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Structural Synergism in Functionalized Polymers: New Catalysts for Transacylation Reactions of Derivatives of Carboxylic and Phosphoric Acids

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The final report summarizes the goals, accomplishments and personnel associated with this project.

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I. Description of Project

This project has focused on the development of new highly-efficient, selective catalysts for widely-used commercial and biological reactions of carboxylic and phosphoric acids and their derivatives. The first phase of the project included the design and synthesis of linear, water-soluble polymers that are expected to self-organize in aqueous solution to form lipophilic substrate-binding domains adjacent to catalytic sites effective in transacylation reactions. Progress toward these objectives was summarized in End-Of-The-Year Report dated May 21, 1990.

The second phase of this work has dealt with the continuing evaluation of synthetic catalysts and the development of new methods for detailed structural characterization of these polymeric materials. Prof. R.G. Cooks (Purdue University, West Lafayette, IN) has been a key collaborator in this effort. The ultimate aim of this phase of the investigation is to ascertain the limits of substrate-selectivity for linear, synthetic polymeric catalysts. Progress toward these goals is summarized in End-Of-The-Year Report dated May 21, 1991.

II. Summary of Accomplishments

The major accomplishments are summarized in Section Part II (e) of the End-O-The-Year Reports of 1990 and 1991. Details of the investigation to-date are contained in seven papers published in refereed journals, one patent, four non-refereed papers and fourteen ONR technical reports. These papers are summarized by author, title and journal below:

A. Papers Published in Refereed Journals

1. M. Zeldin, W. K. Fife, C.-x. Tian and Y. Xin, "Siloxanes with 1-Oxypyridin-3-yl Groups. Part 6. Synthesis of Copolymers and Application as Transacylation Catalysts," *British Polymer Journal*, 21, 481-486 (1989). Additional support is acknowledged from the National Science Foundation for funds to purchase thermal analysis equipment (Grant No. CHE 84-10779).

2. S. Rubinsztajn, M. Zeldin and W.K. Fife, "Synthesis and Characterization of 3-Pyridinyl Substituted Ethoxysilane Monomers," *Synthesis and Reactivity In Inorganic and Metal-Organic Chemistry*, 20 (*4*), 495-502 (1990). Additional support is acknowledged from NSF for funds to purchase thermal analysis equipment (Grant No. CHE 84-10779).

3. P. Ranganathan, M. Zeldin and W.K. Fife, Thermal Properties of N-Substituted 4-Vinylpyridinium Ions and Their Polymers, *J. Polym. Sci.: Part A: Polym. Chem.* Ed. 28, 2711-2717 (1990). Additional support is acknowledged from NSF for funds to purchase thermal analysis equipment (Grant No. CHE 84-10779).

4. S. Rubinsztajn, M. Zeldin and W.K. Fife, "New Transacylation Catalysts. Silanes and Siloxanes Functionalized with 4-(Dialkylamino)pyridine Moieties," *Macromolecules*, 23, 4026-4028 (1990). Additional support is acknowledged from Reilly Industries.

5. K.K. Kasem, W.K. Fife, M. Zeldin and C.R. Leidner, "Lipophile Exchange Membranes as Electroactive Assemblies on Electrode Surfaces," *J. Electroanal. Chem.*, 296, 221-231 (1990). Additional support is acknowledged from Purdue Research Foundation.

6. W.K. Fife, P. Ranganathan and M. Zeldin, "A General Synthesis of 1-Alkyl-4-vinylpyridinium Ions. Alkylation of 4-Vinylpyridine with Primary Alkyl Triflates," *J. Org. Chem. 55*, 5610-5613 (1990). Additional support is acknowledged from Reilly Industries.

7. S. Rubinsztajn, M. Zeldin and W.K. Fife, "Synthesis, Characterization and Solubility Behavior of Polysiloxanes with 4-(Dialkylamino)pyridine Functions," *Macromolecules*, 24, 2682 (1991).

B. Patents Granted

1. Martel Zeldin, Wilmer K. Fife and Slawomir Rubinsztajn, "Aminopyridyl Silanes," US Patent No. 4,997,944, Issue Date: Mar. 5, 1991.

C. Technical Reports Published (ONR Technical Reports) and Papers Published in Non-Refereed Journals

1. Wilmer K. Fife, Prema Ranganathan and Martel Zeldin, "Synthesis, Characterization and Polymerization of 1-Alkyl-4-vinylpyridinium Salts," Polym. Repr. Am. Chem. Soc. Div. Polym. Chem., 30(2), 123-124 (1989). Additional support is acknowledged from Reilly Industries, Indianapolis, IN.

2. Martel Zeldin, Wilmer K. Fife, Slawomir Rubinsztajn and Cheng-xian Tian, "Siloxane Polymers and Copolymers with Pendant 1-Oxpyridin-3-yl Groups as Transacylation Catalysts, "American Chemical Society Division of Polymeric materials: Science and Engineering, Abstracts, 61, 99-100 (1989). Additional support is acknowledged from Reilly Industries, Indianapolis, IN.

3. Martel Zeldin, Wilmer K. Fife, Cheng-xian Tian and Yue Xin, "Siloxanes with 1-Oxpyridin-3-yl Groups, Part 6. Synthesis of Copolymers and Application as Transacylation Catalysts," (ONR Technical Report No. 1, 6 pages). Additional support is acknowledged from the National Science Foundation for funds to purchase thermal analysis equipment (Grant No. CHE-84-10779).

4. Martel Zeldin, Wilmer K. Fife, Slawomir Rubinsztajn and Cheng-xian Tian, "Siloxane Polymers and Copolymers with Pendant 1-Oxpyridin-3-yl Groups as Transacylation Catalysts," (ONR Technical Report No. 2, 3 pages). Additional support is acknowledged from Reilly Industries, Indianapolis, IN.

5. Wilmer K. Fife, Prema Ranganathan and Martel Zeldin, "Synthesis, Characterization and Polymerization of 1-Alkyl-4-vinylpyridinium Salts," (ONR Technical Report

No. 3, 3 pages). Additional support is acknowledged from Reilly Industries, Indianapolis, IN.

6. Slawomir Rubinsztajn, Martel Zeldin and Wilmer K. Fife, "Synthesis and Characterization of 3-Pyridinyl Substituted Ethoxysilane Monomers," (ONR Technical Report No. 4, 10 pages). Additional support is acknowledged from the National Science Foundation for funds to purchase thermal analysis equipment (Grant No. CHE 84-10779).

7. Prema Ranganathan, Wilmer K. Fife and Martel Zeldin, "Thermal Properties of N-Substituted 4-Vinylpyridinium Ions and Their Polymers," (ONR Technical Report No. 5, 11 pages). Additional support is acknowledged from the National Science Foundation for funds to purchase thermal analysis equipment (Grant No. CHE 84-10779).

8. Martel Zeldin and Wilmer K. Fife, "Aminopyridyl Silanes and Siloxanes," (ONR Technical Report No. 6, 41 pages).

9. Wilmer K. Fife, Martel Zeldin and Slawomir Rubinsztajn, "Polymeric Catalysts with Enzyme-Like Properties," Proceedings of 1990 US Army CRDEC Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, MD, Nov. 1990, in press.

10. Wilmer K. Fife, Martel Zeldin, Yue Xin and Carol Parish, "Copolymerization in Self-Organized Systems," Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem., 32(1), 579 (1991).

11. Kasem K. Kasem, Wilmer K. Fife, Martel Zeldin and Charles R. Leidner, "Lipophile Exchange Membranes as Electroactive Assemblies on Electrode Surfaces," (ONR Technical Report No. 7, 11 pages). Additional support is acknowledged from Purdue Research Foundation.

12. Slawomir Rubinsztajn, Martel Zeldin and Wilmer K. Fife, "New Transacylation Catalysts: Silanes and Siloxanes Functionalized with 4-(Dialkylamino)pyridine Moieties," (ONR Technical Report No. 8, 2 pages). Additional support is acknowledged from Reilly Industries.

13. Wilmer K. Fife, Prema Ranganathan and Martel Zeldin, "A General Synthesis of 1-Alkyl-4-vinylpyridinium Ions. Alkylation of 4-Vinylpyridine with Primary Alkyl Triflates," (ONR Technical Report No. 9, 4 pages). Additional support is acknowledged from Reilly Industries.

14. Slawomir Rubinsztajn, Martel Zeldin and Wilmer K. Fife, "Synthesis, Characterization and Solubility Behavior of Polysiloxanes with 4-(Dialkylamino)pyridine Functions," (ONR Technical Report No. 10, 7 pages).

15. Leo Z. Vilenchik, Slawomir Rubinsztajn, Martel Zeldin and Wilmer K. Fife, "Characterization of a Single Sample of an Unknown Polymer by Size Exclusion

Chromatography," (ONR Technical Report No. 11, 5 pages). Additional support is acknowledged from Reilly Industries.

16. Wilmer K. Fife, Martel Zeldin and Slawomir Rubinsztajn, "Polymeric Catalysts with Enzyme-Like Properties," (ONR Technical Report No. 12, 7 pages).

17. Wilmer K. Fife, Martel Zeldin, Yue Xin and Carol Parish, "Polymerization in Self-Organized Systems," (ONR Technical Report No. 13, 3 pages).

18. Wilmer K. Fife, Slawomir Rubinsztajn and Martel Zeldin, "A Synthetic p-Nitrophenyl Esterase with Remarkable Substrate Selectivity," (ONR Technical Report No. 14, 14 pages).

D. Personnel

1.	Post-Doctoral Fellows:	Ying Hu (Full) Prema Ranganathan (Full) Slawomir Rubinsztajn (Full)
2.	Graduate Students:	Eric Granger (Partial) Laurie Lawin (Full) Carol Parish (Partial) Yue Xin (Partial) Zheng-Yun Zhan (Partial)
3.	Undergraduate Students:	Martin Kuntz Michael Ranjbar Donica Schwomeyer