Macromolecules **2000,** *33,* 4281−4284

Hyperbranched Polyesters as Nanoporosity Templating Agents for Organosilicates

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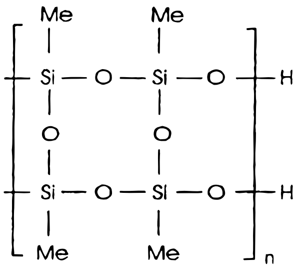
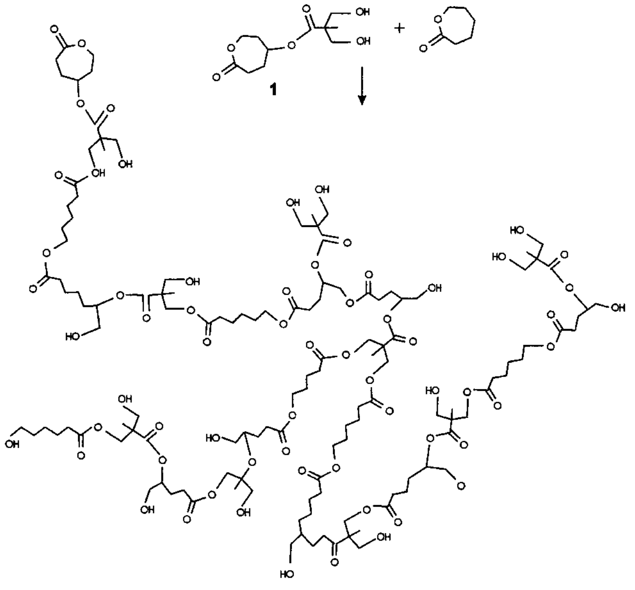
Received August 17, 1999
Revised Manuscript Received March 27, 2000

Scheme 1



MSSQ

Scheme 2



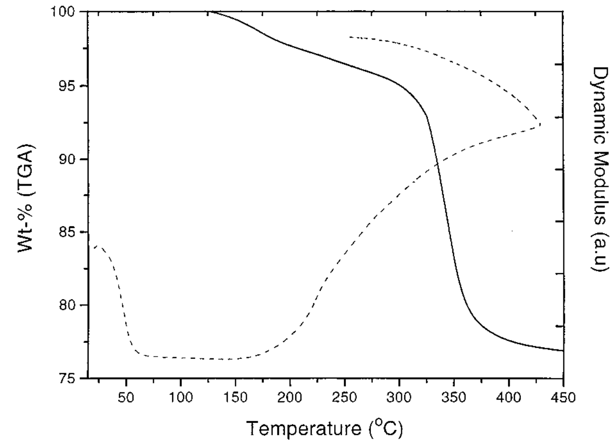


Figure 1. Dynamic mechanical analysis (- - -) and thermogravimetric analysis (—) of the organic−inorganic hybrid containing 20 wt % hyperbranched poly(ϵ-caprolactone).

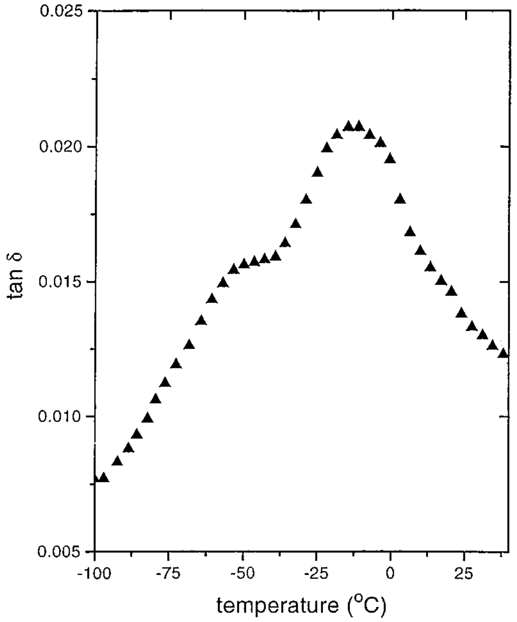


Figure 2. Tan δ versus temperature plot (dielectric spectroscopy) for the organic−inorganic hybrid containing 30 wt % hyperbranched poly(ϵ-caprolactone).

The field of dendritic macromolecules has witnessed explosive growth in recent years with numerous structures and new synthetic strategies being reported.[1] However, for the area's continued growth and development, applications of these novel materials are necessary. In this paper, the application of hyperbranched macromolecules as templating agents for the preparation of nanoporous, ultralow dielectric materials for advanced microelectronic devices is presented. The principal vision for obtaining ultralow dielectric constant materials is the incorporation of controlled porosity,[2] where the reduction in dielectric constant is achieved simply by replacing a portion of the densified film with air, which has a dielectric constant of approximately one. One set of materials that have attracted considerable attention are the porous silicas such as silica aero- and xerogels produced by the sol−gel reactions of orthosilicate esters.[3] Alternatively, porous silica has been prepared from low molecular weight surfactants used as structure-directing agents which self-assemble, leading to kinetically quenched nanostructures.[4] More recently, this concept has been extended to higher molecular weight surfactants (i.e., amphiphilic block copolymers) to permit the organization of larger structural features.[4d−f] Block copolymers offer the possibility of fine-tuning the polymer/solvent phase behavior by adjusting molecular weight, composition, and macromolecular architecture. This general concept was first demonstrated by Hillmyer and coworkers working with mixtures of a thermosetting epoxy resin and a poly(ethylene oxide)−poly(ethylene) copolymeric amphiphile.[5] In another approach, star-shaped macromolecules derived from poly(ϵ-caprolac-

10.1021/ma991407v CCC: $19.00

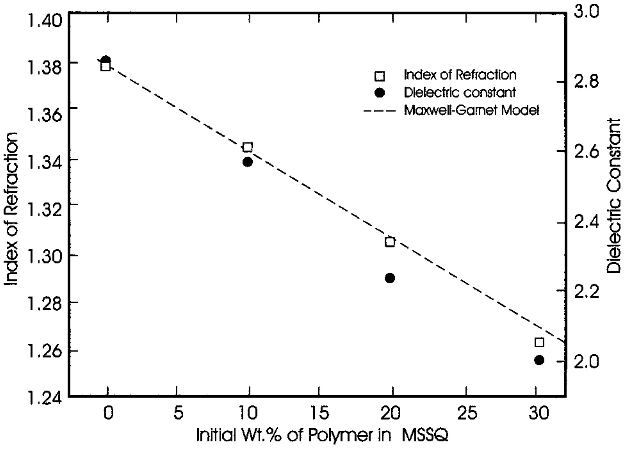


Figure 3. Index of refraction and dielectric constant of porous organosilicates generated from the organic−inorganic hybrids containing 10−30 wt % hyperbranched poly(ϵ-caprolactone).

tone) have been used to template a nanostructured morphology in organosilicates produced by curing silsesquioxanes (MSSQ, Scheme 1) which afford porosity upon thermolysis of the macromolecule.[6] However, the maximum achievable porosity from this hybrid approach has not been realized owing to limited polymer solubility in solvents suitable for the MSSQ, due in part to the semicrystalline nature of poly(ϵ-caprolactone) and the tendency of the solutions with higher concentrations of poly(ϵ-caprolactone) to prematurely macroscopically phase separate.

For these reasons, we have continued to survey aliphatic polyesters having dendrimeric and hyperbranched molecular architectures, since it has been demonstrated that such materials are significantly more soluble and less crystalline than their linear analogues,[7] and previous studies of high-temperature polymer mixtures with MSSQ required hyperbranched macromolecular architectures to facilitate nanoscopic separation.[8] There are only a few reports of dendrimeric aliphatic polyesters, those derived from 2,2′-bis(hydroxymethyl)-propionic acid (bis-MPA)[9] and/or those derived from poly(ϵ-caprolactone).[10] Recently, several groups have reported a new approach to hyperbranched polyesters utilizing a single-step self-condensation procedure involving ROP[11] chemistry which is related to the self-condensing vinyl polymerizations previously reported by Fréchet and others.[12] The bis(hydroxymethyl)-substituted ϵ-caprolactone monomer **1**, prepared in a four-step procedure, was either self-polymerized or copolymerized with ϵ-caprolactone at 110 °C in the presence of a catalytic amount of $Sn(Oct)_2$.[10,11] In this study, the material used for the formation of the inorganic−organic hybrids is a 1:4 copolymer of **1** with ϵ-caprolactone having a molecular weight of 8000 g/mol and a polydispersity of 2.81 (degree of branching = 0.15[11]) (Scheme 2).

The processing conditions to form the nanoscopically phase-separated hybrid morphology with methyl silsesquioxane (MSSQ) and the subsequent removal of the hyperbranched polyester were established using both dynamic mechanical and thermogravimetric analysis. To obtain a stable porous structure, it is critical that vitrification of the MSSQ derivative occurs prior to the decomposition of the polymer. Shown in Figure 1 is the dynamic mechanical spectrum together with the thermogravimetric analysis for a hybrid containing 20 wt % polyester. The MSSQ shows a softening or melting around 40 °C, and the onset of network formation is just below 200 °C. Although vitrification increases with temperature to over 400 °C, as evidenced by the expected increase in modulus, by 300 °C the MSSQ is sufficiently vitrified, a temperature which coincides with the onset of the decomposition temperature of the polyester. Formation of porous thin films was facile and accomplished by spin-coating a solution of MSSQ and the polyester dissolved in propylene glycol methyl ether acetate (PM-acetate) and heating to 430 °C (5 °C/ min). Polyester compositions in the hybrids ranged from 10 to 30 wt %. Unlike previous studies with related star-shaped macromolecules, these hyperbranched isomers allowed the preparation of stable higher solids content solutions and high-quality films with 30 wt % polymer content.[6]

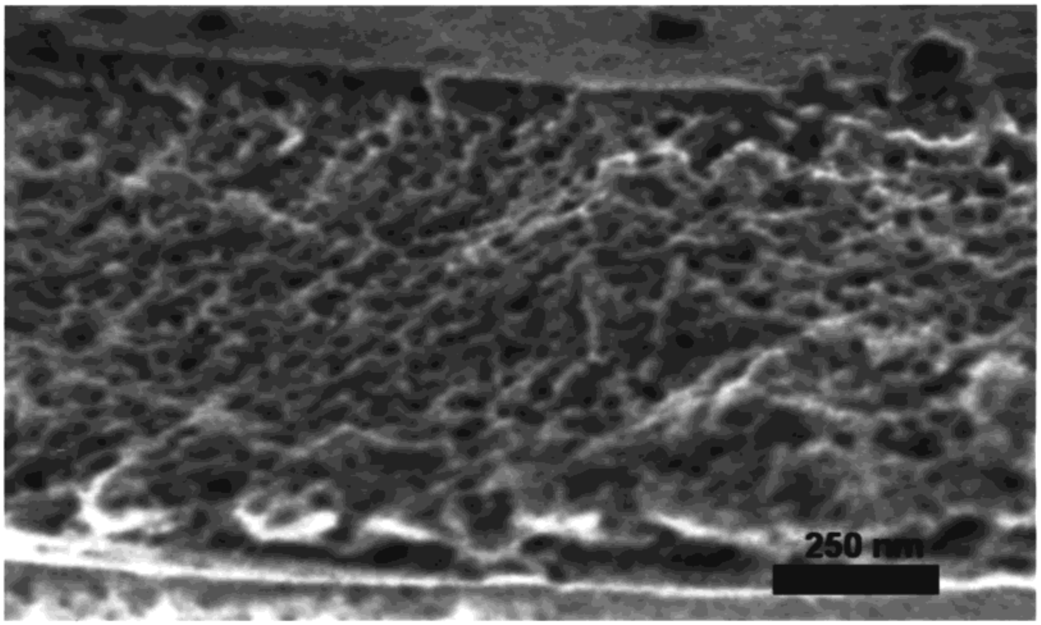


Figure 4. FESEM micrograph of porous organosilicates generated from an organic−inorganic hybrid containing 30 wt % poly(ϵ-caprolactone).

During processing and film formation, it is also critical that phase separation between the polyester and the MSSQ occur during vitrification and that the size scale of kinetic phase separation be limited. This is accomplished by kinetically quenching the film structure prior to coarsening of the morphology, a procedure typical of many thermosetting resin/polymer mixtures proceeding via nucleation and growth mechanisms. Upon spin-coating the mixture from PM-acetate (bp 160 °C), compatiblization is initially facilitated by the presence of residual solvent. Miscibility is maintained upon heating, and once above the boiling point of the solvent, network formation of the SSQ begins. The loss of solvent coupled with the increase in matrix molecular weight accompanied by changes in functionality provides the driving force for phase separation. Dielectric spectroscopy performed on a hybrid cured to 250 °C, a temperature adequate for significant vitrification of the MSSQ but lower than required to effect degradation to the polyester, showed a maximum in the tan δ plot around -30 °C, comparable to that observed for the hyperbranched polyester itself, indicating phase separation.[13] The cured films remained transparent with no visual or microscopic evidence of phase separation. The usual coarsening of the polyester component is presumably precluded by the rapid formation of the MSSQ network, effectively quenching the phase separation and diffusional process.

Porosity in the organosilicate films is generated upon curing the hybrids to 430 °C. The polyester undergoes clean and quantitative degradation, leaving pores which reflect, in principle, the size and shape of the original hybrid morphology. The porosity was verified by IR, refractive index, dielectric constant, and transmission electron microscopy measurements. The IR measurement, corroborated by the TGA results, showed quantitative degradation and loss of the polyester. The refractive index and dielectric constant measurements show the expected decreases, consistent with replacing a portion of the film with air. Shown in Figure 3 is the dielectric constant of the porous thin films as a function of the air content together with the expected values predicted by Maxwell−Garnett theory.[14] Moreover, the porous films with air have dielectric constants below 2.0 and produce high-optical-quality films. Figure 4 shows a FESEM micrograph of the cross section of a porous organosilicate film derived from a hybrid containing 30 wt % polyester. Clearly, a porous structure is obtained with a pore volume fraction that is commensurate with the polyester composition in the hybrid. Discrete porosity is observed with average pore size of $\approx$200 Å.

In summary, a general approach to porous organosilicates is detailed. Hyperbranched polyesters, prepared in a single step using ROP methods, were found to be superior materials for templating nanostructures in organosilicates. Compatibilization of the polyester/MSSQ mixture on the nanoscopic size scale was facilitated by the abundant chain-end functionality of the hyperbranched polyester, similar to hybrids generated from MSSQ with hyperbranched poly(aryl ether phenylquinoxalines).[8] In contrast to the star-shaped poly(ϵ-capolactones) previously surveyed as porosity templates, the hyperbranched materials allowed higher solids content solutions, higher polyester compositions in solution, and better film quality, a manifestation of the higher solubility and lack of crystallinity for this architecture. The porous films, generated by the thermolysis of the hyperbranched polyester, have low dielectric constants and refractive indices that track the polyester composition in the hybrid and are similar to the values obtained from star-shaped poly(ϵ-caprolactone). However, the average pore size obtained from the hyperbranched template was significantly smaller than that produced from the star-shaped architecture while the linear analogues showed macrophase separation. This work represents another example[1] of how polymer architecture can exert a tremendous influence on the physical and solution properties of a material.

Acknowledgment. The National Science Foundation under Grant No. DMR-9808677 for the Center of Polymeric Interfaces and Macromolecular Assemblies is kindly acknowledged for partial support of this work.

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MA991407V