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Templating Organosilicate Vitrification Using Unimolecular Self-Organizing Polymers Prepared from Tandem Ring Opening and Atom Transfer Radical Polymerizations

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Summary: A unimolecular templating star-shaped polymer with a compatibilizing outer corona, prepared by tandem ROP/ATRP procedures, was dispersed into a thermosetting organosilicate. The organic polymer was thermalized to leave behind its latent image in the matrix with a pore size that reflected the size of the polymer molecule, and provided the expected reduction in dielectric constant.

Keywords: ATRP; nanoporosity; ROP; star-shaped polymer

Introduction

Historically, the semiconductor industry has been able to achieve a two-fold increase in microprocessor performance approximately every three years,[1] primarily achieved by a reduction in device dimension, driven by advances in microlithography allowing on-chip device densities to continue to increase. Even though feature dimensions are projected to decrease to 90 nm or less in the near future, this alone may not be sufficient to continue the historic performance improvements. Other innovative technologies and materials are required to maintain the expected performance enhancements at these dimensions and minimize deviation from the expected performance/density "treadmill." The switch to copper metallurgy,[2] silicon on insulator and silicon-germanium are examples of materials breakthroughs that have significantly bolstered performance.[3] This continual increase in device and wiring densities has therefore placed increasing demands on the insulating material. The integration challenges of any new material place a premium on dielectric generational extendibility (i.e., maintaining the same elemental composition while the dielectric constant progressively decreases). The only route to

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true dielectric extendibility is the incorporation of porosity, which will require control of pore sizes so that they are at least 10X smaller than the minimal device dimensions.[4]

Over the last few years, we have developed several techniques for the generation of nanoporosity in thermosetting organosilicates using sacrificial polymers or porogens that template the matrix vitrification to produce nanohybrids that are precursors to nanoporous films. These methods include: a) kinetically quenched nucleation and growth processes from miscible porogen/organosilicate combinations that phase separate upon curing, triggered by both chemical and molecular weight changes in the matrix,[5] b) templation using crosslinked single-chain nanoparticle-like porogens that are dispersed in the organosilicate[6] and c) templation using unimolecular self-organizing polymer porogens.[7] In the first case, the nucleated polymer domains, which consist of many polymer chains, remain nanoscopic in scale with growth inhibited by the crosslinking matrix (kinetically arrested growth), a process that is typically difficult to control. The last example uses a stimuli-responsive, star-shaped copolymer that creates a nano-sized domain through a matrix-mediated collapse of the interior core of the core-corona polymeric structure. The outer corona of the star compatibilizes the insoluble core in the thermosetting resin and suppresses aggregation or precipitation of the insoluble interior so that a single polymer molecule templates crosslinking and ultimately generates a single hole. The unimolecular micellar star polymers were prepared using ruthenium-catalyzed ring opening metathesis polymerization (ROMP) in a tandem core-in/core out approach that provides pore sizes that are identical to the molecule size in the range of 20-30nm.

Our recent efforts have focused on the reduction in pore size to satisfy the criteria for future device features. This requires a sacrificial template significantly smaller in size, yet retaining the same architecture and function. Towards this goal, we have focused on "bottom-up" or core-out approaches to star-shaped templates. Specifically, star-shaped polyesters prepared by the controlled ring-opening polymerization (ROP) of ε-caprolactone or lactide[8], initiated from the numerous chain-end hydroxymethyl groups of the analogous dendrimeric[9] and hyperbranched[10] polyesters derived from 2,2'-bis(hydroxymethyl) propionic acid, bis-MPA,[11, 12] provided number average molecular weights per arm that correlated closely to the monomer to initiator ratio. The bis-MPA units also provide exquisite markers for the spectroscopic analysis of the polymers, as the quartenary carbon and the protons on the methyl group are very sensitive to the substitution of the neighboring hydroxyl groups.[13] Along similar lines, dendrimer-like star polymers provide examples of a new macromolecular architecture characterized by a radial geometry where the different layers or generations are comprised of high molecular weight polymer emanating from a central core.[14] This modular approach to polymer design and synthesis provided the opportunity to systematically address some of the issues of branching in macromolecules.[15] Radial or layered block copolymers were generated by compositional variation between generations. In one example, dendrimer-like star block copolymers were prepared by combining ROP with other living/controlled polymerization methods such as atom transfer radical polymerization (ATRP). In some cases, these dendrimer-like star polymers were found to respond to changes in the polarity of the solvent (^{1}H-NMR) and serve as micelle mimics. This tandem ROP/ ATRP "core-out" approach to star-shaped copolymers will be described together with their utility as single molecule templates to direct the crosslinking of organosilicates.

Experimental

Materials

The 1,1,1-tris(p-hydroxyphenyl)ethane (THPE) (Hoechst Celanese) and stannous(II) 2-ethylhexanoate $Sn(Oct)_2$ (Sigma), were used as delivered. 4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS) was synthesized according to a literature procedure.[16] The ε-caprolactone was dried over CaH_2 (Mallinckrodt), distilled and stored under N_2 prior to use. Toluene was dried over Na, distilled and stored under N_2. The methyl methacrylate and hydroxyethyl methacrylate (HEMA) were distilled under vacuum and refrigerated under N_2 until used. The dendrimers derived from 2, 2-bis(hydroxymethyl)propionic acid (Bis-MPA) were prepared according to a literature procedure.[13] The benzyl 2,2'-bis(hydroxymethyl) propionate was synthesized according to a literature procedure. All other compounds were purchased from Aldrich and used as received.

Measurements

Size-exclusion chromatography (SEC) was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer. Four 5 μm Waters columns (300 X 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5, 10^6 Å) were used with THF as eluant. The SEC results were calibrated with polystyrene standards. The thermophysical properties (Tg) were recorded on a Perker-Elmer DSC-7. ^{1}H NMR spectra were recorded in a solution with a Bruker

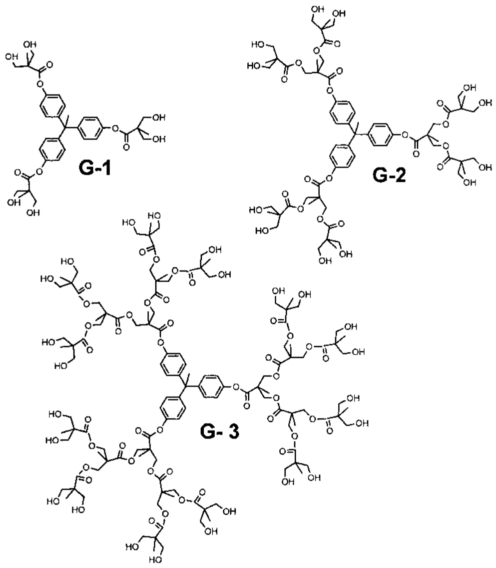
AM 250 (250 MHz) spectrometer. ^{13}C NMR spectra were recorded at 62.9 MHz on a Bruker AM 250 spectrometer using the solvent carbon signal as an internal standard.

General procedure for the modification of the hydroxy functional end groups of the poly(ε-caprolactone) initiators for ATRP. G-1 (6-OH) (8.00 g, 3.20 mmol) was dissolved in 50 mL of dry THF, and to this solution, triethylamine (1.40 g, 17.75 mmol) was added. The 2-bromo-2-methylpropionyl bromide (1.58 g, 6.85 mmol) was added dropwise over a 15 min period and stirring continued at room temperature for 48 hours. ^{1}H-NMR ($CDCl_3$) δ 1.28–1.40(m, poly, -CH_2*CH_2*CH_2-), 1.55–1.70 (m, poly, -CH_2*CH_2*CH_2-), 1.89(s,6H, CH3), 2.24–2.35 (t, poly, -*CH_2*CO-), 4.00–4.05 (t, poly, -*CH_2*O-), 4.11–4.16 (t, 18H, ,-*CH_2OH*), 4.31 (2, 12H,-CH_3(*CH_2*O)$_2$)), 6.89–7.07 (dd, 12H, Ph–). ^{13}C NMR ($CDCl_3$) 17.74, 24.51, 25.47, 28.29, 30.70, 34.05, 46.71, 51.61, 55.88, 64.05, 65.11, 65.70, 120.69, 129.65, 146.23, 148.62, 171.37, 171.57, 172.77, 173.43.

General procedure for ATRP of methyl methacrylate from functional polycaprolactone. G-1 (6-Br) (0.40 g 0.15 mmol) and dibromo-bis(triphenylphosphine)nickel(II) (7.00 mg, 0.009 mmol) were charged into a flask, which was evacuated for 12h and then purged with nitrogen and evacuated . Dry methyl methacrylate (2.00 g, 20.00 mmol) was added through a rubber septum and allowed to stir at room temperature until the macroinitiator dissolved. Optionally, toluene or THF could be added to facilitate the dissolution of the initiator and/or reduce the viscosity of the polymerization. The reaction flask was placed in a hot oil bath (110°C) and allowed to react for 5–8 hours. The polymers were isolated in hexane, stirred with methanol and isolated by filtration.

Results and Discussion

The dendritic initiators used in this study are the first, second and third generation hydroxy functionalized bis-MPA dendrimers (G-1-3), Scheme 1.[13] The synthesis of the six, twelve and twenty-four arm star polymers was accomplished by the reaction of G-1, G-2 or G-3 respectively, with ε-caprolactone in the presence of a catalytic amount of Sn(Oct)$_2$ in bulk,[11,12] and the characteristics of the polymers are shown in Table 1. The targeted degrees of polymerization, DP, for each arm of the star polymers ranged from 10 to 50 and the average DP's, calculated by ^{1}H NMR, were comparable to the targeted values (Table 1). Examination of the ^{13}C NMR spectra and comparison with previous studies demonstrated that initiation occurs from each of the hydroxyl groups of the dendritic initiator.[11,12]

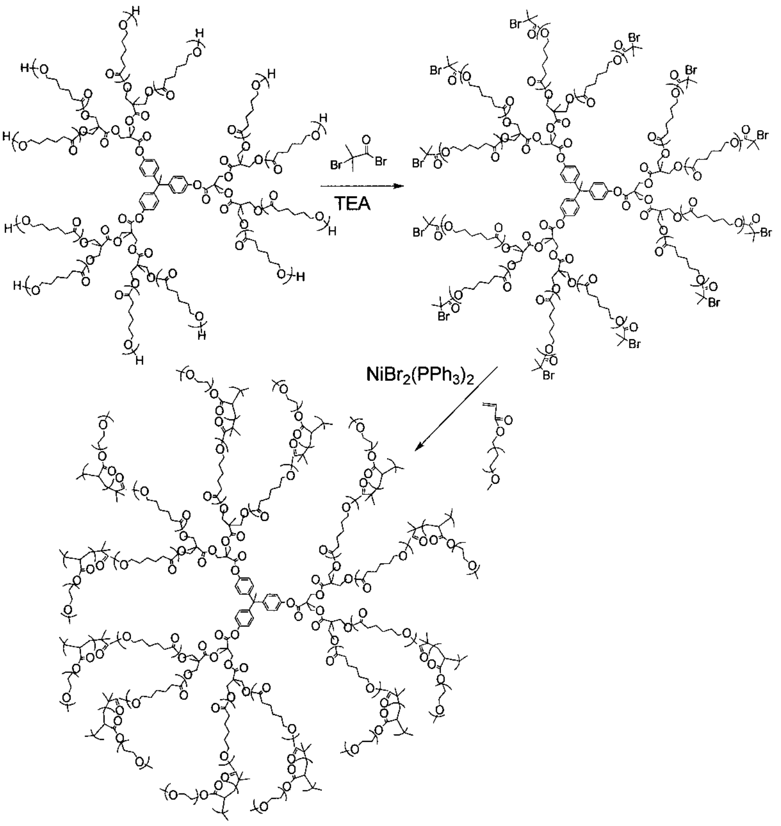


Scheme 1

Table 1. Characteristics of star-shaped polycaprolactones.

Sample Entry	Initiator	Targeted DP, M/I	DP ^{1}H-NMR	Mw/Mn (PDI)	Mw (SEC)
1	G-1	20	19	1.10	14,500
2a	G-2	10	12	1.21	20,000
2b	G-2	20	17	1.12	34,000
2c	G-2	50	48	1.20	62,000
3	G-3	25	24	1.18	70,000

Introduction of initiating centers for ATRP at the chain ends of the star-shaped polycaprolactone was accomplished by esterification of the hydroxyl functional chain ends with 2-bromo-2-methylpropionyl bromide in THF in the presence of triethylamine (Scheme 2).[14g] Isolation of the chain-end functionalized polymers and purification from excess reagents was accomplished by a simple precipitation in methanol. The ^{1}H NMR spectra of the star polymers show a clear shift in the peaks assigned to the methylene group adjacent to the hydroxyl chain end (3.66 ppm) upon the formation of the ester linkage (4.15 ppm). Furthermore, a new peak, from the $-CH_3$ groups of the modified chain end is observed at 1.05 ppm.



Scheme 2

Table 2. Characteristics of amphiphilic radial block copolymers.

Sample Entry	Core	Shell Type	DP (Shell)	Mw (SEC)	Mw/Mn PDI	D_h (DLS nm)
4a	2a	PEO	12	44,200	1.09	13.2
4b	2b	PEO	16	48,700	1.04	13.4
4c	2c	PEO	8	42,600	1.04	16.0
5	3	PEO	18	99,500	1.08	18.0
6	2b	MMA/HEMA 80/20	-	92,000	1.18	-

ATRP of selected vinyl monomers from the star-shaped macroinitiators was accomplished in solution at 85°C using $NiBr_2(PPh_3)_2$ as the organometallic promoter.[17] Polymers derived from hydroxyethyl methacrylate (HEMA) and poly(ethylene oxy) methacrylate-functional macromonomer were found to be miscible with organosilicate oligomers and were chosen to provide the corona of the star polymers. The high concentration of HEMA necessary in the copolymer corona required the use of the trimethylsilyl protected HEMA (Si-HEMA) together with dilution with methyl methacrylate in the polymerization to avoid "gelation" and facilitate processing of the mixtures. Upon completion of polymerization, the polymer was dissolved in a 50/50 mixture of methanol/THF, and the trimethylsiloxy group was readily removed under acidic conditions. Generally, ATRP catalysts are used in near stoichiometric amounts relative to the activated bromide, however, controlled polymerization is possible at $NiBr_2(PPh_3)_2$ levels as low as 10 to 20 mole percent the stoichiometric amount. Reduced catalyst concentrations and diluted polymerization mixtures minimized radical-radical coupling reactions in the preparation of the star polymers. The polymerizations were performed in toluene (20% solids) at 85°C in the presence of 20 mol.% catalyst for 18 hours. These conditions minimize side reactions and limited the conversions so as to minimize the size of the corona. The polymers were isolated in hexane, redissolved in THF and fractionally precipitated by the addition of hexane. This general ATRP procedure, with targeted DP's in the proximity of 10 to 20 for the outer corona (Table 2), was used to survey each of the macroinitiators. Shown in Figure 1 are the SEC traces for the poly(caprolactone) "macroinitiator" and the block copolymers derived from the poly(ethylene oxy) macromonomer. Clearly, from these data, high molecular weight, low polydispersity products are obtained which yield the expected spectroscopic data. The size of the star polymer in THF solution was determined using dynamic light scattering techniques (DLS) (Table 2). In solution, a single star-shaped polymer assumes a solvent-swollen state, and hence the values obtained by DLS represent the upper limit in size. For example, the smaller star **4a** had a Rg of 13.2 nm while that of the larger star **5** was 18.0 nm. The size distribution for both polymers was relatively narrow, consistent with the low polydispersity index measured by size-exclusion chromatography.

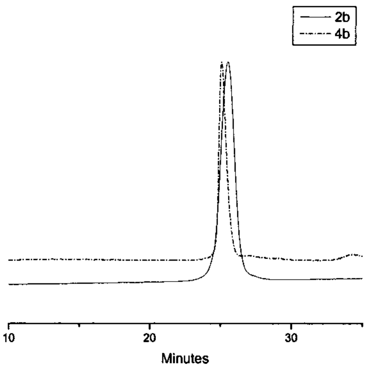


Figure 1. SEC chromatographs of star-shaped polycaprolactone, **2b**, and radial block copolymer, **4b**.

The amphiphilic polymers were dissolved in a solution containing methyl silsesquioxane (MSSQ) prepolymer in propylene glycol monomethyl ether, and the resulting solution was spun on a silicon wafer to produce thin films. Thermal analysis of the micellar star polymers in the hybrid samples by dynamic mechanical analysis (DMA) confirms that at least the internal hydrophobic core of the micellar polymers is phase separated from the MSSQ resin after soft curing (80 and 150 °C), (Figures 2 and 3), consistent with the dispersion and collapse of the core of the amphiphilic pore-generating macromolecule. The compatibilizing PEO arms are ultimately also expelled during further curing (to 200 °C) by frustrated phase separation generating the single polymer templating morphology. Crossectional FESEM and TEM micrographs of porous thin films generated from mixtures of MSSQ with **4a** (40 wt.%) are shown in Figure 4. For a truely templating process, the star polymers should produce foams with hole sizes reflecting the respective porogen dimensions. The dielectric constants of the porous samples decrease predictably from 2.8 to 1.9 with increasing porogen loading (0-40%).

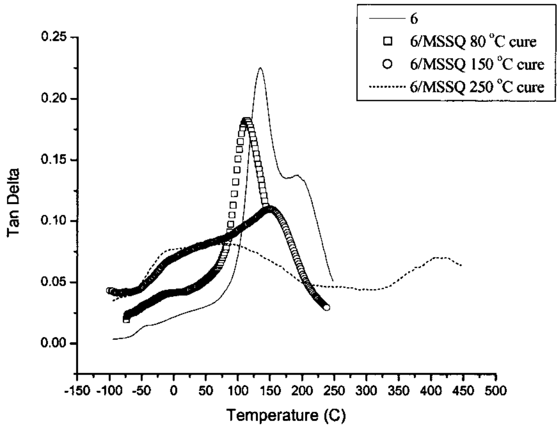


Figure 2. Dynamic mechanical analysis of **6** and mixtures of **6** (40 wt.%) with MSSQ cured to different temperatures.

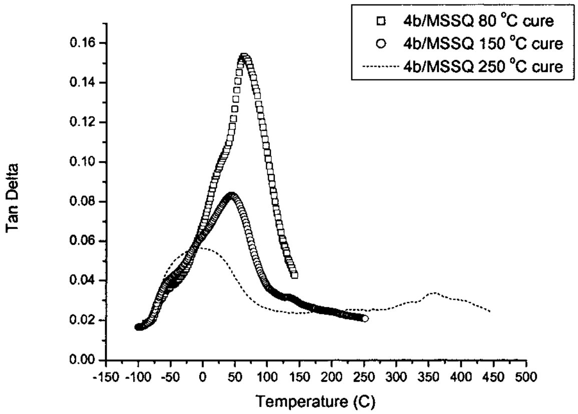


Figure 3. Dynamic mechanical analysis of mixtures of **4b** (40 wt.%) in MSSQ cured to different temperatures.

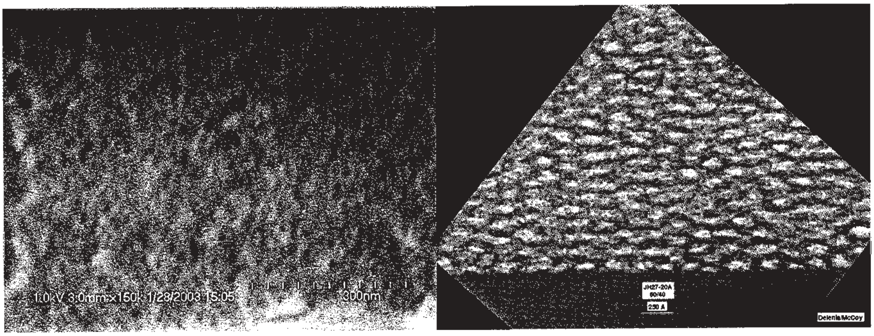


Figure 4. FESEM (left) and TEM (right) micrographs of porous MSSQ derived from **4b** (40 wt.%).

In summary, unimolecular, micellar star polymers, synthesized by tandem ROP/ATRP procedures, provide a controlled templating effect during the thermal cure of organosilicates. The unimolecular nature of the polymeric materials eliminates the complex dynamic assembly characterizing most amphiphilic systems. Porogen burnout results in nanoporous films where the pore sizes and distributions reflect the dimensions of the single polymer molecules.

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