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13. ABSTRACT (Maximum 200 words) Hyperbranched polymers of unique compositions were studied for their mechanical properties and degradation behaviors. Highly branched polymeric architectures have been shown to exhibit properties that are unique to those of linear polymer materials. In the studies supported under this grant, hyperbranched polycarbonates were designed as analogs to common engineering polymers to investigate the effects of branching upon the chain-chain packing and cooperative motions. Remarkably, the local chain-chain interactions were quite similar for hyperbranched and linear polymer isomers. In another design, hyperbranched poly(silyl ester)s were studied as hydrolytically-degradable polymers to determine the effects of branching upon the degradation profile. The hyperbranched poly(silyl ester)s degraded by a two-step degradation profile, whereas the analogous linear polymer gave smooth molecular weight loss with time. The result of these undertakings was the preparation of new materials and the acquisition of improved understanding of the structural conformation, three-dimensional solid-state packing, and physical and mechanical properties of highly-branched polymers.					
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1) **List of Illustrations and Tables.**

Figure 1. Chain ends, monomeric repeat units and a core are the components that comprise a dendritic macromolecule. For clarity, the dendritic structures are drawn with these components emanating from a central point, however, the conformation of the dendrimer is highly dependent upon its composition.

Figure 2. Phenol-terminated hyperbranched polycarbonate was prepared by the condensation, step-growth polymerization of the A_2B monomer bearing two chloroformate groups and one tert-butyldimethylsilyl-protected phenol. Reaction with silver fluoride converts the chloroformates to fluoroformates, then removes the silicon protecting group to allow for polymerization to proceed. Hydrolysis of the fluoroformates then liberates the phenolic chain end functional groups.

Figure 3. The phenol-substituted linear polycarbonate is produced by the condensation of the mono-benzylated triphenolic moiety with phosgene, followed by hydrogenolysis. The phosgene was ^{13}C labeled to incorporate ^{13}C labels at the carbonate functionalities along the polymer backbone. Exchange of a fraction of the phenolic protons with deuterons provides a system that is doubly-isotope-labeled for solid-state NMR studies. Intramolecular ^{13}C - 2H distances are fixed, whereas, the intermolecular distances can be probed.

Figure 4. Dynamic mechanic analysis of several linear and hyperbranched polycarbonates indicate similar sub- T_g transitions, suggesting similar local chain-chain packing and dynamics.

Figure 5. The preparation of an A_2B monomer is followed by cross-dehydrocoupling reactions between the hydrosilanes and the carboxylic acid to yield a hyperbranched poly(silyl ester). The silyl ester linkages are hydrolytically labile, and the hyperbranched polymer was found to degrade via a two-stage degradation profile, which differs from the typical behavior of linear polymers based upon similar chemistry. The silanol hydrolysis product can condense to produce a non-degradable linear polymer as the final material.

2) **Statement of the problem studied.**

Hyperbranched polymers of unique compositions were studied for their mechanical properties and degradation behaviors. Highly branched polymeric architectures have been shown to exhibit properties that are unique to those of linear polymer materials. In these studies, hyperbranched polycarbonates were designed as analogs to common engineering polymers to investigate the effects of branching upon the chain-chain packing and cooperative motions. In another design, hyperbranched poly(silyl ester)s were studied as hydrolytically-degradable polymers to determine the effects of branching upon the degradation profile. The result of these undertakings was the preparation of new materials and the acquisition of improved understanding of the structural conformation, three-dimensional solid-state packing, and physical and mechanical properties of highly-branched polymers.

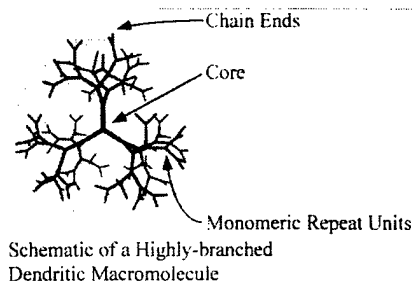


Figure 1. Chain ends, monomeric repeat units and a core are the components that comprise a dendritic macromolecule. For clarity, the dendritic structures are drawn with these components emanating from a central point, however, the conformation of the dendrimer is highly dependent upon its composition.

3) **Summary of the most important results.**

A) *Dendritic Macromolecules—Background*

Dendritic macromolecules (shown schematically in Figure 1) are constructed from the attachment of monomeric repeat units in a manner that results in a branching site at each repeat unit, to

yield a globular structure containing a large number of chain ends that emanate from a single focal point. As such, their properties differ greatly in comparison to linear polymers. For example, dendritic materials have been shown to possess higher solubilities, lower degrees of crystallinity and lower viscosities than linear polymers.

These unique properties have been attributed to a lack of chain entanglement for highly-branched polymers. We have confirmed this by studying the conformation and nature of packing for dendrimers in the solid state, by a combination of stable isotope labeling strategies with solid-state NMR. The lack of chain entanglements imparts these interesting characteristics to dendritic materials, but also prevents the ability to form free-standing films for mechanical properties testing in the solid state. Therefore, in order to evaluate the mechanical properties of dendritic macromolecules, atomic force microscopic experiments performed upon ultra-thin films were developed. Films of dendritic materials underwent significant machining at much lower forces than required to affect films of the corresponding linear polymers. Moreover, direct machining occurred, as opposed to a stick-slip phenomenon of deformation for linear polymer samples. These findings served as the entry into the design of hyperbranched polycarbonates, a branched form of the common polymer engineering materials. Hyperbranched structures, based upon hydrolytically-degradable linkages were also studied, to determine the effect of branching upon the molecular weight breakdown for polymers consisting of large percentages of short-chain segments.

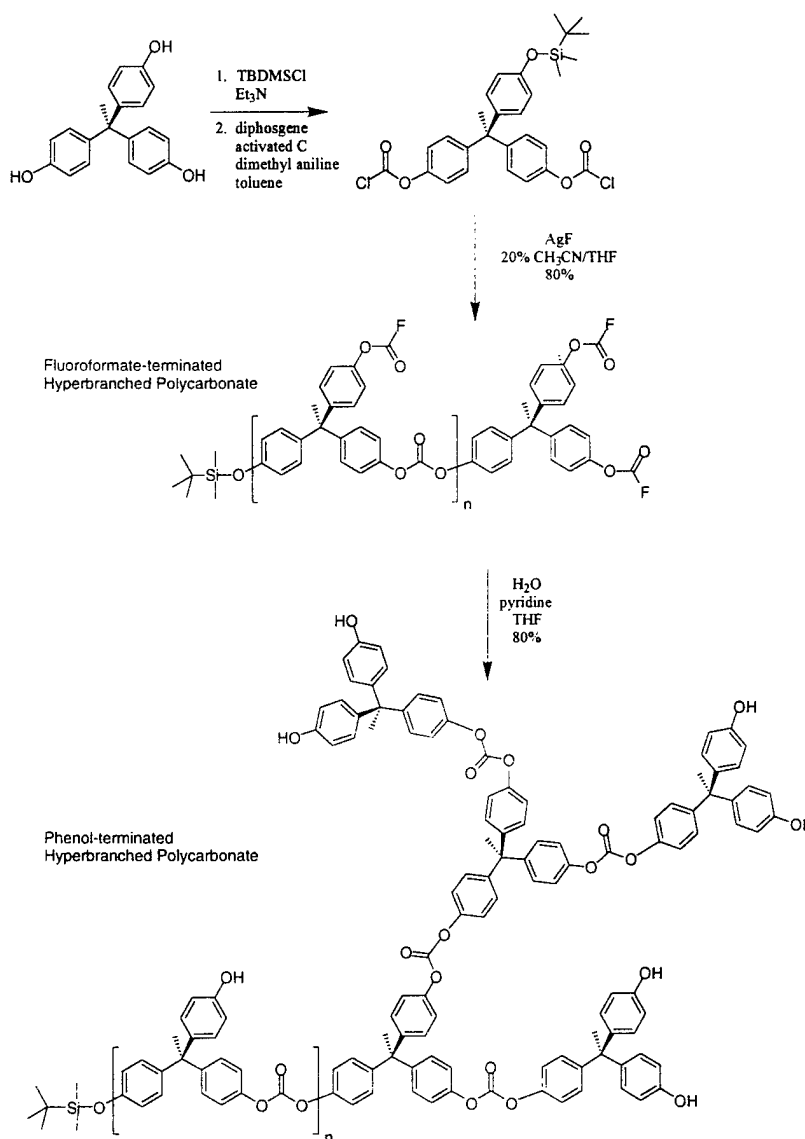


Figure 2. Phenol-terminated hyperbranched polycarbonate was prepared by the condensation, step-growth polymerization of the A₂B monomer bearing two chloroformate groups and one tert-butyl dimethylsilyl-protected phenol. Reaction with silver fluoride converts the chloroformates to fluoroformates, then removes the silicon protecting group to allow for polymerization to proceed. Hydrolysis of the fluoroformates then liberates the phenolic chain end functional groups.

B) Hyperbranched Polycarbonates

(1) Synthesis

Hyperbranched polycarbonates were prepared as an analog of engineering materials to study the effects of branching upon the mechanical properties and the interchain interactions. The synthetic scheme shown in Figure 2 was optimized for the production of the hyperbranched polycarbonates, having degrees of branching of ca. 50% and molecular weights that were tunable based upon the polymerization conditions. The phenol-terminated hyperbranched polycarbonate synthesis is scalable, allowing for the production of multiple grams of material for mechanical properties testing. Linear polycarbonates of analogous chemical composition, but with a non-branched architecture (essentially isomers)

were also prepared. Figure 3 illustrates the chemistry employed to generate the linear polycarbonate materials with phenolic side-chain substituents.

(2) Physical and Mechanical properties of Hyperbranched PC vs. Linear PC's

The compositions of both the hyperbranched and linear polycarbonates are the same and they are similar to the composition of linear bis(phenol A) polycarbonate. Therefore, comparison is made between the dynamic mechanical analyses of each of these three polymers, and also the linear benzyl-substituted polycarbonate, which is the precursor to the phenol-containing polymer. As is shown in Figure 4, each of the polymers exhibit a significant sub- T_g γ transition with a maximum between -106 and -78 °C. In fact, the T_γ for bis(phenol A) polycarbonate and the phenol-terminated hyperbranched polycarbonate are -99 and -92 °C; the activation energy (E_a) for the phenol-terminated hyperbranched polycarbonate transition is larger than that of the bis(phenol A) polycarbonate, which may indicate motion restriction due to either branching or hydrogen-bonding between the phenolic groups. The linear phenolic polycarbonate samples failed during acquisition, likely due to packing defects resulting from the high T_g and high melt viscosity which impair the ability to melt press the samples.

These data indicate that each of the materials (including the hyperbranched polymer!) undergoes sub- T_g relaxations that should result in good mechanical properties. The brittleness of the hyperbranched polymer is therefore expected to be due to the lack of extensive chain entanglements, which also allow for ease of melt processing to form the DMA samples (in comparison to the linear phenolic material). The results are promising toward the hyperbranched polycarbonate finding application as a strong material to be used in composites, or in performance as a nanoscopic scaffold.

The phenol-terminated hyperbranched polycarbonate was the first example of a hyperbranched polymer that formed films of suitable integrity to able to be subjected to traditional mechanical analysis as neat, bulk samples. Instron analysis was performed (ASTM method D-638), which gave tensile strength (ultimate) of 3.92 ± 0.34 MPa, elongation to rupture of 9.2 ± 1.4 % and tensile modulus of 1050 ± 35 Mpa for a hyperbranched polycarbonate of $10,500 M_w$. The low values for each of these measurements agrees with the lack of chain entanglements, which could be due to low molecular weight or the presence of branching. For the linear phenol-substituted polycarbonate material with a $93,000 M_w$, the Instron measurement gave a tensile strength (ultimate) of 80 ± 9 MPa, elongation to rupture of 75 ± 6 % and tensile modulus of 2520 ± 116 Mpa.

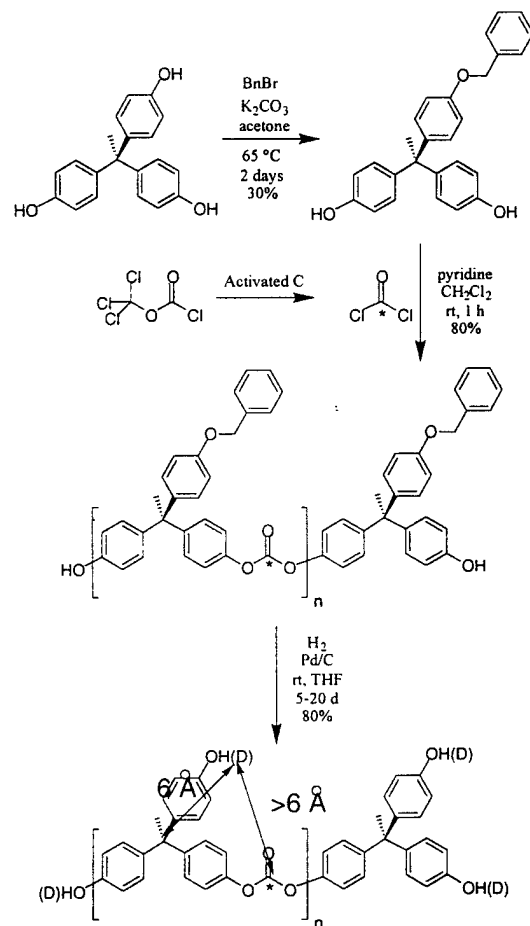
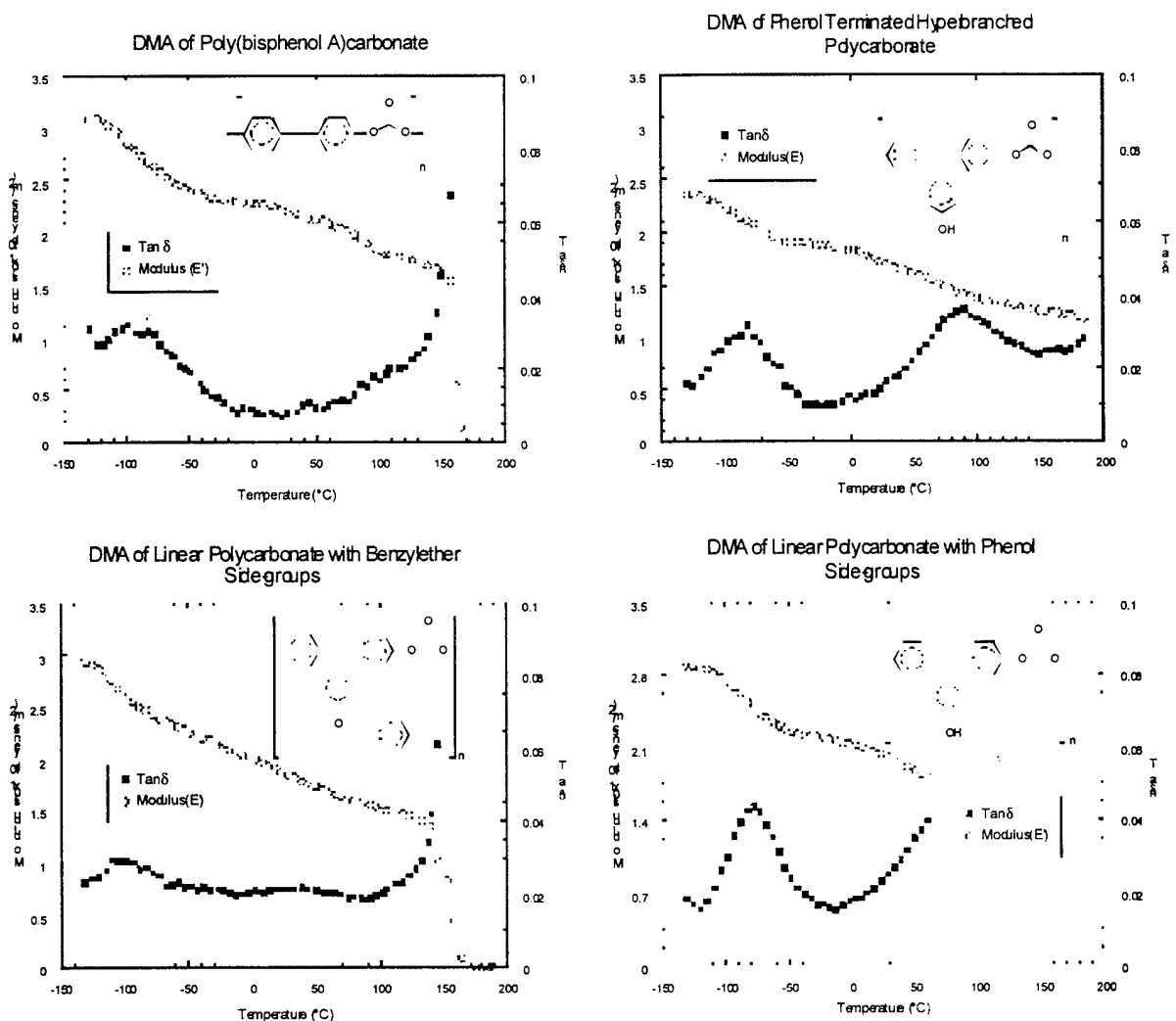


Figure 3. The phenol-substituted linear polycarbonate is produced by the condensation of the mono-benzylated triphenolic moiety with phosgene, followed by hydrogenolysis. The phosgene was ^{13}C labeled to incorporate ^{13}C labels at the carbonate functionalities along the polymer backbone. Exchange of a fraction of the phenolic protons with deuterons provides a system that is doubly-isotope-labeled for solid state NMR studies. Intramolecular ^{13}C - ^2H distances are fixed, whereas, the intermolecular distances can be probed.

Figure 4. Dynamic mechanic analysis of several linear and hyperbranched polycarbonates indicate similar sub- T_g transitions, suggesting similar local chain-chain packing and dynamics.



	T_g °C	T_{γ} °C	E_a (γ) (kcal/mol)
Poly(bisphenol A)carbonate	150	-99	11
Phenol Terminated Hyperbranched Polycarbonate	205	-92	18
Linear Polycarbonate with Phenol Side-groups	210	-78	11
Linear Polycarbonate with Benzylether Side-groups	148	-106	12

(3) Molecular dynamics behavior

In order to microscopically evaluate the molecular motions, solid-state NMR experiments were performed. It was found that the same aromatic ring π (180°) flips that gate molecular motion and dissipate energy upon impact of bis(phenol A) polycarbonate are present in the hyperbranched polycarbonate material (when the phenolic groups are protected as silyl ethers to remove hydrogen-bonding). This indicates that the hyperbranched polycarbonate is able to pack on the molecular level in similar fashion as the linear polycarbonate material, and that the same motions occur even with very different molecular

architecture. Determination of a model for the solid-state local chain packing for the linear and hyperbranched polycarbonates found the materials to be quite similar, by solid-state NMR measurements upon ^{13}C and ^2H labeled samples, in combination with molecular modeling. [This work has been performed in collaboration with Professor Jacob Schaefer, Washington University, St. Louis, MO and is currently being written for publication]

C) Hyperbranched Poly(silyl ester)s

(1) Synthesis

For hyperbranched polymers prepared from AB_2 monomers, the statistical degree of branching of 50% leads to *ca.* 25% of the monomeric repeat units being present as chain ends distributed throughout the macromolecular architecture. Therefore, cleavage of any one of 25% of the backbone linkages will release only a single monomeric unit, resulting in a minimal reduction in the overall polymer molecular weight. This is in contrast to linear polymer chains, which contain only two chain ends. It is then expected that hyperbranched degradable polymers should, in general, exhibit degradation behaviors that differ substantially from linear polymers. The architectural effects between linear and hyperbranched structures upon the degradation properties of polymeric materials were studied for poly(silyl ester)s with differing compositions and architectures. Three poly(silyl ester)s--linear poly(dimethylsilyl benzoate), linear poly(diisopropylsilyl benzoate), and hyperbranched poly(dimethylsilyl benzoate)--were synthesized via cross-dehydrocoupling polymerizations of AB and AB_2 monomers, 4-(dimethylsilyl) benzoic acid, 4-(diisopropylsilyl) benzoic acid, and 3,5-bis(dimethylsilyl) benzoic acid, as 10 M solutions in ethylene glycol diethyl ether in the presence of 0.25 mol% of 10 wt.% palladium on activated carbon at 100 °C under argon for 1-3 days. The synthetic scheme for the preparation of the hyperbranched poly(silyl ester) is shown in Figure 5. The characterization of each polymer included infrared (IR), ^1H NMR, ^{13}C NMR, and ^{29}Si NMR INEPT spectroscopies, size exclusion chromatography (SEC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The degree of branching of hyperbranched poly(dimethylsilyl benzoate) was 51%, as determined by ^1H NMR spectroscopy, with spectral analysis confirmed through comparison with model compounds. The hydrolytic degradation properties of the polymers in solution and in the solid state were studied quantitatively by monitoring the molecular weight reduction over time using SEC. In addition, the erosion processes of solvent-cast polymer films upon hydrolytic degradation were investigated by monitoring the changes in the surface topographies and

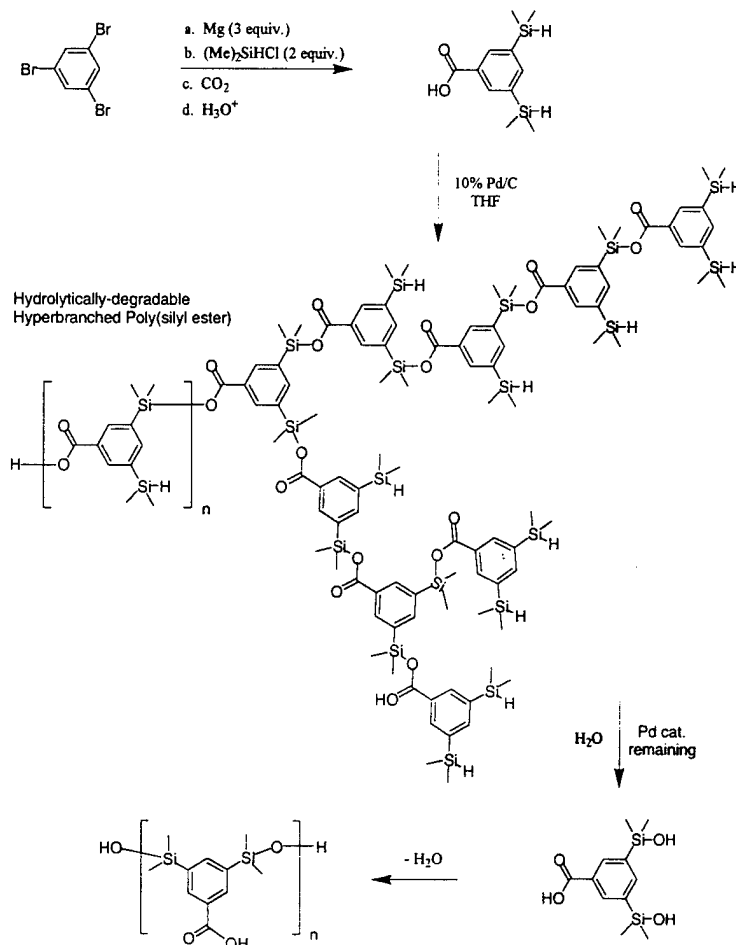


Figure 5. The preparation of an A_2B monomer is followed by cross-dehydrocoupling reactions between the hydridosilanes and the carboxylic acid to yield a hyperbranched poly(silyl ester). The silyl ester linkages are hydrolytically labile, and the hyperbranched polymer was found to degrade via a two-stage degradation profile, which differs from the typical behavior of linear polymers based upon similar chemistry. The silanol hydrolysis product can condense to produce a non-degradable linear polymer as the final material.

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morphologies using atomic force microscopy (AFM). Hydrolysis of each of the linear polymers gave smooth molecular weight loss over time, whereas the hyperbranched material exhibited a two-stage degradation profile. The unique degradative profile observed for the hyperbranched poly(silyl ester)s is of great interest and further modification of the degradation properties is being accomplished by compositional and architectural control for the poly(silyl ester)s.

List of all publications.

(1) *Papers published in peer-reviewed journals.*

- Kao, H.-M.; Stefanescu, A. D.; Wooley, K. L.; Schaefer, J. "Location of Terminal Groups of Dendrimers in the Solid State by Rotational-Echo Double-Resonance NMR", *Macromolecules*, **2000**, *33*, 6214-16.
- Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L. "Cyclization in Hyperbranched Polymer Syntheses: Characterization by MALDI-TOF Mass Spectrometry", *J. Am. Chem. Soc.*, **1998**, *120*, 10180.
- Mueller, A.; Kowalewski, T.; Wooley, K. L. "Synthesis, Characterization and Derivatization of Hyperbranched Polyfluorinated Polymers", *Macromolecules*, **1998**, *31*, 776-86.
- Bolton, D. H. and Wooley, K. L. "Synthesis and Characterization of Hyperbranched Polycarbonates", *Macromolecules* **1997**, *30*, 1890.

(2) *Papers published in non-peer-reviewed journals or in conference proceedings.*

- Straw, T. A.; Mueller, A.; Stefanescu, A. D.; Kowalewski, T.; Wooley, K. L. "The Design, Synthesis, Characterization and Derivatization of Fluorine-Containing Dendrimers and Hyperbranched Polymers", In *Hyper-Structured Molecules II – Chemistry, Physics, and Applications*, Ed. H. Sasabe, Gordon and Breach Science Publishers, Japan, (2001).
- Mueller, A.; Wooley, K. L. "Crosslinked Hyperbranched Fluoropolymer Films", *ACS Polym. Prepr.* **1998**, *39*(2), 960.
- Fields, H. R. Jr.; Kowalewski, T.; Schaefer, J.; Wooley, K. L. "AFM Investigation of Micromechanical Properties of Poly(benzyl ether) Dendrimers and Their Linear Analogs", *ACS Polym. Prepr.* **1998**, *39*(2), 1169.
- Fields, H. R.; Kowalewski, T.; Schaefer, J.; Wooley, K. L. "Synthesis and Micro-mechanical Characterization of Linear Polymer Analogs to Poly(benzyl ether) Dendrimers", *ACS Polym. Prepr.*, **1998**, *39*(1), 333.

(3) *Manuscripts submitted, but not published.*

- Wang, M.; Gan, D.; Wooley, K. L. "Linear and Hyperbranched Poly(silyl ester)s: Synthesis via cross-dehydrocoupling-based polymerization and morphological analysis by atomic force microscopy", *Macromolecules*, submitted.

List of scientific personnel supported and advanced degrees received by them.

- Baroni, Timothy E.—postdoctoral research associate, currently employed as a postdoctoral research associate at the School of Medicine, Washington University (St. Louis, MO)
- Bolton, Daniel H.—graduate student, completed Ph.D. dissertation March 30, 1998, "Synthesis, Characterization and Comparison of Hyperbranched and Linear Polycarbonates", currently employed with Bayer Corporation (Pittsburgh, PA)
- Mashburn, Courtney D.—undergraduate summer research student, B. S. received from Hendrix College, Conway, AR, May 2000
- Mueller, Anja—graduate student, completed Ph.D. dissertation August 17, 1998, "Hyperbranched Fluoropolymers: synthesis, characterization, derivatization and application", currently a postdoctoral research associate with Professor D. O'Brien, U. Arizona
- Wang, Min—Ph.D. student, to complete her dissertation research on "Degradable Poly(silyl ester)s: Synthetic Methodologies and Controlled Macromolecular Architectures" in June 2001