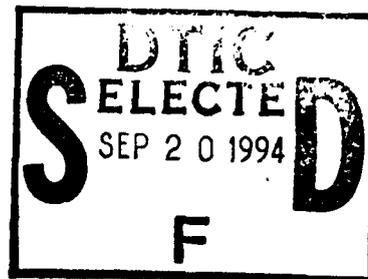


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**OFFICE OF NAVAL RESEARCH**

**FINAL TECHNICAL REPORT**

for

1 October 1989 through 30 September 1992

for

Contract N00014-90-J-1261

**Investigation of Chemical and Physical Properties of  
Surface - Modified Chemically Resistant Polymers**

by

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**94-30239**



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**Papers Published in Refereed Journals**

1. *Macromolecules* **1990**, *23*, 366 (with B.U. Kolb and P.A. Patton)  
"Reactions of Polystyryl Anions with Poly(chlorotrifluoroethylene) Film at the Solution-Solid Interface"
2. *Macromolecules* **1990**, *23*, 2648 (with R.C. Bening)  
"Surface Modification of Poly(tetrafluoroethylene-co-hexafluoropropylene). Introduction of Alcohol Functionality"
3. *Macromolecules* **1990**, *23*, 3916 (with E.M. Cross)  
"Thermal Reconstruction of Surface-Functionalized Poly(chlorotrifluoroethylene)"
4. *Chimia* **1990**, *44*, 11  
"Organic Chemistry at Chemically Resistant Polymer Surfaces: Modification of Surface Reactivity and Surface Properties"
5. *Macromolecules* **1991**, *24*, 982 (with M.S. Shoichet)  
"Convenient Syntheses of Carboxylic Acid Functionalized Fluoropolymer Surfaces"
6. *Macromolecules* **1991**, *24*, 3045 (with N.L. Franchina)  
"Surface Modifications of Poly(ether ether ketone)"
7. *Macromolecules* **1992**, *25*, 2093 (with T.G. Bee)  
"Surface Modification of Poly(chlorotrifluoroethylene): Introduction of Reactive Carboxylic Acid Functionality"
8. *Macromolecules* **1992**, *25*, 2603 (with E.M. Cross)  
"Radical Chlorination of Polyethylene Film: Control of Surface Selectivity"

**Chapters in Books**

1. *Concise Encyclopedia of Polymer Science and Engineering* Kroschwitz, J.I., Ed., John Wiley & Sons, Inc., New York: 1990, 1152 (with W.J. Ward)  
"Surface Modification"

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**(Chapters in Books)**

2. *Materials Synthesis Based on Biological Processes* (M. Alper, P.C. Rieke, R. Frankel, P.D. Calvert and D.T. Tirrell, Eds.), Materials Research Society, 1991 (with M.S. Shoichet)  
"Poly(L-lysine) Adsorption to Fluoropolymer Films"
3. *Chemically Modified Surfaces* (H.A. Mottola and J.R. Steinmetz, Eds.) Elsevier, 1992 (with N.L. Franchina)  
"Poly(ether ether ketone) Surface Chemistry"

**Papers Published in Non-Refereed Journals**

1. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1989**, 30(2), 152  
(with J.V. Brennan)  
"Surface Modification of Poly(vinylidene fluoride): Introduction of Reactive Handles"
2. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1990**, 31(1), 416  
(with N.L. Franchina)  
"Carbonyl Surface Chemistry of Poly(ether ether ketone)"
3. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1990**, 31(1), 418  
(with M.S. Shoichet)  
"Shortcuts to Carboxylic Acid - Functionalized Fluoropolymer Surfaces"
4. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1990**, 31(1), 422  
(with E.M. Cross)  
"Controlled Chlorination of Polyethylene Surfaces"
5. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1990**, 31(2), 627  
(with D.R. Iyengar and J.V. Brennan)  
"Design of Polymer-Polymer Interfaces: Adsorption of Polystyrene to PVF<sub>2</sub>"
6. *Polym. Matl. Sci. Eng.* **1990**, 63, 94 (with T.G. Bee)  
"Frictional Studies of Surface Modified Poly(chlorotrifluoroethylene)"

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**(Papers Published in Non-Refereed Journals)**

7. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1991**, 32(3), 627  
(with M.S. Shoichet, D.R. Iyengar and J.V. Brennan)  
"Spontaneous Adsorption of Polymers from Solution to Solution-Polymer Interfaces"
8. *Proc. Adhes. Soc.* **1992**, 15, 43 (with R.J. Fleming and R.J. Farris)  
"Adhesion of Surface Modified Poly(chlorotrifluoroethylene to Epoxy"

**Overview of On-going Research Program**

We are carrying out fundamental research on organic chemistry at condensed phase surfaces and interfaces. We have developed (and continue to develop) new techniques for introducing specific organic functionality onto the surfaces of chemically resistant polymers - poly(chlorotrifluoroethylene), poly(tetrafluoro-ethylene), poly(vinylidene fluoride), poly(ether ether ketone), polyethylene. The techniques are designed to place versatile and reactive centers in the outer few tens of angstroms of the polymer samples. We are studying the chemical reactivity of surface-confined hydroxyl groups and carboxylic acid groups in detail and are developing a set of rules for reactivity at interfaces: structure-reactivity correlations are being drawn. The mobility and accessibility (to reagents in solutions in contact with the solid polymers) of the functional groups are being studied. The extent to which polymer surface properties can be manipulated by organic surface chemistry is being detailed. Adsorption of polymer monolayers and graft polymerization from surface-confined initiators is being studied. The adsorption of polypeptides and polysaccharides from aqueous solutions to specifically modified surfaces is being studied. The overall goal of the research is to simultaneously understand the structure, properties and reactivity of polymer surfaces, particularly as a function of their environment (interfaces).

**Specific Progress During this Reporting Period**

- (1) We completed research on grafting end-functionalized polymers to solid fluoropolymers. The structure of the resulting "phase-segregated polymer

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blends" was a strong function of end-group identity. Details are in *Macromolecules* **1990**, *23*, 366.

(2) We completed the research on the study of processes by which modified polymer surfaces reconstruct on heating. The distance scale of these motions is small; the majority of the modified repeat units remains in the outer 10 Å. Details are in *Macromolecules* **1990**, *23*, 3916.

(3) We have continued to develop PVF<sub>2</sub> surface chemistry, introducing reactive handles by dehydrofluorination and subsequent reactions with the unsaturation. Details are in *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1989**, *30(2)*, 152.

(4) We completed the work on the reductive surface chemistry of poly(tetrafluoroethylene-co-hexafluoropropylene) detailing the control of the depth of reaction and developing routes to alcohol functionality. Details are in *Macromolecules* **1990**, *23*, 2648.

(5) We built an instrument to measure the coefficient of sliding friction of surface modified films showed that the incorporation of fluorine into modified surfaces (prepared by esterification of PCTFE-OH with fluorinated acid chlorides) renders surfaces with higher coefficients of friction than hydrocarbon analogs. Details are in *Polym. Matl. Sci. Eng.* **1990**, *63*, 94.

(6) We completed research on poly(ether ether ketone) surface chemistry and published the first paper and a book chapter. The reactivity of five alcohol surfaces derived from the diaryl ketone was assessed. This has turned out to be an extremely versatile surface substrate. Details are in *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1990**, *31(1)*, 416, *Macromolecules* **1991**, *24*, 3045, and *Chemically Modified Surfaces* (H.A. Mottola and J.R. Steinmetz, Eds.) Elsevier, 1992

(7) Carboxylic acids were introduced to three different fluoropolymer surfaces by indirect methods. Selective modification followed by oxidation produced sub-monolayer levels of acids. The wettability and reactivity were assessed. Details are in *Macromolecules* **1991**, *24*, 982.

(8) We completed work on the surface-selective chlorination of polyethylene. We showed that the depth of reaction and the chain density of chlorination could

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be independently and simultaneously be controlled by chlorine partial pressure and photointensity. Details are in *Macromolecules* 1992, 25, 2603.

(9) A reactive carboxylic acid - containing poly(chlorotrifluoroethylene) surface was prepared by using a protected alcohol - containing lithium reagent. The reactivity of this surface has been assessed. Details are in *Macromolecules* 1992, 25, 2093.

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