizing them from coalescence, and upon further evaporation, an ordered three-dimensional honeycomb structure is obtained.

Microporous polymer films with self-assembled honeycomb morphology produced by the BF method have distinct advantages; it is a simple, inexpensive process, the pore sizes of the film can be controlled by varying casting conditions,¹⁹ and removal of

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templates is not necessary. Similar films have been made from a variety of polymers: for example, rod-coil block copolymers,^{18,20} block copolymers,²¹ conjugated polymers,²² amphiphilic copolymers,²³ dendronized polymers,²⁴ star polymers,^{25–27} and core cross-linked star (CCS) polymers.^{15,28,29} This process has been the topic of a recent review.¹⁹

Usually, polymers with a high glass transition temperature (T_g) are used to make such films. This is because of the inherent mechanism of film formation—relying on the precipitation of the polymer around water—achieved easily by high T_g polymers. However, to make useful films capable of forming on curved or nonflat surfaces, a high T_g polymer system is too brittle, especially with such a high void volume. The extension of the BF technique that we have recently reported¹⁵ utilizes a CCS polymer with an ultralow T_g (−122 °C) based on poly(dimethyl siloxane) (PDMS). We presented the formation of homogeneous, honeycomb-like porous films on nonplanar TEM grids in a single step, without the need for transferring the film. Simply by casting of this low T_g star polymer solution in a humid environment, a porous material could be formed with a hierarchy of surface features, originating from the self-assembly of water droplets, and the pattern of the TEM grid. We have also extended this further to coat particulate surfaces with a PDMS star honeycomb coating.²⁹ However, for this process to be widely adapted and utilized in applied areas, a wide range of polymer compositions need to be capable of forming such unique, ordered structures. It is envisaged that a number of factors will influence the ability of a polymer to form these flexible honeycomb films such as T_g of the polymer, polymer architecture, mechanical properties of the polymer, polymer viscosity, and surface free energies between the polymer and substrate and between polymer and water droplets. We postulate that a combination of the architecture of the star polymer and the associated low T_g are critical features which enabled the replication on nonplanar substrates. To investigate this, herein, a range of star polymers with different compositions, and thus a range of T_g 's, were prepared. Star polymers were prepared by the “arm first” strategy utilizing atom-transfer radical polymerization (ATRP) with the synthesis optimized by systematically varying the reaction conditions. These optimized star formulations were then used to prepare honeycomb films by the BF technique. It was found that a range of star polymers—with their T_g below a critical value—were able to act as precursors for the fabrication of homogeneous honeycomb films on nonplanar substrates, demonstrating the versatility of this approach.

Experimental Section

Materials. All chemicals were purchased from Aldrich unless otherwise stated. Methyl acrylate (MA, 99%), ethyl acrylate (EA, 99%), *tert*-butyl acrylate (*t*BA, 98%), and methyl methacrylate

(MMA, 99%) were passed over an aluminum oxide (basic) column immediately prior to use. *N,N,N',N''*-Pentamethyldiethylenetriamine (PMDETA, 99%) was distilled from calcium hydride. Divinyl benzene (DVB, 80% mixture of isomers) and ethylene glycol dimethacrylate (EGDMA, 98%) monomers were washed three times with 5% sodium hydroxide solution and once with distilled water; the solutions were dried over $MgSO_4$, filtered, and distilled from calcium hydride. 2-(2'-Bromo-2'-methylpropanoyloxy)ethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate³⁰ was synthesized by a previously reported procedure. 2-Methyl bromopropionate (2-MBP, 97%), *p*-toluenesulfonyl chloride (TsCl, 99+%), 2-bromoisobutryl bromide (98%), 2,2'-bipyridine (bpy, 99+%), *p*-xylene (anhydrous, 99+%), anisole (anhydrous, 99+%), and copper(I) bromide (CuBr, 98%) were used without further purification. Monohydroxy-terminated poly(dimethyl siloxane) was purchased from Gelest and used without purification.

Methods. ¹H NMR spectra were measured on a Varian Unity Plus 400 spectrometer operating at 400 MHz. Spectra were run in deuterated chloroform using tetramethylsilane as a reference. Gel permeation chromatography (GPC) was performed on a Shimadzu system with a Wyatt DAWN DSP multiangle laser light scattering (MALLS) detector (690 nm, 30 mW) and a Wyatt OPTILAB EOS interferometric refractometer (690 nm). Tetrahydrofuran (THF) was used as the eluent with three Phenomenex phenogel columns (500, 10⁴, and 10⁶ Å porosity; 5 μm bead size) operated at 1 mL min^{−1} with the column temperature set at 30 °C. Astra software (Wyatt Technology Corp.) was used to process the data using known dn/dc values to determine the molecular weight or an assumption of 100% mass recovery of the polymer where the dn/dc value was unknown. Monomer conversion was determined by gas chromatography using a Shimadzu GC 17-A gas chromatograph equipped with a DB-5 capillary column (30 m, 5% phenylsiloxane) and coupled to a GCMS-QP5000 mass spectrometer (injection temperature, 250 °C; initial column temperature, 40 °C; final column temperature, 250 °C heated at 10 °C min^{−1}). Monomer conversions were calculated from standard response versus concentration curves generated using pure monomers. Scanning electron microscopy (SEM) was conducted on an XL 30 Philips Head SEM. Samples were coated with a gold coating using a Dynavac Mini Sputter Coater prior to imaging. Differential scanning calorimetry (DSC) was performed on a TA 2920 modulated DSC equipped with an LNCA cooling system. Measurements were repeated three times with data taken on the second run. The temperature range was varied according to the literature T_g value of the polymer being measured while the heating/cooling rate was kept constant at 10 °C min^{−1}.

Synthesis of Poly(methyl methacrylate) Macroinitiator. A mixture of methyl methacrylate (12.8 mL, 0.12 mol), CuBr (0.17 g, 1.20 mmol), PMDETA (0.25 mL, 1.20 mmol), and TsCl (0.51 g, 2.7 mmol) in *p*-xylene (17.20 mL) was added to a Schlenk flask and degassed by three freeze-pump-thaw cycles. The flask was then immersed in an oil bath at 80 °C and heated for 40 h. The reaction mixture was diluted with THF (100 mL) and precipitated into MeOH (2 L). The precipitate was collected by vacuum filtration and the precipitation repeated to afford PMMA macroinitiator as a white solid (55% yield, $M_n = 1.00 \times 10^4$ g mol^{−1}, PDI = 1.19).

General Procedure for the Synthesis of Core Cross-linked Star Poly(methyl methacrylate-co-divinyl benzene). A mixture of PMMA macroinitiator ($M_n = 1.00 \times 10^4$ g mol^{−1}, 620 mg, 0.062 mmol), EGDMA (0.18 mL, 0.93 mmol), CuCl (6.2 mg, 0.062 mmol), and bpy (29 mg, 0.19 mmol) in *p*-xylene (12.20 mL) was added to a Schlenk flask equipped with a magnetic stirrer. The mixture was degassed by three freeze-pump-thaw cycles and then heated to 100 °C at atmospheric pressure. After 40 h a sample was taken from the reaction mixture and analyzed directly by GC. The mixture was diluted with THF (20 mL), precipitated into MeOH (1 L), and collected by filtration to afford a colorless solid (SP1) which was analyzed by GPC-MALLS ($M_n = 5.69 \times 10^5$ g mol^{−1}, PDI = 1.23).

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Synthesis of Poly(*tert*-butyl acrylate) Macroinitiator. A mixture of *t*BA (15.00 mL, 113.6 mmol), CuBr (272 mg, 1.80 mmol), PMDETA (396 μ L, 1.80 mmol), and 2-MBP (211 μ L, 1.80 mmol) was added to a Schlenk flask and degassed by three freeze–pump–thaw cycles. The flask was then immersed in an oil bath at 60 °C and heated for 1 h. A sample of reaction mixture was taken for GC analysis. The reaction mixture was diluted with THF (100 mL), passed through a column of basic alumina and celite (4:1), concentrated, and precipitated into 50% methanol/water (2 L) at –15 °C. The precipitate was collected by vacuum filtration and the precipitation repeated to afford *t*PrBA macroinitiator as a white solid which was analyzed by GPC-MALLS (70% yield, $M_n = 1.05 \times 10^4$ g mol⁻¹, PDI = 1.19).

Optimized Conditions for the Synthesis of Core Cross-linked Star Poly(*tert*-butyl acrylate-co-divinyl benzene). A mixture of *t*PrBA macroinitiator ($M_n = 1.05 \times 10^4$ g mol⁻¹, 2.00 g, 0.20 mmol), DVB (252 μ L, 1.80 mmol), CuBr (29 mg, 0.20 mmol), and PMDETA (125 μ L, 0.60 mmol) in *p*-xylene (13.00 mL) was added to a Schlenk flask equipped with a magnetic stirrer. The mixture was degassed by three freeze–pump–thaw cycles and then heated to 100 °C at atmospheric pressure. After 40 h a sample was taken from the reaction mixture and analyzed directly by GC. The mixture was diluted with THF (100 mL), passed through a column of basic alumina and celite (4:1), concentrated, and precipitated into 50% methanol/water (1 L) at –15 °C and collected by filtration to afford a colorless solid (SP2), which was analyzed by GPC-MALLS ($M_n = 3.97 \times 10^5$ g mol⁻¹, PDI = 1.12).

Synthesis of Poly(methyl acrylate) Macroinitiator. A mixture of MA (15.69 mL, 0.15 mol), CuBr (166 mg, 1.10 mmol), PMDETA (484 μ L, 2.3 mmol), and 2-(2-bromo-2-methylpropanoyloxy)ethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (430 mg, 1.10 mmol) was added to a Schlenk flask and degassed by three freeze–pump–thaw cycles. The flask was then immersed in an oil bath at 80 °C and heated for 4 h. The reaction mixture was diluted with THF (100 mL), passed through a column of basic alumina and celite (4:1), and precipitated into methanol. The precipitate was collected by vacuum filtration and analyzed by GPC-MALLS (67% yield, $M_n = 7.00 \times 10^3$ g mol⁻¹, PDI = 1.10).

Optimized Conditions for the Synthesis of Core Cross-linked Star Poly(methyl acrylate-co-divinyl benzene). A mixture of PMA macroinitiator ($M_n = 7.00 \times 10^3$ g mol⁻¹, 300 mg, 0.04 mmol), DVB (91.5 μ L, 0.60 mmol), CuBr (6.0 mg, 0.04 mmol), and PMDETA (20 μ L, 0.08 mmol) in anisole (2.50 mL) was added to a Schlenk flask equipped with a magnetic stirrer. The mixture was degassed by three freeze–pump–thaw cycles and then heated to 100 °C at atmospheric pressure. After 40 h a sample was taken from the reaction mixture and analyzed directly by GC. The mixture was diluted with THF (100 mL), passed through a column of basic alumina and celite (4:1), concentrated, and precipitated into cold methanol (250 mL) and collected by filtration to afford a colorless solid (SP3), which was analyzed by GPC-MALLS ($M_n = 3.80 \times 10^5$ g mol⁻¹, PDI = 1.23).

Synthesis of Poly(ethyl acrylate) Macroinitiator. A mixture of EA (16.30 mL, 0.15 mol), CuBr (143 mg, 1.00 mmol), PMDETA (417 μ L, 2.00 mmol), and 2-(2-bromo-2-methylpropanoyloxy)ethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (370 mg, 1.00 mmol) was added to a Schlenk flask and degassed by three freeze–pump–thaw cycles. The flask was then immersed in an oil bath at 80 °C and heated for 4 h. The reaction mixture was diluted with THF (100 mL), passed through a column of basic alumina and celite (4:1), dried under reduced pressure, and analyzed by GPC-MALLS (70% yield, $M_n = 7.00 \times 10^3$ g mol⁻¹, PDI = 1.14).

Optimized Conditions for the Synthesis of Core Cross-linked Star Poly(ethyl acrylate-co-divinyl benzene). A mixture of PEA macroinitiator ($M_n = 7.00 \times 10^3$ g mol⁻¹, 300 mg, 0.04 mmol), DVB (91.5 μ L, 0.60 mmol), CuBr (6.0 mg, 0.04 mmol), and PMDETA (20 μ L, 0.08 mmol) in anisole (2.14 mL) was added to a Schlenk flask equipped with a magnetic stirrer. The mixture was degassed by three freeze–pump–thaw cycles and then heated to 100 °C at atmospheric pressure. After 40 h a sample was taken from the reaction mixture and analyzed directly by GC. The mixture was

diluted with THF (100 mL), passed through a column of basic alumina and celite (4:1), concentrated, precipitated into cold methanol (250 mL), and collected by filtration to afford a colorless solid (SP4), which was analyzed by GPC-MALLS ($M_n = 4.70 \times 10^5$ g mol⁻¹, PDI = 1.20).

Synthesis of Poly(dimethyl siloxane) Macroinitiator. Mono-hydroxy-terminated poly(dimethyl siloxane) ($M_n = 1.05 \times 10^4$ g mol⁻¹, PDI = 1.60, 20.0 g, 2.0 mmol) was dissolved in 400 mL of dry THF and triethylamine (2.78 mL, 20.0 mmol) was added to the mixture followed by 2-bromoisobutyryl bromide (1.24 mL, 10.0 mmol). The reaction mixture was kept at 0 °C for 3 h and then left overnight. The volatiles were taken off by rotary evaporation and the resultant yellow oil was redissolved in dichloromethane and washed with saturated hydrogen carbonate solution. The organic layer was dried over MgSO₄ and filtered, and the solvent was removed to afford a colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ 0.00 (m, 6H), 0.52 (m, 4H), 1.28 (m, 4H), 1.58 (m, 2H), 1.92 (s, 6H), 3.42 (t, 2H), 3.72 (t, 2H).

Optimized Conditions for the Synthesis of Core Cross-linked Star Poly(dimethyl siloxane-co-divinyl benzene). A mixture of PDMS macroinitiator ($M_n = 1.05 \times 10^4$ g mol⁻¹, 2.00 g, 0.19 mmol), DVB (312 μ L, 2.40 mmol), CuBr (28.6 mg, 0.20 mmol), and PMDETA (125 μ L, 0.6 mmol) in anisole (5.00 mL) was added to a Schlenk flask equipped with a magnetic stirrer. The mixture was degassed by three freeze–pump–thaw cycles and then heated to 100 °C at atmospheric pressure. After 40 h a sample was taken from the reaction mixture and analyzed directly by GC to check DVB conversion. The mixture was then diluted with THF (5 mL), precipitated into MeOH (500 mL) twice, and collected by filtration to afford an off-white solid (SP5), which was analyzed by GPC-MALLS ($M_n = 8.90 \times 10^5$ g mol⁻¹, PDI = 1.30).

Preparation of Honeycomb Materials. Humid air was generated by the mixing of wet and dry air with humidity controlled through variation of the mixing ratio as described previously.³¹ A TEM grid was placed on a glass cover slip; a drop (20 μ L) of star-polymer (10 g/L)/benzene solution was cast onto this grid. A humidified flow (70% R.H. @ 25 °C) of air was directed onto these samples at a rate of 3 L min⁻¹.

Results and Discussion

It is well-documented that the T_g of polymers is generally affected by three factors: (1) the inherent flexibilities/backbone bond rotation barriers of their individual chains, (2) the size or steric bulk of their side chains, and (3) the interactions (steric, dipolar, and hydrogen bonding) between chains.³² In general, anything that restricts the rotation should increase the T_g of the polymer. In this work, we take advantage of this generalization by synthesizing star polymers based on PDMS. The bond angle and bond length of Si–O (130° and 1.63 Å, respectively) are greater than a C–C bond (112° and 1.54 Å, respectively). Therefore, polymer chains based on Si–O bonds have backbones that are extremely flexible, and hence, PDMS polymers have an extremely low T_g .³³ Conversely, PMMA with the tertiary carbon in the backbone adds stiffness to the polymer chain and increases the T_g . In this work, CCS polymers with differing backbone stiffness (PDMS and PMMA) will be synthesized to prepare star polymers with varying T_g values.

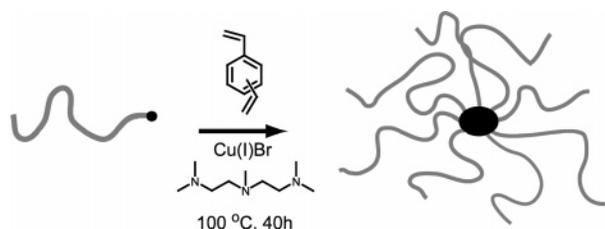
Changing the pendant group of polyacrylates is another way to tune the T_g . It has been well-established that when the length of the pendant group is increased, a decrease in T_g occurs until a threshold point, at which, with a further chain increase, the T_g then begins to rise. This is attributed to a plasticization effect of

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Scheme 1. Synthesis of Core Cross-linked Star (CCS) Polymers



the side chains.³⁴ In addition, by introduction of branched substituents, a markedly different trend is observed. The branched side chains cannot induce plasticization, and hence only increase the stiffness in the chain; therefore, higher T_g values are reported.³⁵ Both of these trends (plasticization effect and bulky pendant groups) are also utilized to synthesize star polyacrylates (PEA, PMA, and PtBA) with varying T_g values.

Preparation of Core Cross-linked Star Polymers with Varying Glass Transition Temperatures. The “arm first” technique was used to synthesize a series of CCS polymers with a range of T_g 's. This technique involves the preparation of a dormant linear chain by living free radical polymerization, which is consequently reacted with a divinyl monomer, forming a star structure (Scheme 1). CCS polymers consist of a highly cross-linked core and linear chains emanating from this core. These structures have been synthesized by living radical polymerization techniques, including nitroxide-mediated radical polymerization,³⁶ atom-transfer radical polymerization (ATRP),³⁷ and reversible addition-fragmentation chain-transfer polymerization.^{38,26}

Poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), poly(*tert*-butyl acrylate) (PtBA), and poly(ethyl acrylate) (PEA) star polymers were all synthesized in two steps via ATRP; an alkyl halide was used to initiate homopolymerization, and the macroinitiators (MI) were then isolated and reacted with divinyl benzene under ATRP conditions (Scheme 1). Poly(dimethyl siloxane) star polymer was made in a similar fashion; however, the homopolymer (monohydroxyl functional) was purchased from Gelest and reacted with 2-bromoisobutyl bromide to form a MI capable of initiating polymerization by ATRP.³⁹

The formation of linear polymers PEA, PMA, PtBA, and PMMA all showed living/controlled characteristics. Good control over the polymerization was achieved with very narrow distributed polymers being prepared over a range of molecular weights (for full details see Supporting Information).

The star formation conditions were optimized by varying the initial concentration of the macroinitiator $[MI]_0$ and the ratio of

MI to cross-linker (r_0). Both effects were found to significantly alter the star structures formed (see Supporting Information for optimization experiments). Figure 1 summarizes these two factors. As the initial concentration of the macroinitiator, $[MI]_0$, was increased, the molecular weight of the star increased. This may be attributed to the greater probability of the “arms” coming into contact with another star species in the more concentrated solution; therefore, more “arms” are attached to the final star, resulting in an increased molecular weight. The second is the influence of cross-linker stoichiometry relative to the macroinitiator, r_0 . As r_0 was increased, the number of arms and hence the molecular weight increased. This could be due to the fact that more cross-linker ensures the growth of a larger core, enabling more arms to link to the core structure, resulting in an increase in the molecular weight. However, there is a limitation for r_0 as when this ratio approaches high values, gelation can occur.

The discussion above is related only to the star structure formed (i.e., ignoring the linear component) and does not discuss the overall yield of the star polymer. In all experiments there is some unconverted linear component remaining; however, unlike a previous report,⁴⁰ no specific trends were observed relating r_0 or $[MI]_0$ to the yield of star polymer. All systems were optimized in terms of star yield and as a result all star polymers were obtained in above 70% yield and in most cases above 80%. For the preparation of honeycomb materials these mixtures do not need to be separated.^{28,26} In fact, the removal of the linear component can increase the brittleness of such films.²⁸ For this reason, the star/linear mixtures were used in the following sections of this manuscript. Table 1 summarizes the conditions and characterization data for the CCS polymers produced in “optimized” conditions. All polymers reached a molecular weight more than $2.50 \times 10^5 \text{ g mol}^{-1}$ with arm numbers greater than 19. These polymers were used in the subsequent sections of this manuscript to study their film-forming behavior.

Differential scanning calorimetry (DSC) was used to investigate the T_g values of the optimized star mixtures, as synthesized above. Each sample was heated and cooled at a rate of $10 \text{ }^\circ\text{C/min}$ and this was repeated three times. The T_g data were taken on the second run; Figure 2 displays the data and Table 1 summarizes the results. These results show that a range of star polymers with extremely different T_g values have been synthesized.

The T_g values reported here displayed the expected trends.^{34,41} We have utilized two distinct strategies to prepare star polymers with a range of T_g values. (1) Changing the polymer backbone: the PDMS star (SP5) showed an ultralow T_g ($-123 \text{ }^\circ\text{C}$) attributed to the extremely flexible Si–O main-chain bonds. The PMMA star (SP1) displayed a high T_g ($100 \text{ }^\circ\text{C}$) because of the methyl group on the main chain giving rise to a “stiffer” polymer. (2) Tuning the pendant group: increasing the side group of the polyacrylate stars from a methyl (SP3) to an ethyl group (SP4) decreased the T_g from 2 to $-30 \text{ }^\circ\text{C}$ because of a plasticization effect. When the pendant group was increased further to a branched *tert*-butyl group (SP2), the T_g increased to $48 \text{ }^\circ\text{C}$ as a result of the inherent stiffness the bulky *tert*-butyl group gives to the polymer chain.

All star polymers displayed only one transition, which were in accordance with literature values for the linear analogs of the arms. No glass transitions were observed from the core of the star molecule, possibly due to its rigid structure and small contribution to the overall mass (<25%).

Formation of Honeycomb Films from Star Polymers: Flat Surfaces. All star polymers (SP1–5) were tested under standard

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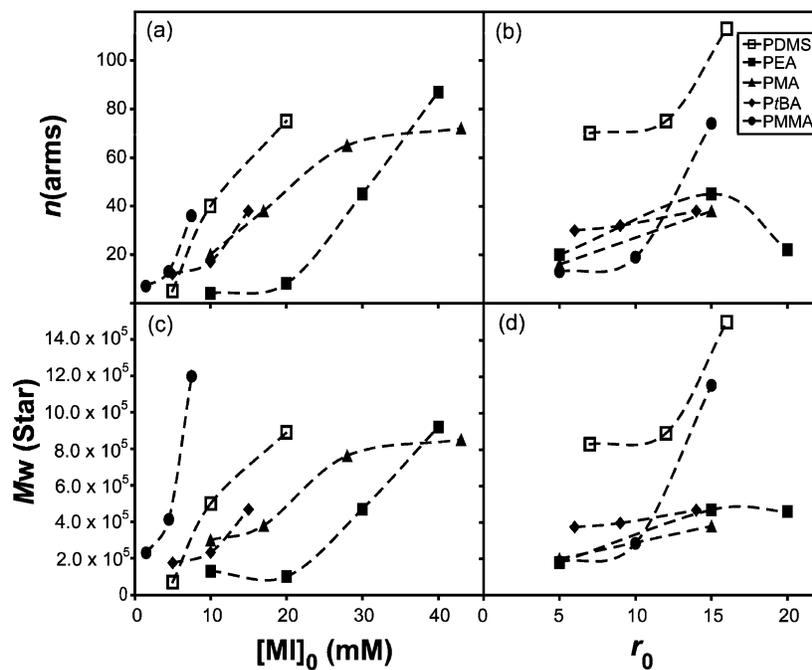


Figure 1. Summary of the effect of reaction conditions on the star structures formed with different arm compositions: (a) effect of macroinitiator concentration ($[MI]_0$) on the number of arms per star, (b) effect of cross-linker added (relative to MI) (r_0) on the number of arms per star, (c) effect of macroinitiator concentration ($[MI]_0$) on the molecular weight of the star, and (d) effect of cross-linker added (relative to MI) (r_0) on the molecular weight of the star. Poly(dimethyl siloxane) (PDMS), open squares; poly(ethyl acrylate) (PEA), closed squares; poly(methyl acrylate) (PMA), closed triangles; poly(*tert*-butyl acrylate) (PtBA), closed diamonds; and poly(methyl methacrylate) (PMMA), closed circles.

Table 1. Summary of Star Synthesis^a Demonstrating Varying Glass Transition Temperatures

linear macroinitiator (MI)		core cross-linked star polymer							
entry	repeat unit	M_n^c ($g\ mol^{-1}$)	$[MI]_0^d$ (mM)	r_0^e	M_w^c ($g\ mol^{-1}$)	PDI ^c	no arms ^f	arm conv. ^g (%)	T_g^h (°C)
SP1	methyl methacrylate ^b	1.05×10^4	5	15	5.69×10^5	1.23	29	84	100
SP2	<i>tert</i> -butyl acrylate	1.05×10^4	15	9	3.97×10^5	1.12	32	85	48
SP3	methyl acrylate	7.00×10^3	17	15	3.80×10^5	1.23	38	72	2
SP4	ethyl acrylate	7.00×10^3	20	15	2.80×10^5	1.14	29	76	-30
SP5	dimethyl siloxane	1.05×10^4	20	12	2.55×10^5	1.30	19	90	-123

^a Reaction conditions: $[MI]_0 = [CuBr]_0 = [PMDTA]_0/2$ and divinyl benzene in anisole heated at 100 °C for 40 h. ^b Reaction conditions: $[PMMA]_0 = [CuBr]_0 = [bpy]_0/3$ and ethylene glycol dimethacrylate in *p*-xylene heated at 100 °C for 40 h. ^c Polydispersity (PDI) and weight average molecular weights (M_w) were measured by gel permeation chromatography equipped with multiangle laser light scattering (GPC-MALLS). ^d $[MI]_0$ = overall initial concentration of macroinitiator (MI). ^e r_0 = initial molar ratio of cross-linker to MI. ^f Number of arms calculated from the formula = $Wf_{arms} \cdot M_{w,star} / M_{w,arms}$. ^g Calculated based on the integration from GPC concentration detector (DRI), arm conv. = $Wf_{arms} \cdot A_1 / (A_1 + A_2)$, where A_1 is the area corresponding to star polymer, A_2 is the area corresponding to the remaining linear polymer, and Wf_{arms} is the weight fraction of arms in CCS polymer. ^h Determined by differential scanning calorimetry (DSC).

breath figure conditions. Aliquots (20 μ L) were cast onto glass cover slips from benzene solutions (10 mg/mL) and evaporated under a flow of humid air (3 L min^{-1} ; 70% R.H.). Scanning electron micrographs of the resulting honeycomb films are displayed in Figure 3. All star polymers were able to form honeycomb structures with PEA (Figure 3b) and PtBA (Figure 3d) showing a slightly irregular pattern. The PMMA-based honeycomb showed a high level of cracking throughout the film, although the packing of pores showed regions of high order (Figure 3e). The other films, cast from the low T_g star polymers, showed more homogeneous films with much less cracking. None of the original linear precursors was able to form stable, ordered porous structures. When the PDMS linear polymer was cast under the same conditions as above, no evidence of water precipitation was observed (i.e., the solution did not turn opaque). The film was analyzed by light microscopy and a featureless, transparent film was observed. The three acrylate linear precursors (PtBA, PEA, and PMA) were also cast as linear precursors; these polymers showed evidence of precipitation (i.e., initially an

opaque surface was observed). However, extremely disordered pores were observed and the films had become transparent and lost their features with time. This result was similar to a recent report of a low T_g dendrimer that formed porous films but also lost its structure with time.⁴² The linear PMMA precursor formed stable porous films under BF conditions, however, with no regularity in porous structure. We have found this to be consistent with our previous results;²⁸ without the star structure in the casting mixture, ordered honeycomb films could not be prepared.

Formation of Honeycomb Films from Star Polymers: Nonplanar Surfaces. This series of CCS polymers were then used for the preparation of porous materials with two levels of ordered surface features as developed previously.¹⁵ TEM grids were placed on the surface of glass cover slips, and a solution of star polymer (10 mg mL^{-1}) in benzene was cast onto this grid, and a humid flow (3 L min^{-1} ; 70% R.H) was directed onto the

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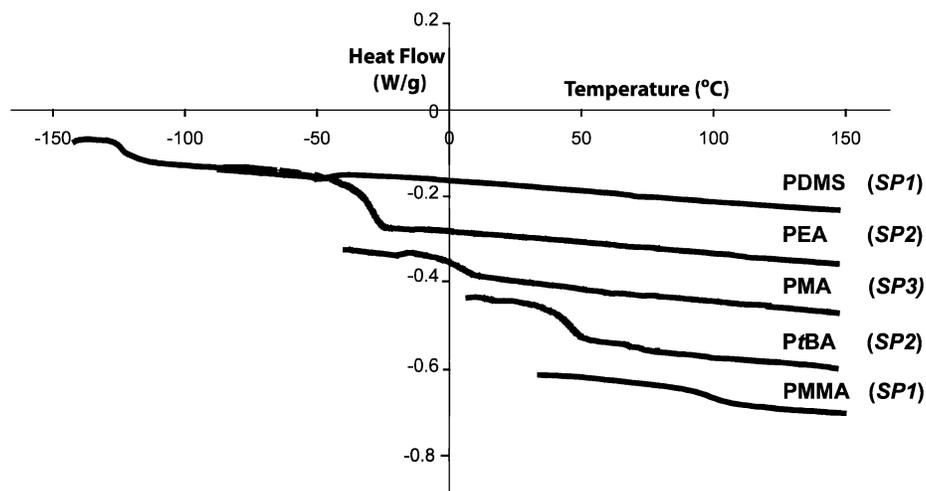


Figure 2. Differential scanning calorimetry results of star polymers displaying different glass transition temperatures (T_g): poly(methyl methacrylate)-based CCS polymer (PMMA, **SP1**) $T_g = 100$ °C, poly(*tert*-butyl acrylate)-based CCS polymer (PtBA, **SP2**, $T_g = 48$ °C), poly(methyl acrylate)-based CCS polymer (PMA, **SP3**, $T_g = 2$ °C), poly(ethyl acrylate)-based CCS polymer (PEA, **SP4**, $T_g = -30$ °C), and poly(dimethyl siloxane)-based CCS polymer (PDMS, **SP5**, $T_g = -123$ °C).

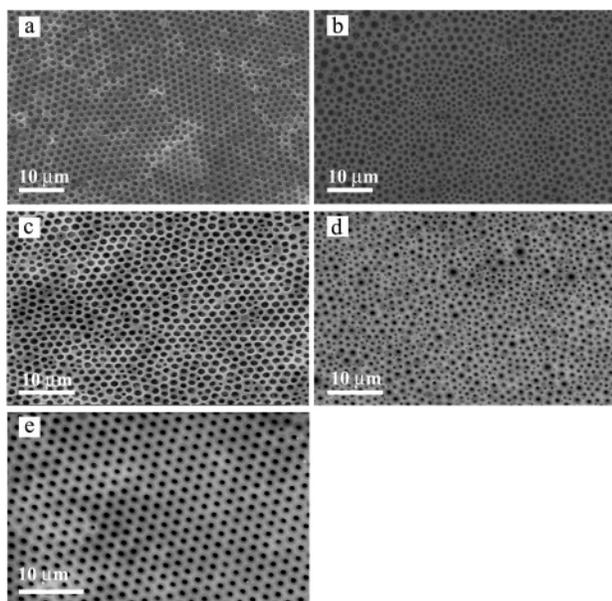


Figure 3. Scanning electron micrographs of honeycomb materials formed from different star polymers: (a) poly(dimethyl siloxane) (**SP5**); (b) poly(ethyl acrylate) (**SP4**); (c) poly(methyl acrylate) (**SP3**); (d) poly(*tert*-butyl acrylate) (**SP2**); and (e) poly(methyl methacrylate) (**SP1**).

surface. The structures formed were then analyzed by SEM. Figure 4 shows the scanning electron micrographs of the structures obtained. Films cast from PDMS, PEA, PMA, and PtBA (Figures 4a–4d) all showed that they can conform to the nonplanar surface while still displaying the ordered porous structure, with importantly little to no cracking. This result was somewhat surprising, showing that star polymers with T_g as high as 48 °C can show enough “fluid-like” character to conform to the surface of the TEM grids. The CCS polymer with PMMA arms (**SP1**), with a higher T_g ($T_g = 100$ °C, Figure 4e), was the only system that has shown to be incompatible with this technique, displaying an ordered porous structure but a high amount of cracking, hence not replicating the TEM grid surface.

Figure 5 illustrates, schematically, how the process could occur. The star polymer solution is cast onto a nonplanar surface, in this instance a TEM grid (Figure 5a). This solution is exposed to a humid airflow, the rapid evaporation of the volatile solvent causes

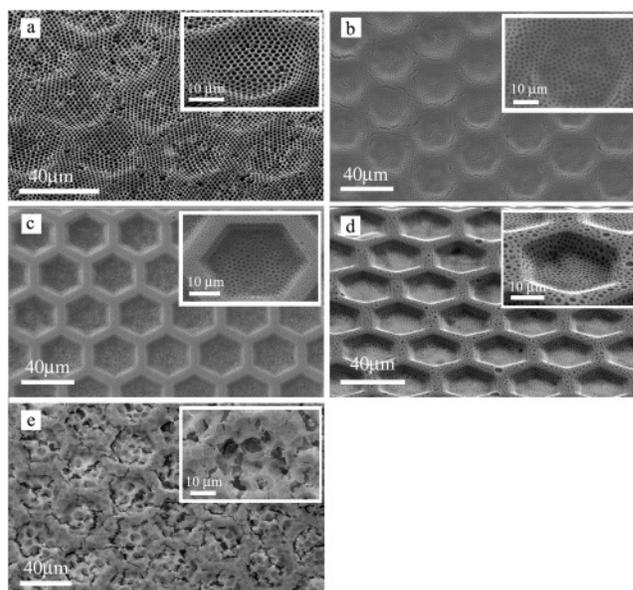


Figure 4. Scanning electron micrographs of honeycomb materials formed from different star polymers cast on to a TEM grid surface: (a) poly(dimethyl siloxane) (**SP5**); (b) poly(ethyl acrylate) (**SP4**); (c) poly(methyl acrylate) (**SP3**); (d) poly(*tert*-butyl acrylate) (**SP2**); and (e) poly(methyl methacrylate) (**SP1**).

a decrease in the surface temperature, and as a result water precipitates at the interface (Figure 5b). These droplets self-assemble, possibly due to convection currents and surface tension instabilities. The star polymer in the solution precipitates around these water droplets, stabilizing them from coalescence (Figure 5c). As more solvent evaporates, the formed honeycomb film makes contact with the surface of the TEM grid (Figure 5d). With complete evaporation of the solvent, the honeycomb film drapes across the surface, contouring to the nonplanar surface features (Figure 5e). It is envisaged that the surface free energy between the polymer and substrate may play an important role in promoting nonplanar honeycomb film formation. However, it is likely that the surface energy will be most influential in the formation of conformal films rather than in affecting the polymers ability to form homogeneous films on nonplanar surfaces. With a low surface energy between polymer and substrate, the film is likely to have better conformity than for a high surface energy between polymer and substrate.

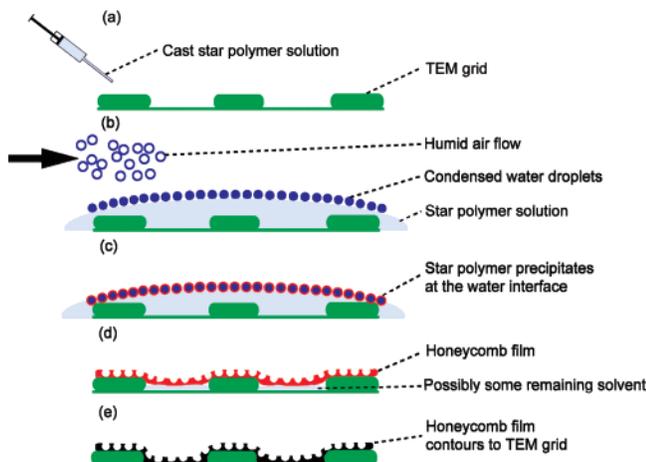


Figure 5. Schematic illustration of honeycomb film formation on nonplanar substrates. (a) A low T_g star polymer is cast onto the surface of a TEM grid. (b) A humid air flow is introduced; water droplets (breath figures) condense onto the cooled solution surface. (c) Star polymer in the solution precipitates around the water droplets. (d) As the solvent evaporates, the film comes into contact with the TEM grid. (e) After complete evaporation, the honeycomb film has contoured to the nonplanar surface because of the visco-elastic star polymer used.

This final step (Figure 5e) is where the extension of BF technique and the flexible nature of the star polymers with low T_g are demonstrated. The PMMA system, on the other hand, successfully formed honeycomb films, as evident from the porous structures in Figures 3e and 4e; however, the film cracked upon drying (Figure 4e). This system (PMMA based) is most likely successful in the initial steps, represented in Figure 5, up to Figure 5d, but fails at the final step (Figure 5e), whereas with the low T_g star polymers (below 48 °C), the film is able to deform and contour to the grid surface, without cracking the honeycomb film. Interestingly, these films are quite stable; we have tested a PDMS film over a period of 1 year and the porous structure remains. This polymer has a great balance of “fluid-like” and “solid-like” properties; the film is capable of contouring to nonplanar surfaces in the initial film formation, while forming stable porous structures over long time periods. It must be noted that this is a complex vitrification process; here, we have concentrated on the thermal properties of the polymer film. Other properties, such as viscosity of the evaporating polymer solution, the viscosity of the polymer film, and mechanical properties of the film may also prove to be important in the successful formation of flexible honeycomb films. It is apparent that the PMA star polymer (SP3) shown in Figure 4c produces by far the best structure and shows excellent conformity to the TEM grid. This polymer allows the film to conform to the surface without the underlying topography being lost, possibly due to relaxation of

the very low T_g films. This in fact may be a combination of optimal mechanical properties in conjunction with T_g and star architecture; this relationship is currently being investigated further.

Conclusions

We have synthesized a series of core cross-linked star polymers with varying T_g via the arm first technique utilizing ATRP. A series of experiments were conducted to optimize the star formation. We found that two reaction conditions, the initial macroinitiator concentration $[MI]_0$ and the stoichiometry of cross-linker (r_0) relative to the amount of MI, can considerably influence the star's formation. Increasing the $[MI]_0$, which also corresponds to an increase in cross-linker concentration, results in a star polymer with an increased number of arms, and hence a higher molecular weight. The relative amount of cross-linker to the macroinitiator (r_0) shows a similar effect whereby increasing (r_0) produces CCS polymers with a higher number of arms and higher molecular weights. Optimized conditions for star formation were established for five different arm compositions; these compositions were carefully chosen to prepare star polymers with a range of glass transition temperatures. High molecular weight star polymers, with T_g ranging from -123 to 100 °C were prepared in yields greater than 72%. All optimized star polymer formulations were shown to effectively form porous films with a honeycomb morphology by the BF technique. When honeycomb films were formed on the surface of TEM grids, star compositions with a T_g of 48 °C and below were able to conform to the nonplanar surface, effectively replicating the surface features of the grid. This work has greatly expanded the potential of honeycomb materials made by the BF technique, indicating a range of star polymers, prepared from common monomers, are capable of forming homogeneous films on nonplanar surfaces. Work is currently underway to prepare functional star polymers with low T_g values and to investigate their use as precursors for functional honeycomb films. This combination will create functionally addressable and flexible honeycomb films for applications such as biosensors. We envisage that these surfaces can be coated onto existing platforms, for example, microfluidic channels, enabling facile incorporation of a functional porous surface.

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Supporting Information Available: Detailed synthesis of linear macroinitiators and core cross-linked star (CCS) polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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