Arborescent Polystyrene via Ambient Temperature ATRP: Toward Ordered Honeycomb Microstructured Templates

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ABSTRACT: The arborescent polystyrene (APS) is used as a precursor to form ordered honeycomb-like microstructured template through self-assembly of water molecules at the air−solution interface via breath-figure mechanism. The APS is synthesized by successive cycles of functionalization (bromination) of polystyrene and grafting reactions via ambient temperature ATRP using the *graft-from-graft* approach. The resulting polymer film self-assembles to a micrometer-sized honeycomb-like arrangement. The morphology is investigated using AFM and SEM.

The application of self-assembled microstructures[1,2] depends critically on the feasibility of their fabrication. The conventional approach of constructing a pattern into the material[3−5] at the level of a micrometer requires expensive, complicated installations and offers insufficient control over the desired microstructures.[6−8] One of the simplest way of fabricating microstructure is by water evaporation technique, also known as "breath figure" mechanism.[9−13] This method (self-assembly) provides a divergent technique for the fabrication of periodic array structures. Literature search indicates that microporous thin films with honeycomb structure have attracted much attention due to their potential uses in sensors[14] and optical[15] and light emitting[16] applications. Several polymeric materials have been used to prepare honeycomb-like microstructured films through "breath figure" technique. This includes homopolymers,[12] block copolymers,[17−20] star polymers,[21,22] amphiphilic copolymers,[23−25] and conducting polymers.[26,27] The development of new synthetic routes should allow the design of specific molecular architectures such as arborescent polymeric materials, in which the rigidity of the polymeric chain versus flexibility can be tailored. A more rigid polymer chain can be used for the formation of well-organized assemblies that would organize like hard-spheres, which in turn can be used for the fabrication of devices at nanoscale.[24]

The progress in the synthesis of dendrite polymers, a class of highly branched polymers[28] containing multiple branches, continues to evoke interest. The dendrimeric building blocks are low molecular weight compounds and a number of steps are required to produce a material of high molecular weight. In particular, arborescent polymers[29−31] with a highly branched structure combine inherent features of dendrimers and star polymers. Arborescent polymers possessing high molecular weight can be obtained in fewer steps. The arborescent graft polymer (AGP) has been synthesized through anionic polymerization.[32] This complex macromolecules was obtained from successive functionalization and grafting reactions of the linear analog. Further functionalization and grafting cycles lead to generation of AGP (G2, G3 etc.). The disadvantage of this *graft-to-graft* strategy is that it leads to a mixture of graft copolymers along with the reactant and it is a tedious process to remove the AGP from the polymer mixture.[33,34] To overcome this disadvantage, the *graft-from-graft* approach is employed to develop a shorter pathway for the synthesis of arborescent polystyrene (APS) via ATRP, as represented in the Scheme 1.

The control of macromolecular architectures has received much attention in recent years. Atom transfer radical polymerization (ATRP) has been attracting increasing interest because of its adaptability to a wide range of functional monomers under less stringent experimental conditions.[35,36] As a controlled radical polymerization technique, ATRP facilitates the control over the molecular weight, macromolecular architecture, specific functionality and ability to synthesize novel materials.[37,38] The use of ATRP to design and obtain AGP has not been explored much.[39,40] The use of ambient temperature ATRP toward the synthesis of new polymeric materials has not been explored to a great depth despite its advantage in terms of lower propensity for side reaction.[41−44]

In this note, a new type of AGP, APS, composed of polystyrene (PS) was employed for the fabrication of ordered honeycomb-like microstructure through moist air flow. The novel APS is synthesized via ambient temperature ATRP, in conjunction with CuBr/PMDETA catalyst system through "*graft-from-graft*" process using polystyrene as the precursor. The APS were cast on glass substrates from various solvents to form films. The water molecules self-assemble onto these film leaving behind pores in the matrix of arborescent polymer. The ordered array of microstructure was investigated using AFM and SEM. This is the first report on the use of well defined dendigraft (AGP) toward the design of highly ordered honeycomb-like microporous films via breath figure mechanism.

A macroinitiator Br−C−PS, synthesized by the allylic bromination of polystyrene (**PS**) was employed for the successive grafting through "*graft-from-graft*" process, as shown in Scheme 1. The chemical structures and the synthetic route for **G1** AGP are shown in Scheme 2. The characterization data (GPC) for PS, PS-*graft*-PS (**G0**) and (PS-*graft*-PS)-*graft*-PS (**G1**) are shown in Table 1. At first, PS of $M_{n,SEC}$ = 14 000 (number average degree of polymerization ∼ 135) and PDI = 1.19 was synthesized by TEMPO. This was subjected to allylic bromination as reported in an earlier paper of ours.[44] A 7% (mol %; ^{1}H NMR) brominated polystyrene [Br−C−PS] was used in this study for grafting polystyrene. On the basis of the SEC and ^{1}H NMR analysis, the approximate composition of Br−C−PS is ∼9 repeat units of styrene with benzylic bromide functionality and 126 repeat units of unfunctionalized styrene repeat units. The PS-*graft*-PS (G0) obtained exhibited a $M_{n,SEC}$ = 47 800 and a PDI of 1.45. On the basis of the SEC data, it could be estimated that on an average 36 repeat units of styrene is present in each one of the 9 repeat units of the brominated PS (precursor to G0). The PS-*graft*-PS (G0) was subjected to allylic bromination. The stoichiometry of the reactants was such that an additional 7 mol % of allylic bromination (total) is achieved. This was followed by further graft polymerization of styrene. The (PS-*graft*-PS)-*graft*-PS (G1) obtained exhibited a $M_{n,SEC}$ = 85 000 and a PDI of 1.63 (Table 1). The PDI of G1 is higher in comparison with G0. This increase in PDI could be attributed to one of the following two reasons: (1) intramolecular radical−radical coupling reaction (Supporting Information) that could terminate some of the chains before complete

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Scheme 1. Generalized Scheme for the Synthesis of Arborescent Polystyrene through a "*Graft-from-Graft*" Approach

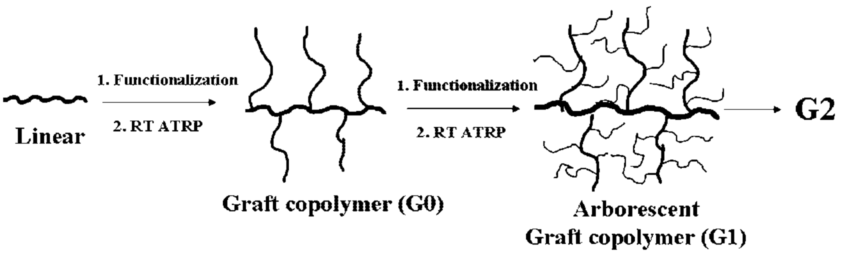
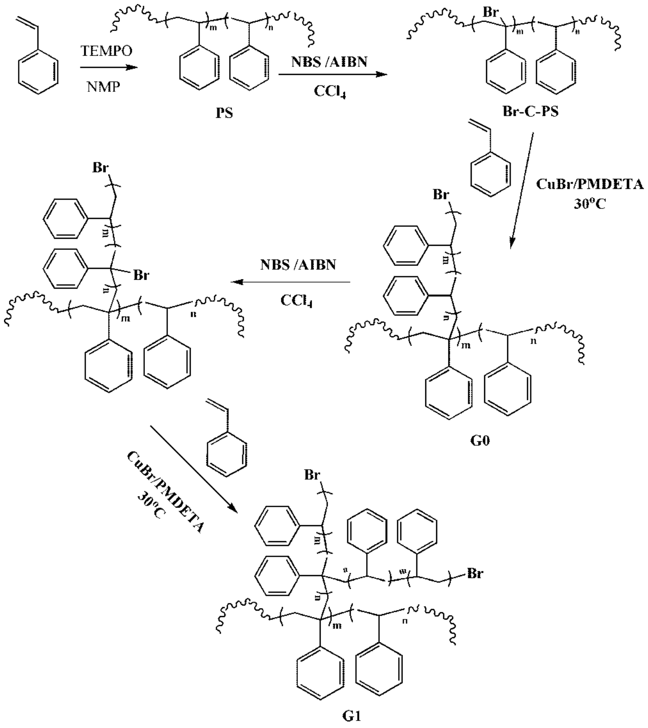


Table 1. Synthesis of APS (G1) by Successive Grafting of Styrene via Ambient Temperature ATRP[a]

entry	samples	reaction time	conversion	$M_{n,SEC}$	PDI	grafting yield (%)
1	PS			14 000	1.19	
2	PS-*graft*-PS (**G0**)	24 h	28.18	47 800	1.45	68.3
3	(PS-*graft*-PS)-*graft*-PS(**G1**)	15 h	33.12	85 000	1.63	83.4

[a] Entry 2: Br−C−PS:CuBr:PMEDTA:styrene (mole ratios) = 0.076:0.2731:0.2731:34.9; $M_{n,SEC}$ of Br−C−PS = 14 000 and mol % bromide = 7 (^{1}H NMR). Entry 3: Br−C−PS-*g*-PS:CuBr:PMEDTA:styrene (mole ratios) = 0.2783:1:1:127.8; $M_{n,SEC}$ of Br−C−PS-*graft*-PS = 47 800 and mol % bromide = 7 (from reaction stoichiometry); graft yield (% G) = $(W_g - W_0)/W_g \times 100$; $M_{n,SEC}$ = number average molecular weight obtained by SEC using narrow molecular weight PS standards; conversion calculated by gravimetric method; W_g is the mass of the graft copolymer; W_0 is the mass of the polymeric initiator.

Scheme 2. Synthetic Strategy Used for Arborescent Polystyrene (G1)



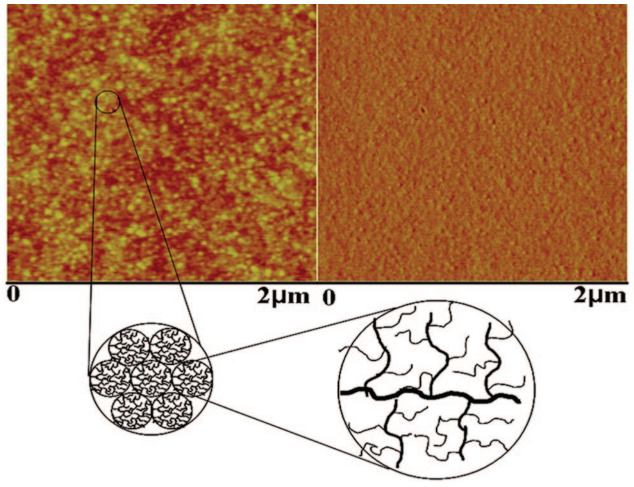


Figure 1. AFM image of the monolayer structure of arborescent polystyrene (G1), spun coated on mica: a spherical particle corresponds to individual molecules of M_n = 85 000 g/mol; PDI = 1.65; the extended picture (∼160 nm) shows the spherical morphology.

propagation; (2) poor initiation efficiency of the brominated polystyrene. It may be also be noted that the allylic bromination is not selective and hence it could take place with equal probability on the ∼325 repeat units of styrene introduced at the G0 stage as well as with the 126 repeat units of styrene that remain unfunctionalized in the initial stage (precursor for G0). Although an approximate number of styrene units per branching unit can be calculated from the SEC data no such attempt is being made here as this method of evaluating apparent molecular weight is inadequate and absolute molecular weight measurements are required to draw more meaningful conclusion. The grafting yield was estimated from the gravimetry by weighing the purified graft polymer recovered after precipitation (no fractionation). These results are shown in Table 1.

The topology of the dendigraft arborescent polystyrene (APS) was investigated by AFM. The use of AFM for investigating topology of arborescent polymers (AGS) has been reported.[45,46] Thus it has been show that films produced from G3 arborescent polymers display long-range ordering that is characteristic of hard spheres of uniform diameter. The tapping-mode AFM phase image of APS that was spun cast from THF solution is shown in Figure 1. This shows the presence of large spherical bumps that are probably caused due to the lateral ordering of the polymer chain. The spherical bumps were 200 nm in dimension, suggesting that they are probably aggregates[47,48] (extended picture of Figure 1). The AFM section analysis revealed that the bumps were 5 nm in height with lateral dimensions of approximately 100−200 nm, which is significantly larger than the dimension of a single PS chain. This indicated that the expanded conformation features were probably aggregates of single molecules. The shape persistence is due to high branching and is achieved here through arborescent polymer, synthesized via ambient temperature ATRP.

The APS was used for preparing films via a simple solution casting of the polymers on to a substrate, under moist air flow. In this method, under suitable conditions, the solvent evaporates;

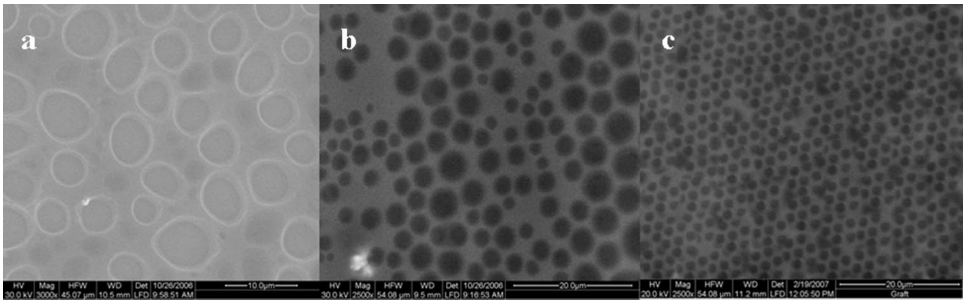


Figure 2. SEM pictures of disordered honeycomb-like structure formed from arborescent polystyrene (G1; 10 mg/mL): (a) THF; (b) DCM; (c) CS_2. Molecular weight of the AGP is 85 000 and PDI = 1.65.

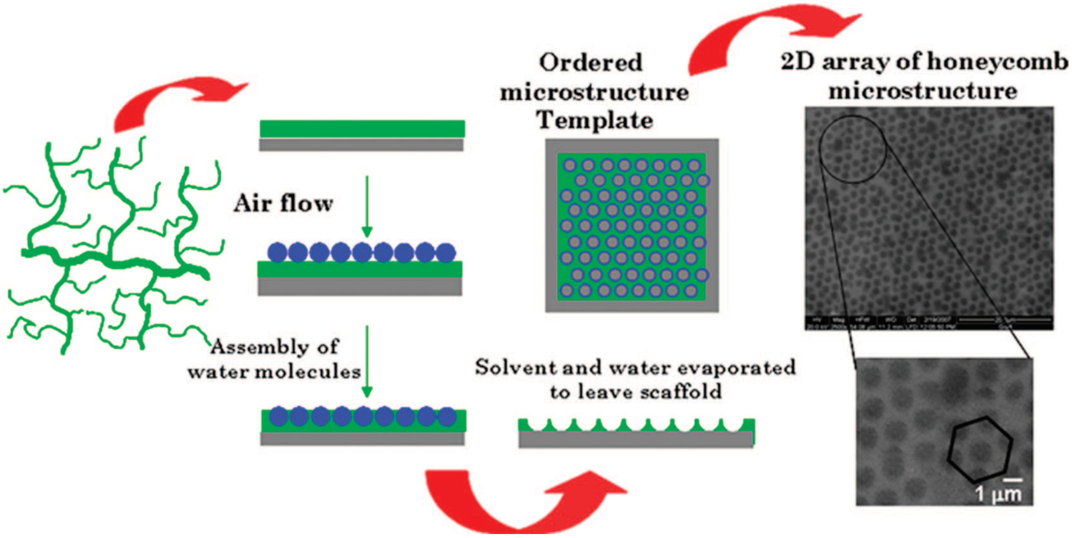


Figure 3. Schematic illustration of the self-assembly of water molecules to form ordered microstructure of arborescent polystyrene, resulting in honeycomb-like film formation on a planar substrate; solvent = carbon disulfide. The ordered arrangement is circled and expanded.

the film containing empty cells organize into ordered arrays leaving behind pores in the matrix of the polymer, commonly known as breath-figure mechanism. The water droplets that condense, act as the template around which the organization occurs. The APS (M_n = 85 000; 10 mg/mL) was dissolved in various solvents such as THF, CH_2Cl_2 and CS_2 and films were cast on microscopic glass slides for investigating template formation. An SEM image of a polymer film, obtained from THF, is shown in Figure 2a. This clearly reveals that the arrangement of the pores was into distorted ordered array. The pore size distribution is seen to vary from 5 to 8 μm. Regular pattern formation was not observed in THF, as it dissolves in water and forms bigger size pores. In contrast, the film formed from dichloromethane, showed somewhat regular patterns as depicted in the SEM image shown as Figure 2b. The bigger pores are due to the arrangement of water molecules on the already arranged array. The shape of the pore at the film surface was ellipsoidal. The pore size distribution was very broad because too many droplets condense onto the solution surface (due to rapid evaporation of the solvent). The morphology of these porous surfaces was found to be distorted and the size varied from 2 to 5 μm. It can be concluded that in dichloromethane this APS is capable of forming disordered homogeneous porous arrays on a planar surface.

The best microstructure formation was observed from CS_2 in contrast to the above observations made using THF and dichloromethane. The film formed from CS_2 was noticed to result in porous surfaces that showed an essentially homogeneous ordered array of microstructures, as shown in Figure 2c. The average diameter of pores was found to be 1.25 μm and the distance between adjacent pores (center of one pore to the center of the adjacent pore) was 0.65 μm. This observation demonstrates that an ordered array of a polymer in a typical honeycomb-like architecture can be formed using a simple and easy process. Thus a number of microstructures of various dimensions can be created by using various solvents, concentration of polymer solution and by adjusting the moist air-flow, as illustrated in Figure 3.

In conclusion, repetitive allylic bromination followed by ambient temperature ATRP grafting sequences can lead to the formation of well-defined arborescent polystyrene with a very compact globular structure. These arborescent graft copolymers synthesized via *graft-from-graft* techniques, at ambient temperature, can result in the formation of highly ordered honeycomb-like microstructures by a simple solution-casting method. This method allows for the rapid and simple fabrication of ordered arrays. Furthermore, control of the pattern can be varied by varying experimental conditions.

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Supporting Information Available: Text giving the experimental section and figures showing the SEC elution curves and an SEM image. This material is available free of charge via the Internet at http://pubs.acs.org.

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