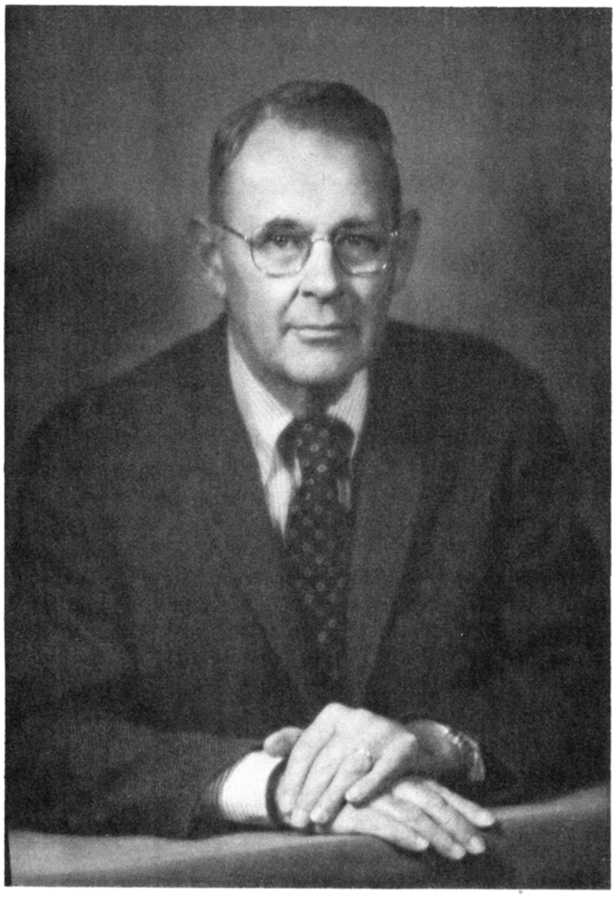

John D. Ferry

John Douglass Ferry, Professor of Chemistry Emeritus at the University of Wisconsin, in Madison, Wisconsin, celebrates his 75th birthday on May 4, 1987. Probably no individual in this country, or, for that matter, in the world at large, has done more for the rheology of polymers than John Ferry. When he established his laboratory at the University of Wisconsin in 1945, rheology was just emerging from an industrial art into a science. The scientific papers that issued forth from Madison until well past his retirement in 1982 contributed immensely to that development.

The theme underlying John Ferry's research has always been the relationship of the modes of molecular motion in macromolecules to their mechanical and other physical properties. He has pioneered the use of rheological methods as primary tools in his investigations. His work on the viscoelastic and other aspects of the dynamics of macromolecules concerns a broad spectrum of systems, ranging from dilute and concentrated solutions to undiluted synthetic bulk polymers, both cross-linked and uncross-linked, and to biological macromolecules, including proteins and nucleic acids.

The list of his scientific co-workers comprises over 60 Ph.D. and M.S. students and close to 30 postdoctoral and other associates. Many are active in various fields of polymer physics today.

His celebrated text, *Viscoelastic Properties of Polymers*, became a classic immediately after the appearance of its first edition in 1961. It has since seen two more revised and thoroughly updated editions, one in 1970, the last in 1980. One or the other of these editions has been translated into Japanese, Russian, and Polish. Ferry's encyclopedic knowledge of his field and his strong sense of professional responsibility made his text the leading publication in the field. The words: "Let's see what Ferry says about it" must have been heard in innumerable discussions all over the world.

John D. Ferry was born in Dawson, Yukon Territory, as the son of a mining engineer working in the gold country. After obtaining his B.Sc. from Stanford University, alma mater of his father, mother, and an aunt, he spent a year in London at the National Institute for Medical Research and later obtained his Ph.D. from Stanford in 1935. In 1936 John Ferry joined the Harvard Faculty as a part-time instructor and was appointed to Harvard's Society of Fellows in 1938. This allowed him to pursue studies of his own choice with complete freedom. He devoted his time to seeking an understanding of the viscoelastic properties of polymers. During World War II John Ferry worked at the Harvard Medical School on plasma substitutes and for the U.S. Navy at Woods Hole Oceanographic Institute. Here he met Barbara Mott, who became Mrs. Ferry in 1944.

In 1946 Ferry joined the Chemistry Department of the University of Wisconsin and became a Full Professor in 1947. From 1959 to 1967 he was Chairman of the Department and in 1973 was given the distinguished title of Farrington Daniels Research Professor.

John Ferry is a member of the National Academy of Sciences, a Fellow of the American Academy of Arts and Sciences, and a member or fellow of many scientific societies, among them The Society of Rheology, of which he was Vice President and President. He has received numerous awards and distinctions and has served as editor or on the editorial boards of many scientific journals. More detailed accounts of his achievements and scientific contributions may be found in two publications. The first[1] contains the remarks by J. L. Schrag during the presentation to John Ferry of the Charles Goodyear Medal in 1981; the second[2] was written by R. F. Landel on the occasion of his retirement in 1982. Two papers by John Ferry himself, *Contemporary Topics in Polymer Science*[3] and *Probing Macromolecular Motions through Viscoelasticity*,[4] are excellent reading for anyone wishing to pursue his work in greater detail. Another publication[5] summarizes the results of some 40 papers on fibrinogen and fibrin and the fibrinogen-to-fibrin conversion which Ferry first described correctly. Much of the work of Ferry and his many students and collaborators is, of course, described in the three editions of his book.[6]

John Ferry's greatest contribution, however, may well be the profound and lasting effect that his gentle, patient, and understanding personality has made on anyone who has had the good fortune to work with him. He is not only a great scientist but also a broadly educated man with a vast range of interests who treats everybody, under all circumstances, with the courtesy of the true gentleman. Research cannot be learned from books. The "right stuff" is acquired by working with the right man. No one embarking on a scientific career could have wished for a wiser, more caring, and more knowledgeable mentor.

On the occasion of his 75th birthday we all who know him personally and, I am sure, those also who know him only through his work wish John Ferry the best of good health, happiness, prosperity, and, certainly, continuing success in his scientific endeavors.

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Articles

Synthesis and Characterization of Poly(alkyl/arylphosphazenes)

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ABSTRACT: Several alkyl/aryl-substituted phosphazene polymers $[R(R')PN]_n$ (**1**, R = R′ = Me; **2**, R = R′ = Et; **3**, R = Me, R′ = Ph; **4**, R = Et, R′ = Ph) and copolymers $\{[R(Ph)PN]_x[R_2PN]_y\}_n$ (**5**, R = Me; **6**, R = Et) were prepared by the thermally induced condensation polymerization of the corresponding *N*-silyl-*P*-trifluoroethoxyphosphoranimines $Me_3SiN{=}P(OCH_2CF_3)RR'$. With the exception of the diethyl derivative **2**, which is insoluble in all common solvents, these polymers were characterized by a variety of dilute solution techniques (viscosity measurements, membrane osmometry, size-exclusion chromatography, and light scattering), by thermal analysis (DSC and TGA), by multinuclear NMR spectroscopy, and by X-ray diffraction measurements. The polymers have molecular weights ($\bar{M}_w$) ranging from ca. 25 000 to 200 000 with symmetrical molecular weight distributions ($\bar{M}_w/\bar{M}_n \sim 2.0$) and, in general, exhibit solution behavior typical of random coil polymers in "good" solvents (e.g., THF or $CHCl_3$). The Mark–Houwink constants for polymer **3** were estimated from the viscosity and light scattering results. The DSC measurements show that (a) poly(dimethylphosphazene) (**1**) is a semicrystalline thermoplastic with T_g = −46 °C and T_m = 143 °C, (b) poly(diethylphosphazene) (**2**) is highly crystalline with T_m = 217 °C, and (c) the phenyl-substituted polymers **3**–**6** are amorphous with glass transition temperatures ranging from −5 °C (**6**) to 37 °C (**3**). The crystallinity of **1** and **2**, presumably the reason for the insolubility of **2**, was confirmed by X-ray diffraction measurements. The thermal stability of these polymers is generally quite high as indicated by decomposition onset temperatures (TGA) of ca. 350–400 °C. High-field ^{13}C NMR spectral data show that the structure of the homopolymer **3** is completely atactic even though there are two different substituents present on each phosphorus atom. A chain growth process is suggested as the polymerization mechanism on the basis of studies of the polymer molecular weight vs. the extent of reaction.

Introduction

Inorganic polymers with a backbone of alternating phosphorus and nitrogen atoms, known as poly(phosphazenes), $[R_2PN]_n$, have attracted increasing attention in recent years.[1] Many such polymers with a variety of substituents at phosphorus have been prepared, and they often exhibit useful properties including low-temperature flexibility, resistance to chemical attack, flame retardancy, stability to UV radiation, and reasonably high thermal stability.[2] Compounds containing biologically or catalytically active side groups are also being investigated.[3]

The most commonly used synthetic route to poly(phosphazenes) is the ring-opening/substitution method developed by Allcock and co-workers. This procedure involves the initial preparation of poly(dihalophosphazene), $[X_2PN]_n$, (X = Cl, F) by the ring-opening polymerization of the cyclic trimer and subsequent nucleophilic displacement of the halogens along the chain (eq 1). In each

$$\begin{aligned}(Cl_2PN)_n &\xrightarrow{NaOR} -[P(OR)_2{=}N]_n- \\ (Cl_2PN)_n &\xrightarrow{RNH_2} -[P(HNR)_2{=}N]_n-\end{aligned} \qquad (1)$$

case, the substituents at phosphorus must be introduced after polymerization since the fully substituted cyclic phosphazenes do not polymerize.[4,5]

A common feature of poly(phosphazenes) prepared in this manner is that the organic substituents are bonded to phosphorus through oxygen or nitrogen links, thereby providing pathways for decomposition or depolymerization on heating above about 200 °C. It has been postulated that

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