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Tribute to H. K. “Hank” Hall, Jr.

On December 7, 2004, a group of faculty, students, family, and friends gathered on the sixth floor outside the office of Professor H. K. “Hank” Hall, Jr., in the C.S. Marvel Laboratories Building on the campus of the University of Arizona to wish him a happy 80th birthday and to enjoy some very good chocolate cake, provided by his wife Wini and his son Doug.

Professor Hall’s fundamental contributions over the span of five decades have profoundly influenced both the theory and practice of organic polymer chemistry. He has been the pivotal scientist at the interface of organic and polymer chemistry who understood that the application of sophisticated synthetic procedures and reaction mechanisms is essential to the design of novel polymer structures and to the elucidation of polymerization mechanisms.

Hank Hall was born in New York City in 1924 and received a B.S. degree in Chemistry from the Polytechnic Institute of Brooklyn in 1944. After a M.S. degree from Pennsylvania State University in 1946, Hank earned a Ph.D. Degree from the University of Illinois in 1949. For his postdoctoral studies Hank went in two distinct directions, which would define his industrial and academic career and interests. He first joined Prof. Paul Flory at Cornell University, a pioneer in theoretical polymer chemistry, and then went to UCLA to work with Prof. Saul Winstein, an expert in physical organic chemistry and reaction mechanisms.

Hank Hall joined E.I. DuPont de Nemours in Wilmington, DE, in 1952, first in the Pioneering Research Laboratory of Textile Fibers Department and later in the Central Research Department as a Group Leader. In 1969, Hank was recruited by Carl S. “Speed” Marvel to join the Chemistry Department at the University of Arizona, Tucson, AZ, to help build up the polymer research efforts in this growing department. He was the Head of the Chemistry Department from 1970 until 1973. During his career, Hank has been a Visiting Professor at Imperial College in London, the University of Rochester, the Polish Academy of Sciences Macromolecular Institute in Lodz, Poland, the Weizman Institute in Israel, the Chinese Academy of Sciences, the Society for the Advancement of Polymer Science in Japan, and the Max Planck Institute for Polymer Research in Mainz, Germany. Hank became Professor Emeritus at The University of Arizona in July 1995 and, in spite of his “retirement”, has continued his research at full speed and maintains his high profile in the polymer chemistry community. Hank Hall received numerous awards and honors during his career, most notably the 1996 American Chemical Society Award for Polymer Chemistry, sponsored by the Mobil Corp.

Professor Hall made major contributions in erasing the artificial boundary between organic and polymer chemistry. His first assignment at DuPont was to explain their recently discovered interfacial polycon-

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densation, whose success appeared to contradict all the established rules and presented a kineticist's nightmare: heterogeneous, extremely fast, etc. Hank found a model monofunctional acyl chloride, ethyl chloroformate, which hydrolyzed only slowly in water solution so that its competitive reactions with amines could be studied.[1] The latter were so fast that buffered solutions were required. Hank synthesized a unique series of sterically hindered phenolic buffers with varying pK_as which suppressed free amine concentration and rate to a measurable range. The amidation proceeded with the astoundingly high rate constants of ca. 10^4 M^{-1} s^{-1}, faster than many vinyl propagation reactions! The data enabled him to understand the interfacial polymerization process: diamine, largely in the aqueous phase, partitions into the organic phase where the diacyl chloride snaps it up as fast as it enters and forms high polymer.

Turning his attention to ring-opening polymerization, he was the first to use the newly developed concept of conformational analysis to ring-opening polymerization and used it to explain the ability of many monocyclic compounds, including lactams, lactones, cyclic ureas, urethanes, imides, and amines, to polymerize.[2] The polymerizability of the corresponding atom-bridged bicyclic compounds was determined by the type of ring structure, involving both angle and conformational strains. Hank explained the anionic polymerization of lactams by slow formation of an intermediate *N*-acyllactam, followed by rapid propagation. Deliberate addition of a small amount of *N*-acetyllactam led to rapid controlled anionic polymerization of pyrrolidone and caprolactam.[3] Hank also synthesized bicyclic monomers, such as 2,6- and 2,7-dioxabicyclo[2.2.1]heptanes and 2,6,7-trioxabicyclo[2.2.2]octane, by subliming the monomers out of the reaction mixture as soon as they formed.[4] These highly strained monomers readily polymerized by a cationic mechanism.

Hank extended his investigations to the rather extreme bicyclo[1.1.0]butane-1-carbonitrile, which polymerized by anionic and free radical mechanisms, and also readily copolymerized.[5] Poly(cyclobutanecarbonitrile) (PCBN) is very similar to poly(acrylonitrile), PAN, but has far superior properties with higher air stability, higher melting point and glass transition temperatures, and superior film and fiber strength. If an economically viable synthesis route to bicyclobutanecarbonitrile were devised, it would easily replace PAN in many high-temperature applications.

The search for a facile synthesis for bicyclobutanecarbonitrile monomers led Hank Hall to an in-depth investigation of the reactions of electron-poor and electron-rich olefins in which spontaneous polymerizations competed with cycloadditions. At that time, "charge-transfer" polymerizations were a hot topic of investigation, but no clear and logical explanation for the initiation reactions was proposed. Here Hank's knowledge of physical organic chemistry led him to the seminal papers of Rolf Huisgen describing the intermediates in [2 + 2]-cycloadditions.[6] According to Huisgen, the tetramethylene intermediate is either predominantly zwitterionic or diradical in nature, depending on the terminal substituents. This proved to be the vital piece of information Hank used to formulate his Bond-Forming Initiation Theory.[7] If the tetramethylene has zwitterionic character, it can initiate cationic homopolymerization of the donor olefin or anionic homopolymerization of the acceptor olefin. If the tetramethylene has diradical character, then it can initiate free radical copolymerization, usually alternating.

Hank set out to prove this theory by analyzing specific and clear examples.[8] Reaction of electron-rich *N*-vinylcarbazole with tetrasubstituted electrophilic alkenes forms cyclobutane adduct, but the reaction is reversible. Thus, the cyclobutane adduct is the initiator for the cationic polymerization of excess *N*-vinylcarbazole by reversion to the zwitterion; the influence of solvent polarity and kinetic data support this. Hank then switched to the investigation of the reactions of a pair of much more moderately electron-rich and electron-poor olefins: *p*-methoxystyrene and dimethyl cyanofumarate, which led to alternating copolymers. The propagation is first order in each monomer, the molecular weight increases with time, and the polymerization is independent of solvent polarity, which are all consistent with an initiation by the tetramethylene diradical. In collaboration with Eberson et al., Hank was able to show the existence of the initiating tetramethylene diradical by spin trapping experiments.[9]

Following the basic methods of a physical organic chemist, Hank extended these findings to new monomer systems and applied it to previously published findings. Analysis of literature data led to a framework with predictive power.[6] Depending on the electrophilicity and nucleophilicity of the two olefins, different reaction pathways predominate: cycloaddition or spontaneous polymerization. A logical picture emerged in the form of a periodic table. As the difference in electronegativity between the two olefins increases, initiated free radical copolymerizations gives way to spontaneous alternating copolymerization, followed by ionic homopolymerizations. Bond formation between the two reacting olefins shows the way to a more energetically favorable and predictable pathway to the spontaneous polymerizations than the previously proposed charge-transfer complexes.

Hank extended the applicability of his Bond Forming Initiation Theory with a systematic study of the reactions of 1,3-dienes with electrophilic olefins, proving that previously observed "tar formations" were real polymerizations.[10] The yield of polymer was maximized when equal amounts of each reactant were used, and the yield of the [4 + 2]-cycloadduct was also highly predictable. Two independent pathways occur: the *s*-cis conformer of the diene undergoes concerted cycloaddition, while the *s*-trans conformer reacts with the alkene to form an initiating hexamethylene diradical. Adding Lewis acids to mixtures of olefins renders the electrophilic olefin more electrophilic and leads to increased reactivities in the spontaneous polymerizations. Resulting from a long-standing collaboration with Drs. Iwatsuki and Itoh, the Bond-Forming Initiation Theory was also applied to the spontaneous homo- and copolymerizations of quinodimethanes substituted with electron-withdrawing groups.[11]

Photochemical "spontaneous" initiations of electron-rich and electron-poor olefins were brought into the same framework.[12] Irradiation of mixtures of the olefins in absence of photoinitiator results in the formation of an excited triplet biradical of one olefin, which adds to another monomer to form a tetramethylene diradical and then either cyclizes or initiates copolymerization.

Henry Hall contributed to other areas of polymer chemistry. He investigated the polymerizability of the C═N bond, intermediate between the polymerizable

C═C and C═O bonds.[13] A great dependence of polymerizability on the substitution pattern was found. Polyquinonimines, synthesized by polycondensation of benzoquinone, anthraquinone, or their derivatives with aromatic diamines, are novel polyaniline analogues with third-order nonlinear optical properties.[14]

These days Hank devotes a lot of time to the elucidation of the mechanisms of liquid crystal polymer formation, in particular the copolymer of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid, i.e., Vectra, in cooperation with researchers at Celanese/Ticona. A totally unique polymerization emerged: originally it is an acidolysis reaction, but the hydroxybenzoic acid end groups are prone to decarboxylation, morphing into phenyl ester end groups, while the acetoxy groups at the other end gradually expel ketene with formation of phenoxy end groups. But the polymerization proceeds anyway by switching to a phenolysis.[15] This is a unique case in polymer chemistry. Hank is now testing the limits of MALDI-TOF spectroscopy by designing specific matrices and sample preparation techniques to elucidate this polymerization mechanism.[16]

Hank Hall has an extensive consulting career providing service to many Fortune 100 companies. He has been in great demand over the years for his services due to his extensive and very profound knowledge of both organic synthetic and applied polymer chemistry.

Hank is also a very effective educator. His more than 40 Ph.D. students and 80 postdoctoral associates, not to mention the numerous undergraduates who have been in his group at Arizona and have spread his expertise throughout this country and the international chemical community. Professor Hall has been a complete teacher at every level at The University of Arizona since his appointment in 1969.

One of Hank's notable attributes is his knack to surround himself with highly capable students and colleagues, which always created a very upbeat and challenging atmosphere in his laboratory. Their friendship and collaborations continue to the present day. He is the first to very graciously acknowledge their contributions to his career, and they are extremely appreciative for his guidance during their studies and complete career.

Hank's philosophy is to work hard, find interesting problems (and financial support!), attract fine colleagues, distribute credit widely, push responsibility down, stay fit and socially active, and have fun! This philosophy has served him well throughout his life and career.

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Anne Buyle Padias

The University of Arizona

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