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MENTATION PAGE

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Technical report

2

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6. AUTHOR(S) Bruce M. Novak			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of California, Berkeley Department of Chemistry Berkeley, CA 94720		8. PERFORMING ORGANIZATION REPORT NUMBER	
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13. ABSTRACT (Maximum 200 words) We, as well as others, have been interested in the sol-gel process for the synthesis of hybrid inorganic/organic composite materials. Since our first report on the application of tetraalkoxysilanes possessing polymerizable alkoxides for the production of non-shrinking sol-gel composites, we have extended our efforts towards increasing the glass content in these composite materials. The stoichiometry in the tetraalkoxysilanes limits the maximum glass content in the original non-shrinking composites to 10-18%. In order to increase the glass content to greater than 50%, we focused our efforts toward the use of silicic acid oligomers. Molecular weights of the poly(silicic acid) materials have been varied from $M_n = 5,000$ to 2,000,000 by controlling reaction conditions. In addition, branching ratios (i.e., linear vs. spherical particles) can be controlled by changing the catalysts used. The properties of the resulting composite can range from a transparent flexible material to a transparent hard material simply by changing the organic polymer in the composite.			
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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT Number: N00014-91-J-1772

START DATE: APRIL 15, 1991

R&T CODE: 413m027

**Ultra-Low Density Organic-Inorganic Composite Materials
Possessing Thermally Insulating and Acoustic Damping Properties**

Bruce M. Novak

**Department of Chemistry
University of California
Berkeley, California 94720**

May 7, 1992

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**Office of Naval Research
Publications/Patents/Presentations/Honors Report**

R&T Number: 413m027

Contract/Grant Number: N00014-91-J-1772

Contract/Grant Title: Ultra-Low Density Organic-Inorganic Composite Materials Possessing Thermally Insulating and Acoustic Damping Properties

Principle Investigator: Bruce M. Novak

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University of California
Berkeley, California 94720

Phone Number: 1-510-643-7536 **FAX Number:** 1-510-642-8369

E Mail Address: novak@violet.berkeley.edu

- a. Number of papers submitted to refereed journals, but not published: 1
- b. Number of papers published in refereed journals (list attached): 2
- c. Number of books or chapters submitted, but not yet published: None
- d. Number of books or chapters published (list attached): None
- e. Number of printed technical reports & non-refereed papers (list attached): 2
- f. Number of patents filed: 1
- g. Number of patents granted (list attached): None
- h. Number of invited presentations at workshops or professional society meetings: 19
- i. Number of presentations at workshops or professional society meetings: N/A
- j. Honors/Awards/Prizes for contract/grant employees (list attached): See Attached List
(This might include Scientific Society Awards/Offices, Promotions, Faculty Awards/Offices)
- k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period, under this R&T project number: 3
 - Graduate Students: 3
 - Post-Doctoral Associates: 0
 - including the number of
 - Female Graduate Students: 1
 - Female Post-Doctoral Associates: 0
 - the number of
 - Minority Graduate Students: 0
 - Minority Post-Doctoral Associates: 0
 - and, the number of
 - Asian Graduate Students: 0
 - Asian Post-Doctoral Associates: 0
- l. Other funding: N/A

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**Office of Naval Research
Publications/Patents/Presentations/Honors Report**

PART I:

ONR Grant, R&T Number: 413m027

Project Start Date: April 15, 1991

Funding Received: \$72,000

b. Published Papers in Refereed Journals:

1. "Mutually Interpenetrating Inorganic-Organic Networks. New Routes into Non-Shrinking Sol-Gel Composite Materials;" Ellsworth, M. W.; Novak, B. M. *J. Am. Chem. Soc.* 1991, 113, 2756.
2. "Inverse" Organic-Inorganic Composite Materials 2. Free Radical Routes into Nonshrinking Sol-Gel Composites;" Novak, B. M.; Davies, C. *Macromolecules* 1991, 24, 5481.

e. Published Non-Refereed Journals:

1. "Inverse" Organic-Inorganic Composite Materials 2. Free Radical Routes into Nonshrinking Sol-Gel Composites;" Novak, B. M.; Davies, C. *Polymer Preprints* 1991, 32, 512.
2. "Functionalized Silicic Esters for the Synthesis of Non-Shrinking Sol-Gel Composites;" Ellsworth, M. W.; Novak, B. M. *Polymer Preprints*, 1992, 33, 1088.

f. Patents Filed:

1. "Mutually Interpenetrating Inorganic-Organic Networks. New Routes into Non-Shrinking Sol-Gel Composite Materials;" Ellsworth, M. W.; Novak, B. M. US Patent, Pending, 1991.

h. Invited Seminars/Presentations:

1. May 21, 1991, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" Corning Glass, Corning, NY.
2. June 12, 1991, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" Chevron Research, Richmond, CA.
3. August 28, 1991, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" American Chemical Society National Meeting, New York, NY.

4. September 12, 1991, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" Materials Science Department, University of California, Berkeley, CA.
5. October 18, 1991, "Polymer Synthesis: From Organic-Inorganic Composite Materials to Water-Soluble Rigid Rod Polymers;" Procter & Gamble Corporation, Miami Valley, OH.
6. October 24, 1991, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" Air Force Workshop on Ceramic Materials, Bolling AFB, Washington, DC.
7. October 25, 1991, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" Dow Corning Corporation, Midland, MI.
8. October 26, 1991, "Transition Metals in Polymer Synthesis;" Dow Corning Technical Exchange Seminar, Dow Corning Corporation, Midland, MI.
9. November 22, 1991, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" Applied Science and Technology Seminar, University of California, Berkeley, CA.
10. December 17, 1991, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" Rohm and Haas Corporation, Philadelphia, PA.
11. January 6, 1992, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" Polymers West Gordon Conference, Ventura, CA.
12. February 26, 1992, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" E. I. DuPont de Nemours and Company, Philadelphia, PA.
13. March 5, 1992, "Architectural Design in Polymer Synthesis via Living Transition Metal Complexes;" University of California, Los Angeles, CA.
14. March 13, 1992, "Biodegradable Polymers: Sand and Potato Composite Materials;" Procter & Gamble Company, Miami Valley, OH.
15. March 26, 1992, "Frontiers in Polymer Synthesis;" National Research Conference on the Frontiers in Polymer Chemistry, Washington, DC.
16. April 28, 1992, "Architectural Design in Polymer Synthesis via Living Transition Metal Complexes;" Moretonhampstead High Polymer Meeting,

Moretonhampstead, United Kingdom.

17. May 5, 1992, "Architectural Design in Polymer Synthesis via Living Transition Metal Complexes;" University of Chicago, Chicago, IL.
18. May 12, 1992, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" Eastman Kodak Company, TN.
19. May 13, 1992, "Inverse Organic-Inorganic Composite Materials: New Routes into Nonshrinking Sol-Gel Composites;" BF Goodrich, Brecksville, OH.

j. Honors/Awards/Prizes :

1. Principal Investigator:

- a. NSF Presidential Young Investigator Award, 1991-96
- b. Alfred P. Sloan Research Fellow, 1991-1992
- c. Lawrence Berkeley Laboratory Young Investigator Award, 1991-1994
- d. DuPont Young Investigator Award, 1991
- e. Rohm and Haas Summer Faculty Fellowship, 1992
- f. 3M Nontenured Faculty Award, 1992
- h. Merit Increase, Department of Chemistry

2. Students:

- a. National Science Foundation Graduate Fellowship, Lisa Boffa
- b. Kodak Graduate Fellowship, Mark Ellsworth
- c. Department of Education Graduate Fellowship, David Auerbach

k. Graduate Students

1. Lisa Boffa (Female)
2. Mark Ellsworth
3. David Auerbach

**Office of Naval Research
Publications/Patents/Presentations/Honors Report**

PART II:

- a. **Principal Investigator:** Bruce M. Novak
- b. **Telephone Number:** 1-510-643-7536
- c. **ONR Scientific Officer:** Dr. Kenneth Wynne

d. **Brief Description of Project:** We are investigating the design and synthesis of strong, ultra-low density xerogel and aerogel composites reinforced by either the incorporation of high-modulus, heat-resistant polymers, or by the simultaneous formation of three-dimensional, cross-linked polymer networks, which interpenetrate, and hence, strengthen the inorganic superstructure. Additional synthetic methods are being pursued which should virtually eliminate the truculent shrinkage problem currently associated with the sol-gel technique. These techniques should allow for the first time, room temperature preparation of fully-dense, xerogels which do not require high temperature sintering processes. Ultra-low density materials of this type would have applications in a broad range of areas including lightweight engine components, high temperature coatings, aircraft wings, thermally insulating materials, acoustic damping materials or coatings and numerous other lightweight structural applications. As these materials can be formed optically transparent, they can compete in a number of arenas in which other, low-density graphitic composites are inappropriate. For example, reinforced, sound damping, low-density windows, mirrors, solar panels, insulating portholes and optical devices for vessels and air- and spacecraft can be envisioned. This proposal represents a unique approach which combines three well-developed, but historically separate areas of science; sol-gel derived inorganic glasses, high-modulus, heat resistant polymers and interpenetrating polymer networks. The marriage of these three existing technologies enables us to create a new class of ultra low-density and acoustic damping materials.

e. **Significant Results During Last Year:** Our "genesis" nonshrinking composites involved the formation of tetraalkoxysiloxanes possessing polymerizable alcohols that, after their hydrolysis from the silicon center, are polymerized *in situ* resulting in a nonshrinking, interpenetrated network. One limitation is that the glass/polymer ratio of the resultant composite is fixed by the stoichiometry of the tetraalkoxysilane and ranges from *ca.* 5 - 18% SiO₂. We have recently developed a new class of poly(silicic acid) polymers possessing polymerizable alkoxide moieties that can be hydrolyzed and polymerized in the same fashion to yield exceptionally hard, transparent composite materials with glass contents now ranging up to nearly 70%.

f. **Brief Summary of Plans for Next Year's Work:** We are continuing in the development of these non-shrinking sol-gel formulations in both the low- and high-glass regimes. Further work will include the investigation of new monomers to

provide polymers possessing a greater range of physical properties such as lower T_g 's to provide impact resistance or high modulus polymers to build strength. Accompanying this synthetic work, we will begin to investigate the mechanical properties (compressive yield strengths, modulus of elasticity, etc.). This mechanical testing is anticipated to provide a critical leg in the design of second generation materials. In addition, we plan to investigate the formation of ultra-low density composites using supercritical universal drying (SCUD) techniques. SiO_2 aerogel materials can routinely be formed using SCUD with densities as low as 0.100 g/ml. Inorganic aerogels are, by themselves, extremely brittle and crumble with simple handling, but our recent results indicate that homogeneously blending small amounts of polymer within these materials substantially increases their strength, improves their optical clarity, and decreases their processing times. We have initiated a systematic investigation into polymers that remain soluble, and hence, homogeneously embedded in the SiO_2 matrix under SCUD conditions. We anticipate a new class of ultra-low density composites resulting from this work.

g Names of Graduate Students Working on Project:

1. Lisa Boffa
2. Mark Ellsworth
3. David Auerbach

Office of Naval Research
Publications/Patents/Presentations/Honors Report

PART III:

- a. **Introductory "vu-graph":** Attached
- b. **Figure:** Attached.
- c. **Concluding "vu-graph":** Attached
- d. **Explanation:**

1. **Introductory "vu-graph":** We have been interested in exploring the reverse side of traditional glass-fiber reinforced, organic polymer composites by developing methods for homogeneously embedding organic polymers within inorganic glass matrices. Although "inverted," the basic composite principles remain intact, but now the advantages (and occasionally synergistic) relationship can result from the combination of a high-modulus organic polymer (providing high tensile strength) or an amorphous elastomer (providing improved impact resistance) with a three-dimensionally cross-linked, inorganic matrix (providing high compressive strength). The realization of these inverted organic-inorganic materials requires forming the inorganic matrix under conditions in which the organic polymers will survive. Our approach will be the synthesis of optically-transparent, simultaneous interpenetrating composites through the synchronous formation of both the inorganic and organic components. This will be accomplished by the hydrolysis and condensation of tetraalkenyl orthosilicates (the sol-gel process) to form an inorganic SiO_2 matrix while simultaneously eliminating unsaturated alcohols which are polymerized *in situ* using free radical techniques. This simultaneous approach utilizing polymerizable alkoxides circumvents the insolubility problem often associated with organic polymers in the sol-gel precursor solutions, while at the same time eliminates the ubiquitous shrinkage problem associated with drying of sol-gel derived xerogel materials.

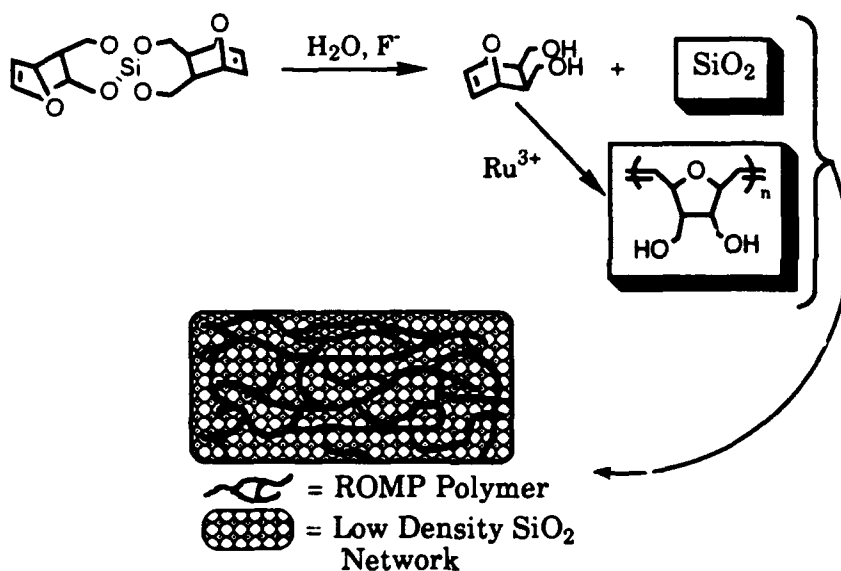
2. **Figure:** We have found that, under the right circumstances, the two components of these simultaneous interpenetrating networks display synergistic, non-additive behavior. The attached figure shows the dynamic storage modulus as a function of time for three reactions: the independent free radical polymerization of 2-hydroxyethylacrylate, the simple hydrolysis of the tetraalkoxyorthosilane to form SiO_2 , and finally, the simultaneous formation of both the inorganic SiO_2 phase and the organic polymer phase.

3. **Concluding "vu-graph":** When forming composite materials such as the one depicted in the figure, the glass/polymer ratio is dependent only upon the stoichiometry of the tetraalkoxyorthosilane monomer. As a result, the glass percentages have been limited to less than 17%. In order to synthesize composites with higher glass contents (i.e., greater than 50%), we have initiated a project based on the

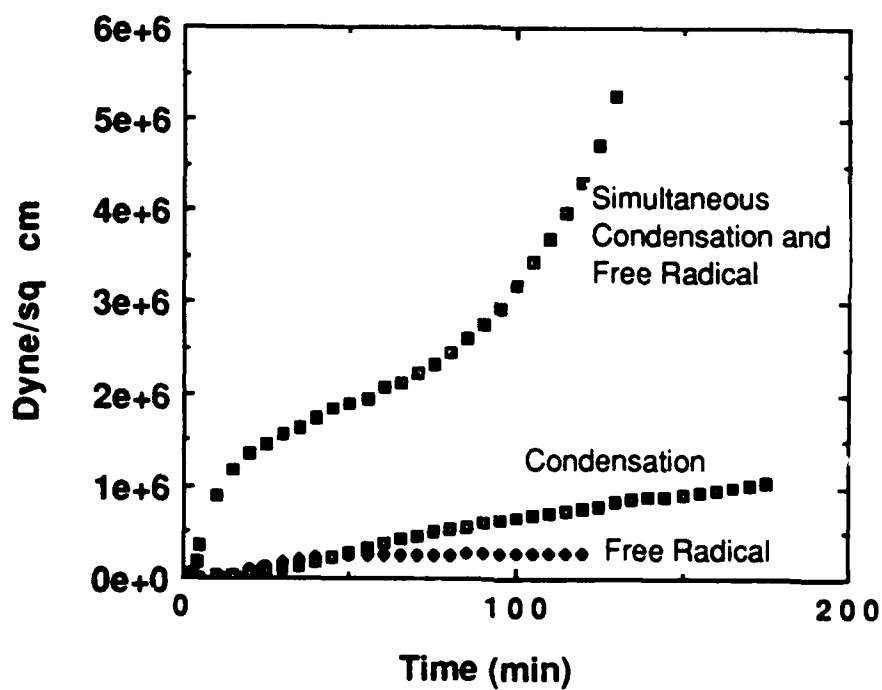
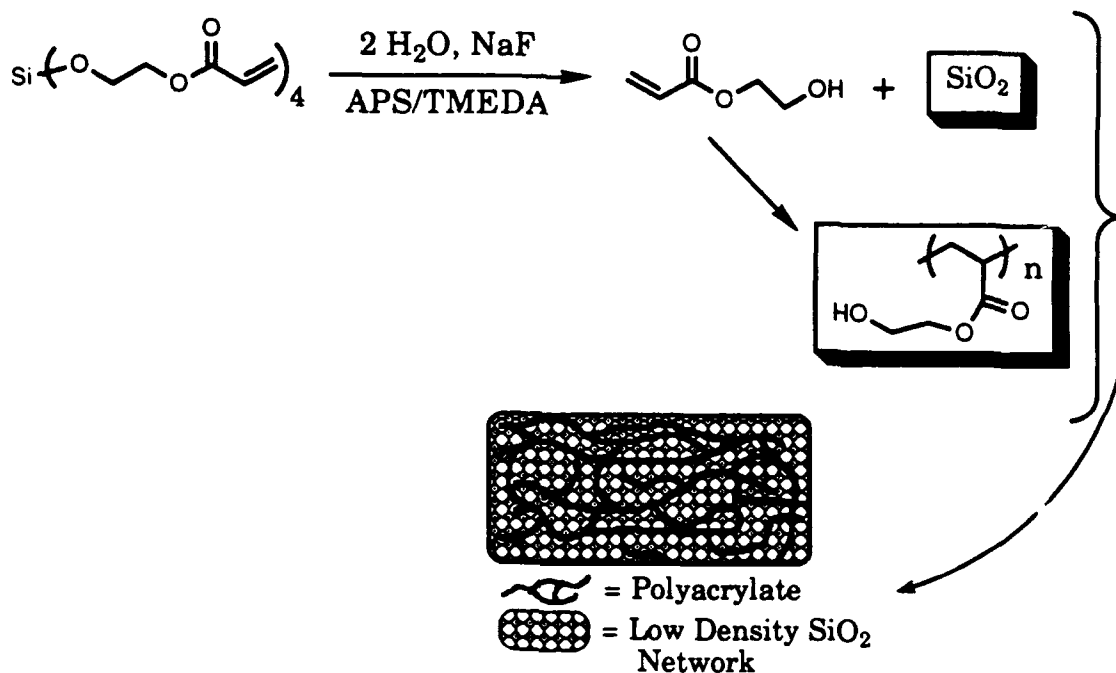
synthesis of soluble, pre-condensed SiO_2 polymers that are substituted with polymerizable alcohols. By controlling both the degree of branching of the poly(silicic acid) chains in these polymers and the substitution level of the alkoxide, composite with glass contents ranging from a few percent to over seventy percent can now be fabricated.

Organic-Inorganic Simultaneous Interpenetrating Networks: New Routes into Nonshrinking Sol-Gel Composites

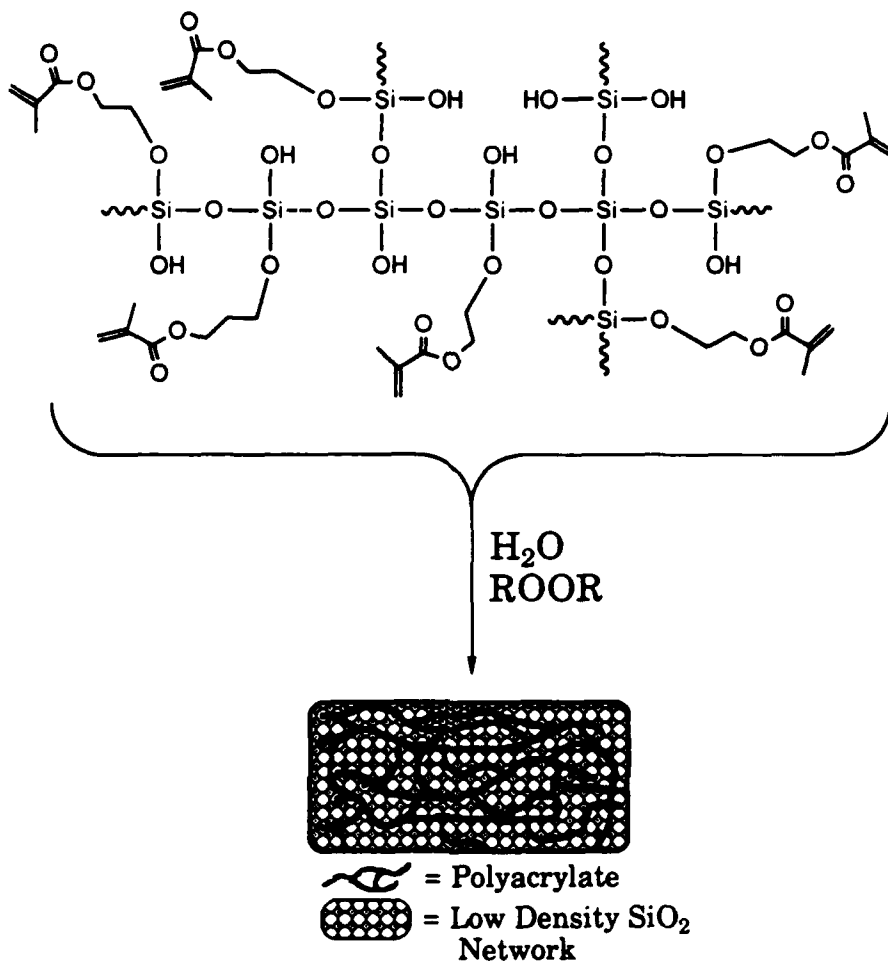
Bruce M. Novak
Department of Chemistry
University of California
Berkeley, California 94720



Dynamic Storage Modulus: Independent vs. Simultaneous Reactions



Poly(Silicic Acid) Precursors to Nonshrinking Sol-Gel Composites



Composite Properties

- Optically Transparent
- Low Densities
- Glass Contents 2 - 70%
- Mechanical Properties Vary:
Rubbery - Brittle Glasses