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Porous Polymer Films and Honeycomb Structures Made by the Self-Organization of Well-Defined Macromolecular Structures Created by Living Radical Polymerization Techniques**

Martina H. Stenzel-Rosenbaum, Thomas P. Davis,* Anthony G. Fane, and Vicki Chen

Macroporous polymers have become materials of high interest in recent years, because of their potential applications in diverse areas from membranes to medical devices.[1] Star and block polymers are known to template around water droplets to form isoporous arrays.[2–5] However, the utilization of this discovery has been severely restricted because the synthetic route used, anionic polymerization, is difficult and limited to a small number of (generally nonfunctional) monomers. A number of other synthetic routes to star polymers have become available in recent years,[6] and the development of living radical polymerization provides a great opportunity to significantly broaden the range of functional materials. We have adopted both metal-mediated radical polymerization and reversible addition–fragmentation transfer (RAFT) polymerization to synthesize star polymers for application in isoporous film and honeycomb-structure production. The porous structures are created from casting solutions of star polymers in an organic solvent onto a glass substrate under a humid atmosphere as described by Francois and co-workers.[4, 7, 8]

The star polymers were synthesized either by metal-mediated polymerization using a copper (atom-transfer radical polymerization, ATRP) or an iron catalyst system or by RAFT polymerization. Both types of polymerization require a multifunctional initiator, from which arm growth occurs. The preparation of 6-arm polystyrene stars by the RAFT process utilized hexakis(thiobenzoylthiomethyl) benzene (**1**) as an initiator.[9] The polymerization process is shown in Scheme 1.[10] The pseudo first-order reaction kinetics and molecular-weight development were both found to be consistent with a living radical polymerization process. This RAFT method yielded narrow polydispersity polystyrene stars with molecular weights of up to 400 000, and six arms, each with a thioester end group. One complication in this process is the parallel synthesis of a linear chain along with the star structure (Scheme 1).

ATRP/metal-mediated polymerization was also utilized to synthesize stars. Two different approaches were taken, both based on the application of sugar initiators. The first approach we took was based on the work of Haddleton and co-workers

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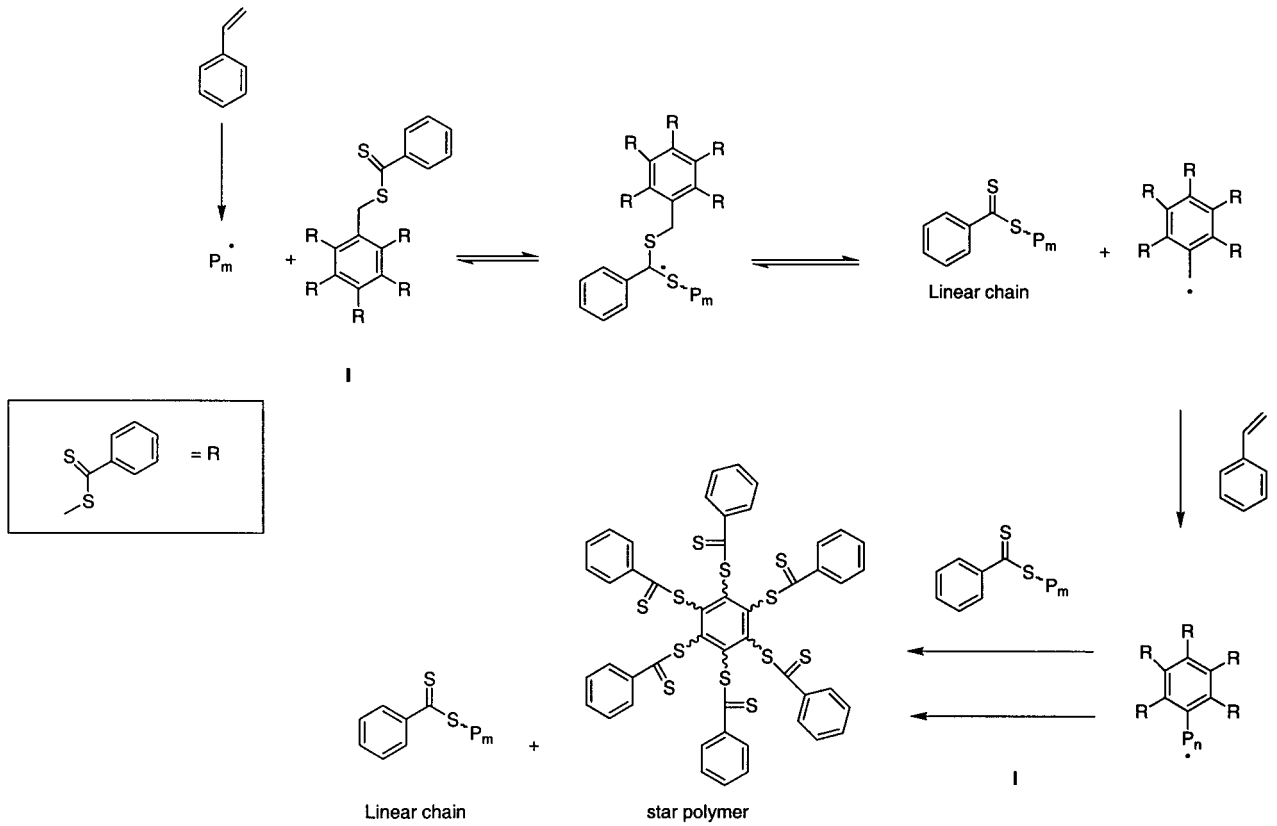
[**] We acknowledge a DAAD (German Academic Exchange Service) Scholarship (HSPIII) for Dr. M. H. Stenzel-Rosenbaum.

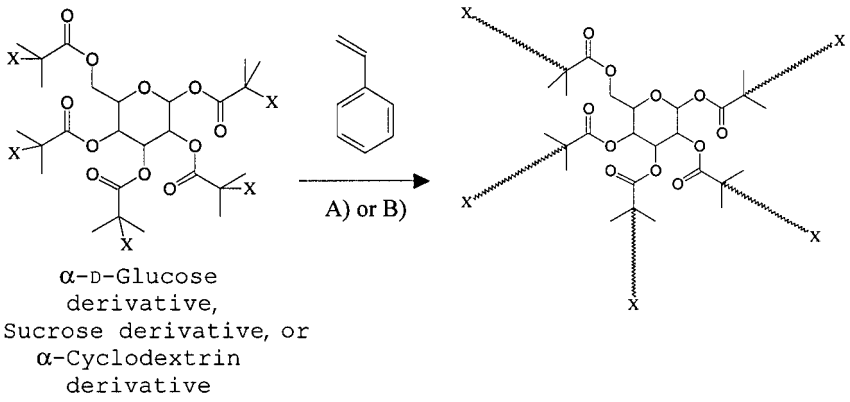
  1433-7851/01/4018-3428 $ 17.50+.50/0



Scheme 1. Star production using the RAFT process. The star synthesis is accompanied by a parallel linear arm synthesis. This is not necessarily a disadvantage in the production of porous films, as some linear-polymer inclusion is often found to be beneficial (see main text); P_m = linear polymer; P_n = single polymer star arm.

who developed a bromide containing initiator based on α-D-glucose[11] for the polymerization of styrene or methyl methacrylate in the presence of CuBr and *N*-propyl-2-pyridylmethanime (Scheme 2). The second approach was to utilize iron-mediated free-radical polymerization as pioneered by Sawamoto and co-workers[12–14] together with a multifunctional iodine-containing initiator based on sugar cores. Utilizing glucose, sucrose, and α-cyclodextrin in this way we prepared star polymers with 5, 8, and 18 arms, respectively,[15] (Scheme 2). In both approaches the kinetics and molecular-weight development were consistent with a living radical mechanism. The copper-based ATRP system proved more versatile and robust. However, we found the porous-film formation was very sensitive to residual copper/ligand and extensive purification was required to ensure reproducible film formation. In contrast, the iron-mediated system, whilst requiring more rigorous reaction conditions (it is also rather slow), necessitated much less purification of the star polymer product. The stars produced by an ATRP route have the advantage of facile end-group functionalization allowing us to produce functional porous films.

The preparation of the honeycomb-structured films seems to require a star polymer which is largely free of impurities (such as residual catalyst) to avoid disturbance of the film formation. The films were cast on a glass slide from a solution of the star polymer in carbon disulfide (10–20 mg L^{-1}) under humid conditions. The type of morphology we attained from a film cast from a polystyrene star polymer made by iron-catalyzed ATRP is shown in Figure 1. The five-arm polystyrene star had a molecular weight of 28000 and a polydispersity index (PDI) of 1.2. The film contains pores organized in a hexagonal array with a monodisperse pore size of ~1 micron. The surface of the porous film can easily be removed with adhesive tape to expose the honeycomb structure underneath (Figure 2). The pores are thought to originate by templating of the polymer stars



Scheme 2. Typical star structures made by ATRP techniques. A) X = Br, CuBr, *N*-propyl-2-pyridylmethanime, bulk, 90 °C. B) X = I, Ti(O-*i*Pr)$_4$, [CpFeI(CO)$_2$], toluene, 80 °C.

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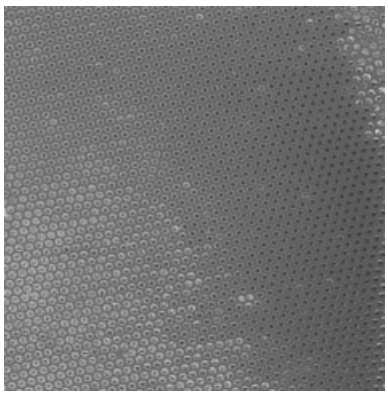

Figure 1. Scanning electron microscope (SEM) image of a porous film made from polystyrene stars. The pore size is approximately 1 micron in diameter.

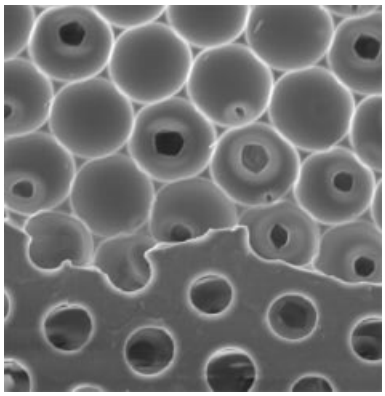

Figure 2. SEM image of the honeycomb structure of the porous film. The structure is revealed when the top layer is removed with adhesive tape.

around condensed water droplets. The precipitating star polymers stabilize the water droplets by forming a solid envelope allowing the self-organization of the stable water droplets in a hexagonal close packed array.[7, 8] It is clear that the molecular dimensions of the stars can directly affect the pore structure (Figure 3). The pore diameter can be altered in the range from 0.4 – 3 microns. The pore size is not only

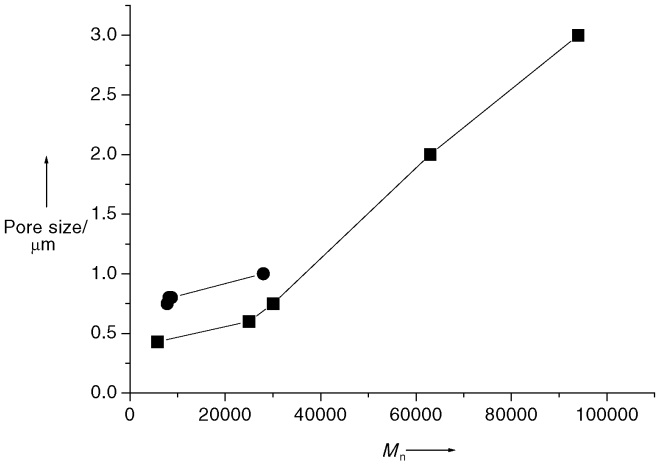

Figure 3. A plot showing the relationship between pore size and the molecular weight of the star arms. The ATRP stars have five arms, and the RAFT stars have six arms; ● ATRP, ■ RAFT.

controlled by the molecular weight of the polymer, but also by the number of arms and the nature of the end groups. This is a remarkable result as it clearly indicates that structure on the micron scale can be controlled by very small changes at the molecular level. The data in Figure 3 indicate that the polystyrene stars made by the RAFT process, with six arms and a thioester end group, form smaller pores than the five-arm polystyrene star of the same molecular weight made with iron-catalyst ATRP (iodine end groups). Confirmation that this observation cannot be solely attributed to the different arm configuration comes from a direct comparison of stars (10000 molecular weight, five arms) made by ATRP utilizing iodine and bromine initiators. Changing the end group from iodide to bromide decreased the film pore size from 750 nm to 650 nm. We also altered the bromine end groups by post-polymerization reaction with sodium pentadecafluoro-1-octanolate or sodium salicylate. The film pore diameters were again found to change to 450 nm (-$OC_8H_2F_{15}$) and 550 nm (-salicyl). The hexagonal honeycomb structure was not disrupted by these structural modifications to the star molecules. We have also observed that we can attain control over the porous morphology by controlling the number of arms grown from the star core, with an 18-arm star (molecular weight 10000, PDI 1.2) produced even smaller diameter pores of 250 nm. One major advantage of living radical polymerization is that it is very simple to synthesize block structures and thus broaden porous-film production to a whole range of functional substrates. To exemplify this we synthesized star-block copolymers of styrene and ethyl acrylate. We prepared stars starting with a polystyrene block, with the subsequent addition of an ethyl acrylate block (and vice versa). The porous-film structure cast from these star-block molecules is shown in Figure 4.

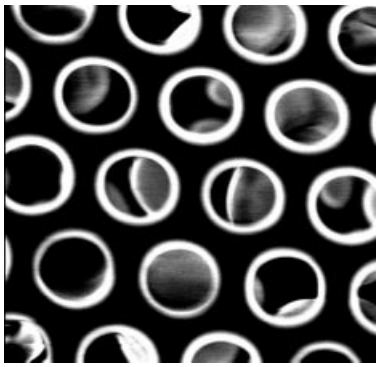

Figure 4. SEM image of a porous film cast from a polystyrene – ethyl acrylate star block. The molecular weight of the star block was measured to be 30000, with a polydispersity of 1.17. The arms consist of (approximately) a block of 50 styrene units followed by 20 ethyl acrylate units.

In our work we also found that it is possible to blend the star polymer with linear polymers, cast down the blend, and maintain highly structured films. We found that up to 30 wt % of narrow dispersity linear polystyrene can be added to the casting solution without any disturbance of the hexagonal orientation. If too much linear polymer is added then the organization of the pores is disrupted, ultimately leading to the disappearance of the pore structure altogether (Figure 5).

  1433-7851/01/4018-3430 $ 17.50+.50/0

The blending of star polymers with linear chains is in fact beneficial, we found that the addition of 20 wt% of linear polystyrene added to a polystyrene star leads to less brittle films and fewer defects during the film formation. The precise relationship between the star and linear polymers and the influence on the porous-film formation is highly dependent on the molecular weight and the chemical composition of the components. The blending process can be extended to mixtures of different polymers as a method of introducing functionality to the films. All of the polymer architectures we utilized and the nature of the resulting cast films are detailed in Table 1.

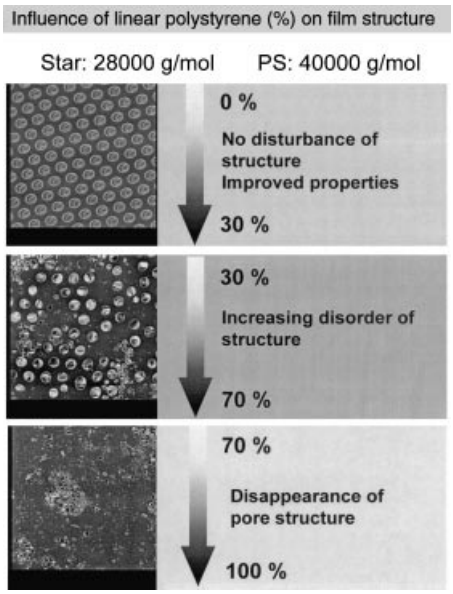

Figure 5. SEM micrographs of porous films made by adding linear polystyrene (PS) to a polystyrene star (five arm).

In summary, we have shown, that living radical polymerization techniques can be easily applied to the preparation of different star polymers. This is a facile approach to highly ordered porous materials with a monodisperse pore size, honeycomb morphology. We have demonstrated strong correlations between arm length, arm number, and end-group functionality with pore diameter. We have also shown that polymer blends can be used to improve the integrity of the films and as a way of introducing functionality into the materials.

Experimental Section

Initiators were prepared according to literature procedures for RAFT[9, 10] and ATRP.[11, 13, 15]

ATRP: A schlenk flask was charged with styrene (10 mL; with inhibitor removed), penta-*O*-isobutyryl bromide-α-D-glucose (173 mg), *N*-propyl-2-pyridylmethanime (291 mg), and CuBr (135 mg). The mixture was immediately degassed by three freeze–pump–thaw cycles and then purged with N_2 under a nitrogen atmosphere. The mixture was stirred continuously and kept in an isothermal oil bath at 90 °C. After 8 h, the polymerization reached a conversion of 50%. The reaction mixture was passed through a short alumina column and then precipitated in methanol or hexane.

A typical iron-catalyzed ATRP experiment was carried out with penta-*O*-isobutyryl iodo-α-D-glucose (100 mg), [$CpFeI(CO)_2$] (26.1 mg), titanium isopropoxide (245 mg), styrene (6 mL), and toluene (3 mL). A typical conversion after 50 h at 80 °C was 20%. The workup procedure was as described above. The star-block copolymers were synthesized by the same method. After the required reaction time, the mixture was cooled and excess styrene was distilled off under vacuum. The styrene star polymer was

Table 1. A summary of synthetic methods and physical properties.

Synthetic approach	Star structure/synthetic method	M_n	End group	Number of arms	Concentration of casting solution [g L^{-1}]	Pore diameter [μm]
metal-mediated/Fe	ref. [15]	4000	I	5	10	no pores
styrene		7800	I	5	10	0.75
80 or 100 °C in toluene	all based on a glucose core	8200	I	5	10	0.8
		9000	I	5	10	0.8
		28000	I	5	10	1.0
ATRP/Cu	glucose core	8000	Br	5	10	0.65
styrene	cyclodextrin core	10000	Br	18	10	0.25
90 °C in bulk	cyclodextrin core	15000	Br	18	10	0.34
ATRP/Cu	end-group modification of polymer with $M_n = 8000$ and Br end group					
styrene	reaction with $HOC_8H_2F_{15}$	8500	-$OC_8H_2F_{15}$	5	10	0.45
90 °C in bulk	reaction Na-salycilate	8500	-salycilate	5	10	0.53
RAFT	all based on a hexakis(thiobenzoyl thiomethyl)benzene core	6000	-S(C=S)Ph	6	10	0.43
styrene		25000	-S(C=S)Ph	6	10	0.6
100 °C in bulk		30000	-S(C=S)Ph	6	10	0.75
		68000	-S(C=S)Ph	6	10	2
		94000	-S(C=S)Ph	6	10	3
ATRP/Cu	glucose core	23000	Br	5	25	1.0
styrene/ethyl acrylate	50 styrene/5 ethyl acrylate units					
star-block copolymers	50 styrene/12 ethyl acrylate units	27000	Br	5	20	1.4
styrene star	50 styrene/20 ethyl acrylate units	30000	Br	5	23	1.0
90 °C in bulk, isolated then diluted with toluene and dissolved in ethyl acrylate						

  1433-7851/01/4018-3431 $ 17.50+.50/0

dissolved in toluene (5 mL) and ethyl acrylate (2.5 mL, inhibitor-free), followed by three freeze–pump–thaw cycles, prior to further chain-extension polymerization.

RAFT: RAFT polymerization was carried out in glass bottles. Hexakis-(thiobenzoylthiomethyl)benzene (50 mg) and styrene (10 mL) were mixed together and degassed by purging with nitrogen. The bottles were sealed and placed in an oil bath at 100 °C. In typical reaction conditions a conversion of 50% was attained after 75 h. The polymer was isolated by evaporation of the styrene.

Analyses: The stars were characterized by size exclusion chromatography and NMR spectroscopy. The porous films were analyzed by SEM. The molecular weights quoted in the paper were determined against linear polystyrene standards and are provided as an approximate guide to the true molecular weight.

Film casting: The films were prepared[4] from carbon disulfide solutions with a polymer concentration of 10 g L^{-1} (unless specified differently in Table 1). The solution was cast on a glass support and dried with a humid air (or nitrogen) flow at 22 °C. The casting process was carried out in a box at a humidity of 85%. The saturation of the air flow was achieved by bubbling the gas through a water reservoir. The air flow was measured with a flow meter to ensure reproducibility.

Received: March 14, 2001
Revised: June 27, 2001 [Z16719]

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Rapid Access to Diverse Arrays of Chiral 3,4-Diazaphospholanes**

Clark R. Landis,* Wiechang Jin, Jonathan S. Owen, and Thomas P. Clark

Chiral phosphine ligands are central to many developments in transition metal catalyzed enantioselective transformations.[1] Recent demonstrations of high enantioselectivity for a wide range of hydrogenation reactions with Rh complexes of DuPHOS,[2] PennPHOS,[3] RoPHOS,[4] BASPHOS,[5] CnrPHOS,[6] and related ligands highlight the unusual efficacy of rigid phosphacycles.[7] Other emerging trends in ligand design include the use of heterofunctional bidentate ligands,[8] implementation of attractive "secondary interactions" between complementary functional groups of the substrate and the catalyst periphery,[9] and the construction of large libraries of chiral phosphines for high-throughput catalyst screening.[10] All these strategies for the discovery of enantioselective catalysts can be accelerated by new synthetic methods for constructing cyclic phosphanes. We report a versatile synthetic route to a large number of new chiral diazaphospholanes that uses aldehydes, hydrazines, and primary phosphines as starting materials.

By analogy with P–C bond formation by means of the classic Mannich condensation[11] reaction, we reasoned that the condensation of primary phosphines with azines (R–CH=N–N=CH–R), prepared by the treatment of hydrazine with two equivalents of the corresponding aldehyde, would yield diazaphospholanes such as **1** (Scheme 1). This procedure yields a variety of 3,4-diazaphospholanes in good yields (25–95%) with *rac* selectivity under mild reaction conditions. All compounds were thoroughly characterized by using ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis, and in most cases, X-ray crystallography (Figure 1). To the best of our knowledge, the only previous report of 3,4-diazaphospholanes involved the stepwise condensation of formaldehyde and phenylphosphane, followed by ring closure with *N*,*N*′-dialkylhydrazines.[12]

The condensation of azines and primary phosphines with one equivalent of dry HCl as acid promoter renders simple 3,4-diazaphospholanes (**1**, **7**, **9**) upon workup. Acid chlorides function as both promoters and N-functionalization reagents to yield *N*,*N*′-dicarboxy-3,4-diazaphospholanes (**2**, **3**, **4**, **6**) directly in a one-step synthesis. The reaction of phenylphosphane with the azine derived from acetyl salicylaldehyde yields **5**, in which one of the salicyl acetyl groups is transferred to the hydrazine moiety. As exemplified by the transforma-

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[**] We thank the Department of Energy, Office of Basic Energy Sciences for financial support of this work. All crystal-structure determinations were performed by Dr. Doug Powell or Dr. Ilyea Guzei. The cone-angle measurements were made with the gracious assistance of Dr. David White of the UNC-Wilmington.

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