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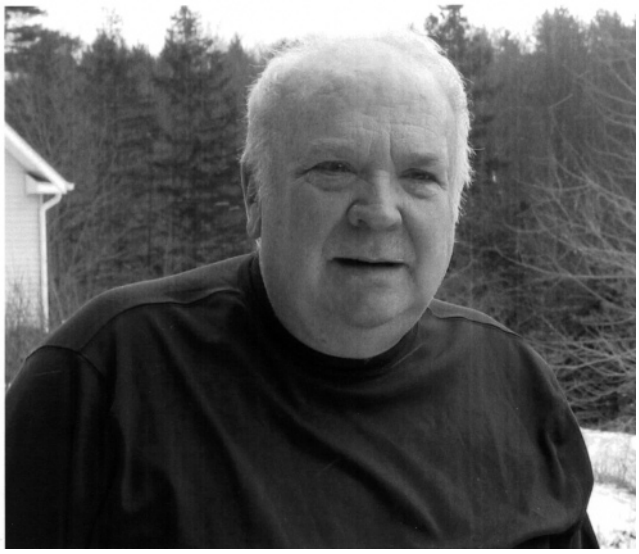

Tribute to Lewis J. Fetters

On March 29, 2006, we will celebrate the 70th birthday of Lewis J. Fetters. Lew is one of the pioneers in the field of anionic polymerization, and he has a richly deserved international reputation for synthesizing well-defined polymers of high purity and controlled architectures. In addition to his synthetic work, Lew has made seminal contributions to fundamental polymer physical chemistry and physics as well as to commercial applications of block copolymers.Lew Fetters received a B.A. in chemistry from the College of Wooster (Ohio) in 1958. He then began graduate studies in the Chemistry Department at the University of Akron with Professor Maurice Morton, defending his Ph.D. dissertation on "The Anionic Polymerization of Butadiene and Isoprene" in 1962. Lew then spent 2 years as a National Academy of Sciences/National Research Council Postdoctoral Fellow in the Polymer Division at the National Bureau of Standards (NBS—now the National Institute for Standards and Technologies, NIST). Following his postdoctoral appointment, Lew remained with the NBS Polymer Division as a member of the technical staff from 1965 to 1967. In 1967, he returned to the University of Akron, joining the faculty of the new Department of Polymer Science. Lew remained at Akron for 16 years, rising to the rank of Professor, before moving to Exxon (now ExxonMobil) Research and Engineering Co. as a Senior Research Associate in 1983. Lew spent the next 17 years at ExxonMobil, before returning to academia in 2000. Lew is presently Visiting Professor in the Department of Chemical and Biomolecular Engineering at Cornell University.

Lew Fetters' career began at a time when the study of organolithium-initiated anionic polymerization was in its infancy, and he quickly established a reputation for his skill in synthesizing high quality polymeric materials by his meticulous attention to detail. As a consequence, over the subsequent years his collaboration has been sought by a dazzling array of many of the best known names in polymer chemistry and physics. Throughout his career Lew has exploited the ability of certain monomers to polymerize anionically without termination to generate near-monodisperse "living" polymers. The introduction of a second monomer results in the formation of a diblock copolymer. Alternatively, coupling using appropriate multifunctional chlorosilanes yields well-defined star-shaped polymers or more highly branched architectures. In the early 1960s such endeavors were often regarded as largely academic exercises although Shell was already mass-producing styrene−diene triblock copolymers (Kratons R*)—thermoplastic elastomers—which exhibit high strength and novel processing characteristics.

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The availability of near-monodisperse materials opened the way for the study of the fundamental physical chemistry/physics of polymers in solution and in the bulk in a more exacting manner than had been possible previously. Lew and his collaborators have measured chain dimensions and characteristic ratios for a wide variety of linear and star polymers in solution using static and dynamic light scattering.[1−3] Other studies were on the rheological behavior of star polymers and the effects of the number of arms on their diffusion. The ability to employ model materials to measure the effect of purposefully adding homopolystyrene or polystyrene−butadiene (SB) diblock to an SBS triblock upon the stress relaxation shed interesting light on such imperfections that exist in commercial materials.[4] The advent of small-angle neutron scattering (SANS) facilities enabled extension of such measurements to the melt state. These include polydienes having controlled microstructures and their polyolefin counterparts obtained by saturation.[5] This also enabled study of the thermodynamics of polyolefin blends and diffusion in them.[6] A particularly important discovery is that the unperturbed chain dimensions in polyolefin and polydiene blends and their associated temperature coefficients measured under theta conditions can differ significantly from those determined in the melt.[7,8] This is at variance with the classic prediction of Flory.[9]

In the early 1960s it was known that the living organolithium-based polymers derived from styrene, butadiene, and isoprene are strongly associated. The observation that their propagation reactions exhibit low fractional kinetic orders had led to the suggestion that propagation is solely via the minute equilibrium content of unassociated ends and that, in consequence, the order should be the inverse of the degree of association—variously reported as between 2 and 6. Fetters showed that this attractively simple mechanism fails to accurately match observation or to explain the profound kinetic effects of the variation of the degree of association during the polymerization as well as the cross-association between initiator and propagating species shown in certain cases.[10] Recently, he has shown by SANS that the reality is much more complex, with self-assembly producing not only dimers and tetramers but also very large-scale structures and multiarm starlike aggregates—the detail changing as propagation proceeds toward completion.[11,12]

Through anionic polymerization, Lew created a host of well-defined linear and star-block copolymer architectures.[13−15] In the course of this work, in collaboration with Professor E. L. Thomas, a previously unknown block copolymer morphology, the ordered bicontinuous double-diamond morphology, was discovered.[16] Although this morphology was later reassigned as a double-gyroid morphology,[17] this discovery was extremely important because it changed the textbook view of polymer morphologies as simple "spheres, cylinders, and lamellae" and led to a marked increase in interest in phase behavior of block copolymers and their blends.

Lew's contributions to industrial polymer science are no less impressive than his academic contributions. His work on hydrogenated model polydienes has led to major advances in several fields. These include controlling polymer−wax interactions,[18] understanding the origins of entanglement in polymer melts,[19] and the miscibility of polyolefin blends.[20]

At the low temperatures frequently encountered in winter the longer chain components of diesel fuels separate as large crystals or spherulites of wax. The ensuing gelation severely reduces or even destroys the ability to flow. Numerous additives—seemingly often chosen on a largely ad hoc basis—have been employed commercially to solve this problem. A novel additive which solves this problem was invented by Lew while working for ExxonMobil. Saturation of a polybutadiene precursor having one block of high 1,4-polybutadiene and one of low 1,4-content forms a new diblock consisting of polyethylene sequentially lightly and extensively decorated with ethyl groups. The former is insoluble in diesel and forms colloidal-sized crystallites—held in suspension by a soluble brush of the latter. The vast number of nucleation sites available markedly lowers the dimensions of the wax particles formed and so lowers the pour point temperature.[21] An ExxonMobil affiliate, Infineum, has now commercialized such block copolymers as diesel fuel additives to prevent crystal formation at low temperatures.[22] Also at ExxonMobil, Lew co-invented block copolymer viscosity modifiers for lubricating oils which were commercialized.

Lew Fetters has received a great deal of recognition for his outstanding contributions to polymer science. He received the first Creative Polymer Chemistry Award from the American Chemical Society (ACS) for his work on synthesis of well-defined polymers. In 1996, he was named a Fellow of the American Physical Society (APS), for contributions to polymer physics, and was named to the Inventors Hall of Fame. In 2000, Lew was named a Fellow of the Polymeric Materials Science and Engineering Division of ACS, was awarded the APS Ford Prize in polymer physics, received the Applied Polymer Chemistry Award from ACS, and was named Distinguished Alumnus by the Department of Polymer Science of the University of Akron. This must be a record for major recognition for a scientist in a single year!

Lew Fetters serves as a role model and inspiration to more than a generation of polymer scientists. Leading by example, he works tirelessly 7 days a week. He is always ready to offer help or advice to a colleague. He opens his home to collaborators and visiting scientists on a regular basis, insisting that they stay there rather than at a hotel. On a personal level, Lew is an avid reader, especially of military history, and a lover and collector of fine art and music. His love of animals is well-known to his collaborators, students, and friends.

As he moves into his eighth decade, Lew is as active today as he has ever been. We look forward to many more important contributions from Lew Fetters, one of our most accomplished polymer scientists.

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