Sir Harry Melville, KCB, FRS

Sir Harry Melville will celebrate his 80th birthday on April 27, 1988, and it is appropriate that at this time we recognize his immense contributions to polymer science.

Sir Harry was born in Edinburgh, Scotland. There he was educated at the George Heriot School and later at Edinburgh University, where he received a Ph.D. degree. He later received a second Ph.D. degree from the University of Cambridge. From 1933 to 1944 he was a Fellow of Trinity College, Cambridge. In 1936 he was awarded the Meldola Medal of the then Royal Institute of Chemistry. In 1941 he was elected a Fellow of the Royal Society and in 1955 he received the Davy Medal of the Royal Society. He was appointed Assistant Director of the Colloid Research Laboratory at Cambridge in 1938, and in 1940 was appointed Professor of Chemistry at the University of Aberdeen. The Second World War prevented his taking up this appointment until 1946. During the war he served the Government, first as advisor to the Superintendent of Chemical Defense at the Ministry of Defense (1940–1943) and later as superintendent of the Radar Research Station (1943–1945). After the war he resumed his teaching career in Aberdeen and in 1947 moved to the University of Birmingham as Mason Professor of Chemistry and Head of the Chemistry Department. He remained at Birmingham until 1956, when he returned to Government service in the prestigious post of Secretary to the Council of the Department of Scientific and Industrial Research. For service in this position, he was knighted in 1958. His last major academic appointment was as President of Queen Mary College in the University of London from 1967 to 1976, but he continued to serve the Government on a wide variety of committees. He also served as President of the Plastics Institute from 1970 to 1975 and received the Colwyn Medal of the Institution of the Rubber Industry.

Early research interests of Sir Harry Melville were chain reactions and photochemistry, especially mercury-photosensitized reactions in gases, but he soon became involved in the elucidation of free radical polymerization. In the mid 1930s, the mechanisms of what are now known to be free radical polymerizations were still uncertain. At a conference of the Faraday society in 1935, there was serious discussion of two alternative mechanisms for the polymerization of monomers such as styrene, namely, a step-wise molecular insertion reaction to the growing macromolecule and the now familiar free radical chain reaction. The second mechanism became the accepted one in the next year or two. At that time, it was believed that the clearest understanding of the mechanism of polymerizations would be obtained from studies of the reactions in the gas phase. Complications were to arise in this work due to the deposition of the nonvolatile polymeric products, but useful observations were made and conclusions drawn.

Sir Harry studied the photopolymerization of methyl acrylate vapor[4] and showed that the rate of polymerization was proportional to the square root of the light intensity, consistent with a free radical chain polymerization with second-order destruction of the free radical chain carriers.[2] This observation, together with observations of retardation or inhibition of the reaction by oxygen and certain other substances, added to the growing evidence of other workers

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for free radical mechanisms of many similar polymerizations. The photopolymerization of the vapor of methyl methacrylate[3] showed particular complications in that the reaction continued in the dark following a period of illumination. Despite this complication, the rotating sector (intermittent illumination) method was applied for the first time in polymerization studies to determine the lifetime of the photoreaction, but the complications described prevented a meaningful interpretation of the results. It was not until the end of the war, in 1945, that Melville and Burnett[4] applied the rotating sector method to measure the lifetimes of reaction chains in the photoinduced polymerization of liquid monomers. This technique permitted the separate determination of the rate constants for the propagation and termination of the growing chains. During the latter part of his time at Aberdeen, and throughout his time at Birmingham, he studied alternative[5] methods of determining these rate coefficients by following the development of the reaction chains during the nonstationary state preceding the main part of the overall reaction. Of the methods tried, the most successful followed the light-induced polymerization in the early stages by the rise in temperature (the thermocouple method).[6] This method could also be applied to measure the lifetimes of reaction chains at high extents of polymerization and thus to study the effects of accumulated polymer on the rate constants of propagation and termination reactions, the latter associated with the "gel effect".

The immediate postwar period was one of intense activity in polymer chemistry, in which many groups of investigators made substantial advances, often almost simultaneously. Sir Harry, first at Aberdeen and later in Birmingham, gathered together a group of collaborators and students with whom he made significant contributions, chiefly in the field of free radical polymerization and polymer degradation. Central to the interpretation of most rates of polymerization is the assumption that the rate constants for propagation and termination are independent of the sizes of the macroradicals. Gee and Melville[7] examined the consequences of some alternative assumptions. The formal kinetic expressions usually obeyed suggest that the simple assumption is at least approximately correct, although some relevant questions remain unanswered.

Much empirical information about copolymerization became available during the 1930s but this could not be rationalized until the copolymer composition equation was derived in 1944.[8] In 1947 Melville[9] gave an expression for the overall rate of copolymerization. A full interpretation of experimental results (for styrene and methyl methacrylate) was published two years later.[10] There followed many similar studies, from the Birmingham group and from others.

Among other contributions, Melville introduced the use of radiotracer techniques.[11] For example, he and Bevington used labeled initiators to determine whether the macroradical–macroradical termination reactions occur with combination of the radicals (as, for example, in the copolymerization of styrene and methyl methacrylate) or by disproportionation (to form two macromolecules as in the case of the polymerization of methyl methacrylate).[12] Apart from its obvious importance, the rate of initiation of free radical polymerization needs to be known in order to measure the rate constants for propagation and termination. Nearly all stable free radicals that act as inhibitors show some complications of behavior. For example, Melville and Bevington[13] were able to show by using labeled *p*-benzoquinone that it copolymerizes with styrene and acts as a retarder in the polymerization of methyl methacrylate.

In the late 1940s, Melville began to make significant contributions to our understanding of the thermal degradation of polymers. Among the first to be studied in detail was poly(methyl methacrylate).[14] The production of monomer by chain unzipping was accompanied by a relatively small decrease of molecular weight of the remaining polymer, showing that most molecules unzipped to the end with little scission.

Among other contributions to polymer chemistry, he was involved in the study of polymers in solution by light-scattering[15] and osmotic pressure[16] and in the study of free radicals trapped in methyl methacrylate–glycol dimethacrylate gels by use of ESR.[17]

He was an enthusiatic teacher who inspired many undergraduates to share his interests. In his lecturing and writing, he had an unusual directness and clarity. Students and collaborators will recall the encouraging stimulation they received from him in discussions of their work. Many projects he initiated were continued successfully by his collaborators (G. M. Burnett, N. Grassie, J. C. Bevington, J. C. Robb, and others). He retained a real interest in polymer chemistry and attended conferences long after his active involvement had ceased.

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References and Notes

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