

**Reactive Hyperbranched Polymers as
Toughening Processing Aids for Composite Matrices**

Final Report
1 Feb 2003 through 31 August 2004

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PROGRESS REPORT

Reactive Hyperbranched Polymers as Toughening Processing Aids for Composite Matrices (F49620-03-1-0084)

**Prof. Patrick T. Mather,
University of Connecticut
Start Date: 1 February 2003**

I. Progress Summary

The overall objective of this proposal is to develop and study for transition new low viscosity thermoset additives – hyperbranched polymers (HBPs) – for use in composites needed for emerging space-based Air Force applications. Specifically, we are studying and developing hyperbranched polymers for use as new low-viscosity thermoset/thermoplastic additives, which have enormous applications in rigid spacecraft structures. The particular projects included: (i) Modification of high performance thermoplastics by non-reactive hyperbranched poly (arylene-ether-ketone-imide) (PAEKI), (ii) Manipulation of DOB by copolymerization with core monomers and study of induced property modification, (iii) Measurement of Degree of Branch (DOB) by model compound studies, and (iv) Synthesis of hyperbranched liquid crystalline polymer. This program began officially 21 months ago, and during this time we have conducted research with several graduate assistants, but primarily Mr. Haihu Qin and Mr. Timothy E. Marsh.

II. Objectives

- The overall objective of this proposal is to develop and study for transition new low viscosity thermoset additives – hyperbranched polymers (HBPs) – for use in composites needed for emerging space-based Air Force applications.
- We are investigating the application of hyperbranched poly (arylene-ether-ketone-imide), the synthesis of which is well established by other researchers in Air Force, as the processing aids for high performance thermosets or thermoplastics.
- We are establishing the detailed understanding of the trends in performance properties with materials characteristics, including macromolecular architecture, blend composition and processing protocol.
- We are developing new hyperbranched polymers (HBPs), which will enhance the use temperature *and* fracture toughness of thermoset materials.

III. Accomplishments and New Findings

a. Modification of high performance thermoplastics with benzophenone terminated hyperbranched Poly(arylene-ether-ketone-imide) (BT-PAEKI).

This aspect of the research was not originally proposed, but has been pursued with an intern (Mr. Olivier Arnoult, now a graduate student in my group) based on a preliminary observation that showed great promise. Here, we have studied the modification of several commercial, state-of-the-art, high performance thermoplastics, specifically, PEEK, PEKK (Figure 1) and Parmax[®]1201 with BT-PAEKI, whose structure is shown in Figure 2, below. This polymer was synthesized in the group of L.-S. Tan of AFRL/MLBP.

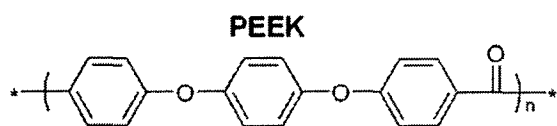
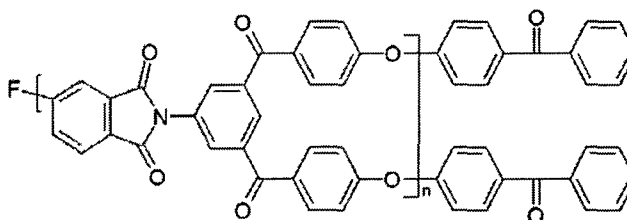


Figure 1. Repeat Unit Structures for PEEK and PEKK.

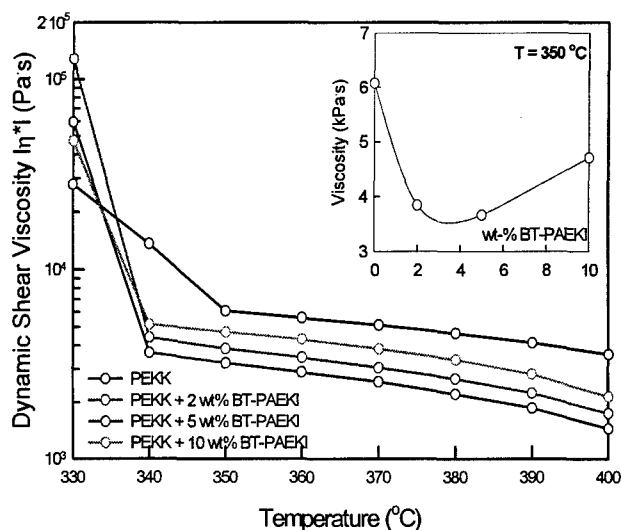


Figure 2. Structure of BT-PAEKI, the non-reactive HBP used in the proposed investigation.



All of the blends were found to exhibit single glass transitions in DSC, suggesting good miscibility with BT-PAEKI, at least for compositions up to 20 wt-% HBP. Among the three systems studied, the PEKK exhibits an observable 50% viscosity decrease in the presence of 5 % BT-PAEKI throughout the temperature region between 350 °C and 400 °C. Notably, the 5% blend viscosity at 340 °C is 40% lower than the lowest viscosity for pure PEKK at 400 °C. Furthermore, BT-PAEKI also has a positive effect in lowering the processing temperature. After a first melt, the blends of PEKK and BT-PAEKI do not recrystallize until 340 °C, which enables processing at temperatures significantly lower than the melting point of neat PEKK, 380 °C. Thus, we conclude that the BT-PAEKI can facilitate the processing of PEKK in two ways: by lowering the viscosity *and* the processing temperature. Benefits of the former include foam process enabling, micromolding, and composite processing.

Figure 3. Dynamic shear viscosity versus temperature for PEKK + BT-PAEKI blends revealing viscosity reduction. Samples were first heated to 400 °C and then cooled slowly to each test temperature.



Despite the observed viscosity reduction, we have found that no compromise in glass transition temperature is observed. In particular, Figure 4 shows example data where DSC trace comparisons reveal a single-T_g intermediate between pure BT-PAEKI and the amorphous fraction of the host PEKK. Quite attractively, the crystallinity of each polymer is also preserved, suggesting that the final mechanical and chemical properties of the resulting foams will be similar to the host polymer, while benefiting from the positive influence of the melt-miscible hyperbranched additive.

Our present and future attention on this portion of the project is to examine in detail modification to the steady shear rheology and steady elongational rheology of PEKK/BP-PAEKI blends of various compositions.

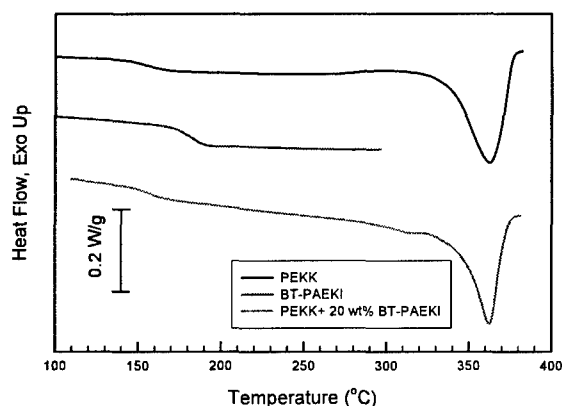


Figure 4. 2nd heating DSC of PEKK, BT-PAEKI, and a 20 wt-% HBP blend. Like for the PEEK blend, a single T_g is seen, while crystallinity of the host is preserved.

b. Synthesis of PAEKI with varying Degree of Branching (DOB) by copolymerization with B₄ monomers.

One of the major objectives of this proposal is to study the influence of the degree of branching on HBP properties and to optimize the toughening effects in high performance thermosets. One method of altering the DOB is to polymerize the AB₂ monomers in the presence of a multi-reactive core molecule. To this end, we have synthesized a polymer with a 20:1 ratio of AB₂ to B₄ core molecule. The chemical structure of this B₄ core molecule is shown in Figure 5. Previous research has shown that incorporation of a core molecule tends to increase the DOB in HBP's. For comparison, we synthesized a polymer with no core molecule. Much to our surprise, DSC analysis (Figure 6) showed that the T_g of the polymer incorporating the core molecule (249 °C) was significantly higher than that of the polymer from only AB₂ monomer (227 °C).

Using GPC and NMR, we plan to characterize the degree of branching of polymers with various ratios of core molecules. After characterizing the polymers themselves, we next plan to incorporate them into BMI thermosets and to study their effect on pre-cure viscosity and toughening in the final thermoset. By correlating the structural characteristics of the PAEKI with performance properties, we will be able to optimize the polymerization parameters to produce an HBP additive that will strengthen the properties of the BMI thermoset.

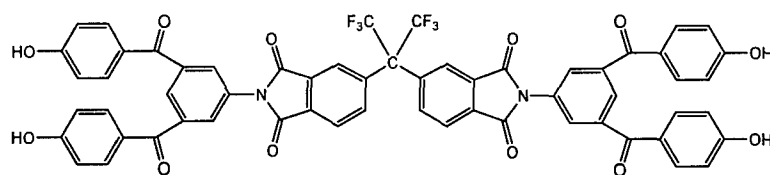


Figure 5. Chemical composition of the B4 core molecule copolymerized with BT-PAEKI monomer.

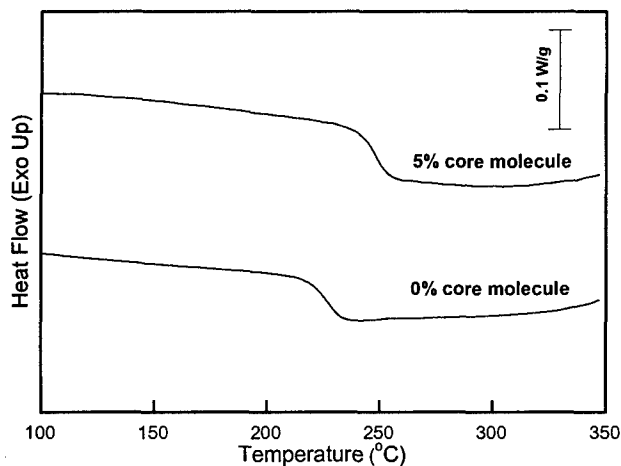


Figure 6: DSC results of the PAEKI homopolymer and copolymer with B₄ core molecule during a ramp of 10 °C/min to 350 °C. With 5 mol-% of B₄ core molecule, the T_g is 249 °C, significantly higher than the PAEKI homopolymer (227 °C).

c. Measurement of DOB of PAEKI by model compounds studies.

A reliable method of measuring DOB with considerable accuracy is needed to better understand the influence of DOB on the properties of hyperbranched additives. Researchers have proved the model compound study as an efficient way to determine the DOB of hyperbranched polymers. We designed model compounds, as shown in Figure 7, to study the DOB in PAEKI.

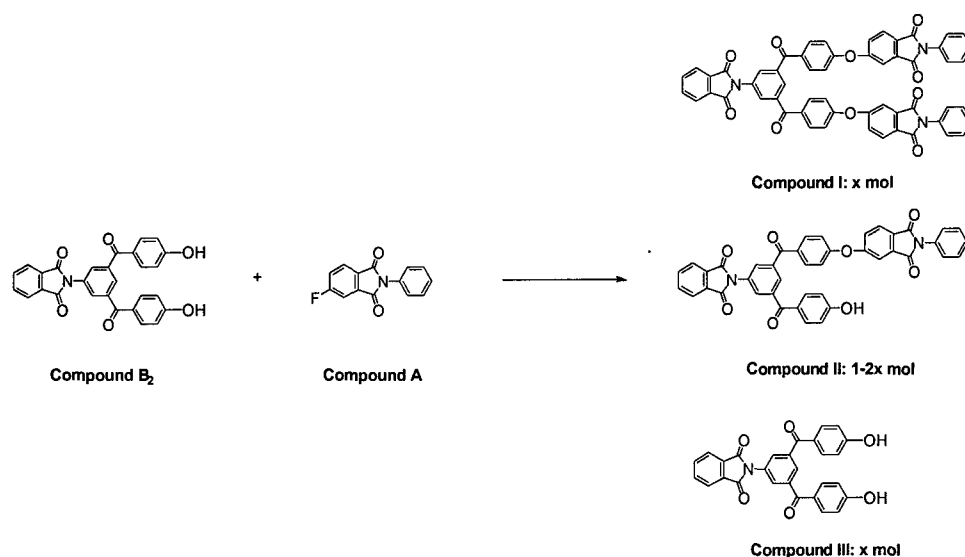


Figure 7: Synthesis and structures of model compounds for DOB measurement of PAEKI.

In Figure 7, the compounds I, II and III are models for branching (**B**), linear (**L**) and terminal (**T**) units of PAEKI, respectively. By analogy, the DOB of PAEKI equals:

$$DOB = \frac{B + T}{B + T + L} = \frac{I + III}{II} = 2x$$

In addition to the indirect method described above, direct measurement of DOB is possible by ¹H-NMR. First, using the model compound study, we can identify the chemical shift of the branching and linear units in PAEKI. By integrating the areas of these peaks, the DOB of PAEKI can be calculated.

So far, we have completed the synthesis of compound A and the first three of five synthetic steps to compound B₂.

d. Synthesis of Hyperbranched Liquid-Crystalline Polymers

We are working on a hyperbranched liquid-crystalline polymer (HB-LCP) for use as a possible additive in liquid-crystalline elastomers (LCEs) and liquid crystalline thermosets (LCTs). Toward this end, we have successfully synthesized a trifunctional liquid crystalline monomer (A₃ monomer) that can be reacted with difunctional silanes (B₂ monomer). The chemistry is shown schematically in Figure 8.

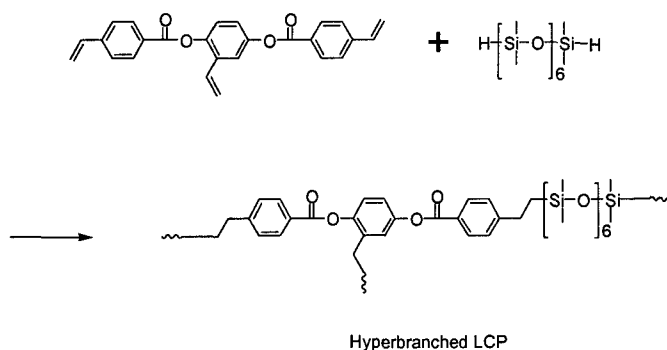


Figure 8: Schematic representative of synthesis of hyperbranched liquid crystalline polymer (LCP) from tri-ene liquid crystalline monomer and difunctional silane.

In addition, we have synthesized a monomer from vinyl benzoic acid and 3-methyl hydroquinone to better understand of the polymerization reaction. It appears to be nematic and homeotropic by POM. Melting occurs at 140 °C, at which point it immediately begins to crosslink (slowly at temperatures just over melting). There is a T_{NI} at about 195 °C for the uncrosslinked material. We have also polymerized this methyl LC monomer with HPDMS-7. The resultant polymer appeared as a clear, yellow, rubbery material. DSC analysis showed no signs of liquid crystallinity. We are presently synthesizing HB-LCPs using the reaction scheme shown in Figure 8. With the materials, we will examine the phase behavior

IV. Personnel Supported

- a. Number of PI's and Co-PI's involved in the research project: **1**
PI: Prof. Patrick T. Mather
- b. Number of Post Doc Supported in the last 12 months under AFOSR: **0**
- c. Number of graduate students supported in the last 12 months: the equivalent of **2** graduate assistants. Haihu Qin and Timothy Marsh
- d. Other researchers supported in the last 12 months by AFOSR: **0**

V. Publications

Publications by PI submitted, accepted, or appearing in the last 12 months period in refereed journals and referencing AFOSR support: **4**

H. Qin, "High Performance Thermosets: Liquid Crystalline Networks and Reactive Hyperbranched Additives," PhD Dissertation, University of Connecticut (2004).

T.D. Dang, P.T. Mather, M.D. Alexander, M.D. Houtz, R.J. Spry, F.E. Arnold, "Synthesis of aromatic benzoxazole polymers for high Tg, low dielectric properties," *Polyimides and Other High Temperature Polymers*, **2**, 205-223 (2003).

H. Qin, P.T. Mather, J.-B. Baek, and L.-S. Tan, "Hyperbranched Poly(arylene-ether-ketone-imide)s: Rheological and Thermomechanical Properties of Blends with a Bismaleimide," in preparation *Polymer* (2003).

G.-M. Kim, H. Qin, X. Fang, F.C. Sun, and PTM, "Hybrid Epoxy-Based Thermosets Based on Polyhedral Oligosilsesquioxane (POSS): Cure Behavior and Toughening Mechanisms," *J. Polym. Sci. B: Polym. Phys. Ed.* **41**, 3299-3313 (2003).

VI. Interactions and Transitions

a. Participation and Presentations at Meetings

Invited Lectures (8)

Army Research Laboratory, AMSRL-WM-MA, "Overview of Structural and Functional Polymers Research," Aberdeen Proving Ground, MD, July 12, 2004.

Materials Integrity Management Symposium, "Shape Memory Polymers: Materials Overview and Application Proposals," Boston, MA, June 8-9, 2004.

ACS International Workshop on Branched Polymers for Performance, "High Tg hyperbranched polymers as thermoset processing and toughening aids," May 23-26, 2004.

SPE Polym. Anal. Div. Founder's Award honoring M.T. Shaw, "Strain Fixing and Recovery in Liquid Crystalline Networks," May 18, 2004.

University of Massachusetts at Lowell Polymer Science Colloquium, "Smectic LC Elastomers," March 11, 2004.

SAMSI Workshop on Multi-scale Challenges in Soft Matter Materials, "Trends in Experimental Studies of Soft Materials," February 15-17, 2004.

Trinity College, "Shape Memory of New Siloxane-Based Liquid Crystalline Elastomers," January 30, 2004.

Crompton Corporation, "Precision Amphiphilic Hybrids: Self-Assembly in Telechelic and Multiblock Architectures" November 6, 2003.

Contributed Talks (11)

C. Liu and P.T. Mather, "High thermal conductivity shape memory polymers," *SPE ANTEC* Polymer Analysis Division, Chicago, IL, May 2004.

Jian Wu and P.T. Mather, "Capillary Instabilities of thin nematic liquid crystalline polymer fibers embedded in a flexible polymer matrix" American Physical Society Annual March Meeting, DPOLY, Montreal Canada, March 25, 2004.

I.A. Rousseau, H. Qin, and P.T. Mather, "Strain Fixing and Recovery in Liquid Crystalline Elastomers," American Physical Society Annual March Meeting, DPOLY, Montreal Canada, March 25, 2004.

Eckrote KA, Rojanapitayakorn P, Mather PT, Weiss RA, Prasad A, Karmaker AC, Goldberg AJ. Glass fiber reinforced thermoplastics for dental CAD/CAM [abstract 1392]. *Journal of Dental Research* 2004; 83(Special Issue A).

C.J. Lefaux, B.-S. Kim, and P.T. Mather, "Layer-by-Layer Deposition of Molecular Composites on Quartz and Nafion Membranes," First International Conference on Fuel Cell Development and Deployment, University of Connecticut, Storrs, CT, March 7-10, 2004.

I.A. Rousseau, H. Qin, and P.T. Mather, "Smectic Liquid Crystalline Elastomers," SAMSI Workshop on Multi-scale Challenges in Soft Matter Materials, Research Triangle Park, NC, February 15-17, 2004.

Jian Wu and P.T. Mather, "The Nematic-Isotropic Interface," SAMSI Workshop on Multi-scale Challenges in Soft Matter Materials, Research Triangle Park, NC, February 15-17, 2004.

Jian Wu, T.S. Haddad, and P.T. Mather, "Rheological behavior of polystyrene (PS) with incorporation of hybrid polyhedral oligosilsesquioxane (POSS)," 75th Annual Meeting of the Society of Rheology, Pittsburgh, PA, October, 2003.

Jian Wu, P.T. Mather, "Orientation effects on the capillary instabilities for thin liquid crystalline fibers embedded in a flexible polymer matrix," 75th Annual Meeting of the Society of Rheology, Pittsburgh, PA, October, 2003.

Changdeng Liu, J. Wu, and P.T. Mather, "Nonisothermal crystallization kinetics of polycyclooctene: Characterization using thermal and optical methods," *ACS National Meeting*, PMSE Division, New York, August, 2003.

I.A. Rousseau, H. Qin, P.T. Mather. "New Siloxane-based Liquid Crystalline Blends, Copolymers and Main-Chain Elastomers with Mixed Mesogens for Tailored Properties," *Second International Workshop on Liquid Crystalline Elastomers*, Bleibach, Germany, September 2003.

- b. Consultation and Advisory Functions with other Laboratories and Agencies
 This project is a close collaboration with Dr. Loon-Seng Tan of AFRL/MLBP on hyperbranched polymers of direct use in this program. Numerous conversations and conferences at scientific meetings have been conducted toward designing of polymers for high toughness and Tg.

c. No transitions to practiced technology exist for this research as yet.

VII. New Discoveries, Inventions or Patent Disclosures. None

VIII. Awards and Honors received by the PI (life-time received): 16

Rogers Corporation Award for Outstanding Teacher in Chemical Engineering	2003
SPE Medical Plastics Division, ANTEC 2002 Best Paper Award	2002
Member of AFOSR Star Team, "Lightweight Low-Cost Membrane Structures"	2002
School of Engineering Outstanding Junior Faculty Award, University of Connecticut	2001
NSF CAREER Award, "Orientational Dynamics in Flows of Thermotropic Polymers"	2001-2006
AFRL-Sponsored Assessment Team, "Applicability of Organic Matrix Composites to Cryogenic Rocket Propulsion applications,"	Spring 2001
Who's Who in Plastics and Polymers	1999
SPE Engineering Properties and Structure Division, <i>Best Paper</i> , 55 th ANTEC	1997
Member of AFOSR Star Team, "Inorganic Synthesis"	1997
USAF Palace Knight Fellowship	1992-1994
National Defense Science and Engineering Grad. Fellowship (A.R.O.)	1989-1992
University Scholars - Penn State Honors Curriculum	1986-1989
Tau Beta Pi	1988-present

Best Summer Research, Rohm and Haas Company

1988

Golden Key National Honor Society

1989-present

George Gleeson Scholarship for Undergraduate Research

1989-1990

REPORT DOCUMENTATION PAGE

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