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FABRICABLE POLYMERS FOR MATRICES AND ADHESIVES WHICH ARE EXTREMELY STABLE TO HEAT, OXIDATION AND HYDROLYSIS

Carl S. Marvel
Department of Chemistry
The University of Arizona
Tucson, Arizona 85721

Final Report

AFOSR ~~Contract~~-77-3112

from

October 1, 1976 to December 31, 1981

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Personnel:

Dr. Richard L. Frentzel	October 1, 1976 - September 30, 1977
Dr. Robert S. Cutler	April 13, 1977 - June 15, 1977
Dr. Steve K. Huang	January 1, 1977 - August 31, 1977
Dr. Steven R. Morehead	September 16, 1977 - December 15, 1977
Dr. Shiow-Ching Lin	November 17, 1977 - August 4, 1978
Dr. Venkatesa Sankaran	December 20, 1977 - October 20, 1979
Dr. Andreas Somers	October 1, 1978 - July 24, 1979
Dr. Paul Chen	December 5, 1979 - May 21, 1980
Dr. George Kriek	November 27, 1979 - July 1, 1980
Dr. See Lin	June 9, 1980 - and continuing
Dr. B. H. Lee	September 1, 1980 - and continuing

United States Air Force
Air Force Office of Scientific Research
Building 410
Bolling Air Force Base, D. C. 20332

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MATTHEW J. KERPNER
Chief, Technical Information Division

Publications:

1. Shioh-Ching Lin and C. S. Marvel, "New Processable Polyaromatic Ether-Keto-Sulfones Curable by Intramolecular Cyclization," J. Polym. Sci., Polym. Chem. Ed., 17, 2337-2350 (1979).
2. V. Sankaran and C. S. Marvel, "Polyaromatic Ether-Ketone-Sulfones Containing 1,3-Butadiene Units," J. Polym. Sci., Polym. Chem. Ed., 17, 3949-3957 (1979).
3. Richard L. Frentzel and C. S. Marvel, "Heat-Curable Polyaromatic Keto-Ether-Sulfones. XIV. More Polymers with 2,2'-Diphenylethynyl-4,4'-Diphenyl Units and Their Rearrangement Products," J. Polym. Sci., Polym. Chem. Ed., 17, 1073-1087 (1979).
4. V. Sankaran, Shioh-Ching Lin and C. S. Marvel, "New Processable Polyaromatic amides Curable by Intramolecular Cyclization. XVI," J. Polym. Sci., Polym. Chem. Ed., 18, 495-503 (1980).
5. A. Somers and C. S. Marvel, "New Processable Poly(ether-Keto-Sulfone)s, Poly(arylene Sulfone)s, and Polyesters Curable by Intramolecular Cyclization. XVII," J. Polym. Sci., Polym. Chem. Ed., 18, 1511-1521 (1980).
6. V. Sankaran and C. S. Marvel, "New Processable Polyaromatic Ether-Keto-Sulfones Curable by Diels-Alder Cycloaddition," J. Polym. Sci., Polym. Chem. Ed., 18, 1821-1834 (1980).
7. Paul Y. Chen and C. S. Marvel, "New Processable Polyaromatic Esters Curable by Intramolecular Cyclization. XVIII," J. Polym. Sci., Polym. Chem. Ed., 19, 619-627 (1981).
8. Byung H. Lee and C. S. Marvel, "New Processable Polyaromatic Ether-Keto-Sulfones as Colorless, Clear Film-Forming Materials," in press.
9. See Lin, George R. Kriek and C. S. Marvel, "New Processable Polyaromatic Keto-Sulfones with Internal Acetylene Units," in press.

Patents:

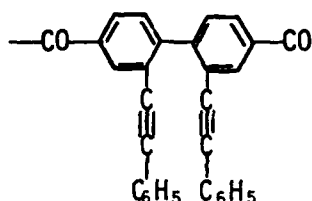
All of the above papers have been converted to patent outlines, and they have all been released to the AFOSR by our University. At the present time, these patent applications are in the hands of Mr. William J. O'Brien, Patent Attorney, Department of the Air Force, AFJACPB Bldg. 104, 424 Trapelo Road, Waltham, MA 02154. I have been in touch with him from time to time to answer questions. I do not have the patent applications numbers or dates to furnish you, since he has taken care of all of that, but I'm certain that none of the patents have been issued yet.



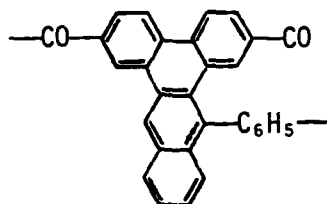
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Brief Summary of Results:

The titles of published papers indicate in general what we have accomplished. Dr. Frentzel and Dr. Cutler worked on polyaromatic ketones containing the unit



which could be cured by heating to give the unit



These polymers produced good laminates but were somewhat intractable and did not have as good oxidation stability as hoped for.

Dr. Shio-Ching Lin developed a satisfactory synthesis of 2,2'-di-bromo-4,4'-diphenic acid which he converted by Friedel-Craft reaction with 4,4'-diphenoxydiphenyl sulfone and isophthaloyl chloride, and he later treated that polymer with copper phenylacetylene to obtain the 2,2'-diphenylethynyl derivative, which gave an interesting laminating resin.

Dr. Sankaran prepared the p,p'-dicarboxylic acid of 1,4-diphenyl-1,3-butadiene, and by Friedel-Craft reaction with diphenyl ether, obtained the polymer which was very difficult to fabricate, and hence not tested further.

Dr. Somers made polyether-ketone-sulfones, polyarylene sulfones, and polyesters which were curable by molecular cyclization. The products were expensive and were not developed further.

Dr. Sankaran and Dr. Shiow-Ching Lin prepared a variety of polyaromatic amides which could be cured by intramolecular cyclization, and these gave promising laminating resins.

Dr. Chen prepared a series of polyaromatic esters which could be cured by the intramolecular cyclization method. These esters were easily soluble and tractable before curing. After curing they were insoluble with increased thermo-stability. The curing process raised the softening temperature by about 20°C and increased the heat stability of the polymers. They lost very little weight at 300°C in circulating air for three days. They made good laminates. The curing requires 270° for 30 hours, which is a drawback to their practical use.

Dr. See Lin and Dr. Lee have worked on the m- and p-dicarboxylic acid derivatives of diphenylacetylene and prepared very interesting polymers by Friedel-Craft reaction with diphenyl ether and diphenoxydiphenyl sulfone. Both the meta and the para isomers gave excellent, clear films which remain clear up to nearly 300°C, and seem to offer promise as replacements for polymethyl methacrylate as a canopy for fighter planes. Although we could get perfectly clear, thin films, we could not melt the product to obtain large pieces such as would be needed for canopies without a yellowing developing, which made them seem less promising than before. They still are under consideration but do not seem as promising as they first did.

At the present time, Dr. See Lin is working on a p-cyclophane derivative in which the bridged portion between the two rings is fluorinated, and then this is converted to the keto ether with isophthaloyl chloride. The product is quite stable to heating and oxidation and can be cured on heating. It does give a laminate but this is still under study and not ready for final evaluation.

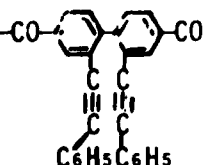
Dr. Lee is currently working with 1,5-diamino-2,6-dimercaptoanthraquinone and condensing it with 2,5-dichlorobenzoquinone to obtain a new type of polymer which is very heat stable but also very intractable. We are still studying it to find a way to convert it into a useful polymer.

Interim reports have been reported to the Air Force Office of Scientific Research in 1977, 1978, 1979, and 1980.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The report covers work on preparation of polyaromatic ketones, polyaromatic sulfones from diphenyl ether, and iso- and terephthaloyl chloride with units of  which can be used to crosslink polymers. We have also worked on the polyether-keto-sulfones and polyesters, polyaromatic amides, and polyaromatic esters of aromatic diphenols.		

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