EDITORIAL

Preface to the special issue

Conceptual Innovation in Polymer Science: Ichiro Sakurada Special Issue

Polymer Journal (2012) **44**, 2–4; doi:10.1038/pj.2011.127

This special issue, ‘Conceptual Innovation in Polymer Science’, is dedicated to Ichiro Sakurada (1 January 1904–23 June 1986), Professor Emeritus of Kyoto University and considered to be the ‘Father of Polymer Science in Japan’. Two early papers on polymer science by Professor Ichiro Sakurada, including historically epoch-making discoveries, are reproduced in English translation in this issue. Their original papers, which were published in Japanese during the World War II, are hardly known to foreign polymer scientists and even to many of the Japanese polymer scientists. Fortunately, Dr Yutaka Sakurada, the son of Ichiro Sakurada, has given his willing consent for these translations.

The two early papers by Ichiro Sakurada are as follows:

PAPER ON THE EMPIRICAL RELATIONSHIP BETWEEN INTRINSIC VISCOSITY AND MOLECULAR WEIGHT, ENTITLED ‘SHAPE OF THREADLIKE MOLECULES IN SOLUTION, AND RELATIONSHIP BETWEEN SOLUTION VISCOSITY AND MOLECULAR WEIGHT’

This paper was originally published in the *Proceedings of the 5th Meeting of Kyoto Imperial University, Research Institute for Chemical Fibers, Japan*, in 1940. The lectures were delivered at the 5th Meeting, held at Osaka Cotton Industry Assembly Hall [Nihon Mengyo Kaikan], now Nihon Mengyo Club, Corp. on 8 October 1940.

For half a year, probably from December 1928 to May 1929, Sakurada stayed in the Laboratory of Prof. Wolfgang Ostwald, Kolloid-Abteilung des Physikalisch-chemischen Instituts der Universität Leipzig. During this period, he studied the viscosity of colloid solutions while publishing four papers on the swelling of acetyl cellulose as a part of a series of papers ‘Reports on the roles of dielectric constant, polarization and dipole moment in colloid systems’ by Wo. Ostwald (I. Sakurada, *Kolloid-Z.* **48**, 277, 353; **49**, 52, 178 (1929)). Then, he moved to the Laboratory of Prof. Kurt Hess, Director of Kaiser-Wilhelm-Institut für Chemie, in Berlin and stayed as a scholar until 1931. As a coworker of Prof. Hess Sakurada took part in the controversy with Hermann Staudinger on the concept of ‘macromolecules’. In the controversy he paid particular attention to the so-called Staudinger’s viscosity law and conducted viscosity measurements in the Hess’s Laboratory. (I. Sakurada, *Ber.* **63**, 2027 (1930); K. Hess, C. Trogus, L. Akim, & I. Sakurada, *Ber.* **64**, 408 (1931); I. Sakurada & K. Hess, *Ber.* **64**, 1174 (1931); K. Hess & I. Sakurada, *Ber.* **64**, 1183 (1931). Also refer to: C. Priesner, *H. Staudinger, H. Mark und K. H. Meyer* (in German) (Verlag Chemie,

Associate Professor Ichiro Sakurada (1934)

Sakurada as, President of Chemical Society of Japan (1968)

1980); I. Sakurada, *Kobunshi Kagaku to Tomoni* [Along with Polymer Chemistry] (in Japanese) (Kinokuniya Shoten, 1969); I. Sakurada, Research reminiscences (9) (in Japanese), *Kagaku* **27**, 867 (1972).) For solving the problem of solution viscosity, Prof. Hess invited R. Eizenschitz, a theoretical physicist who contributed to *dispersion forces* (R. Eizenschitz & F. London, *Z. Physik* **60**, 491 (1930)). He not only published a paper on a viscosity equation for long stretched particles (R. Eizenschitz, *Z. Physik. Chem. A* **158**, 78 (1932); **163**, 133 (1933)), but also cooperated with Sakurada in the viscosity measurements. Thus, Sakurada continued to have a constant interest in the solution viscosity of polymers even after he left the Hess's Laboratory (for examples: I. Sakurada, *Kolloid-Z.* **64**, 195 (1933); *Ber. Deutsch. Chem. Ges.* **68**, 998 (1935)).

In 1938, Sakurada published a paper on the theoretical treatment of solution viscosity of threadlike molecules (I. Sakurada, *Z. physik. Chem. B* **38**, 407 (1938)). Based on the theoretical equations derived for spherical particles and straight rod particles by Einstein and Kuhn respectively, he showed that if the flexibility of a molecule is assumed to increase with its molecular weight, the Staudinger's viscosity law holds approximately for a non-free-draining model.

In 1940, Staudinger and Warth published important experimental data on the molecular weights of various polymers determined by both an osmometric method and a solution viscosity method (H. Staudinger & H. Warth, *J. Prakt. Chem.* **155**, 261 (1940)). Using these data, Sakurada immediately verified his idea of an empirical relationship between the intrinsic viscosity $[\eta]$ and the molecular weight M in polymer solutions, that is,

$$[\eta] = KM^a \quad (1)$$

where K and a are constants for a particular polymer–solvent pair at a particular temperature. He found out that this equation holds very well and announced the results in Osaka, Japan, on 8 October 1940. This translation is the proceedings of its announcement.

On the other hand, R. Houwink had a great interest in the disagreement between the theoretical values calculated by Kuhn's viscosity equation for freely flexible molecules and the observed viscosity values of cellulose and polystyrene solutions. Hence, as soon as the data by Staudinger and Warth were published, he examined the relations between the molecular weights determined by the osmometric method and the solution viscosity method (R. Houwink, *J. Prakt. Chem.* **157**, 15 (1941)), obtaining the following relation:

$$[\eta] = KM^{0.6} \quad (2)$$

In his small book, H. Mark introduced Staudinger's viscosity law and Kuhn's theoretical equation for the solution viscosity of randomly coiled molecules, and described that a more general form may be $[\eta] = KM^a$ (H. Mark, *Der feste Körper*, 103 (Hirzel, Leipzig, 1938)).

Today, equation (1) is well known as the 'Mark–Houwink–Sakurada relation'. (For examples, see text books such as Hans-Georg Elias, *Makromoleküle: Struktur-Eigenschaften-Synthesen Stoffe*, 300 (Hüthig & Wepf Verlag, Basel, Heidelberg, 1975); Gert Strobl, *The Physics of Polymers: Concepts for Understanding their Structures and Behavior*, 295 (Springer-Verlag, Berlin, 1996); L. H. Sperling, *Introduction to Physical Polymer Science*, 3rd edn, 100 (Wiley-Interscience, New York, 2001).) However, Mark did not confirm equation (1) using experimental data, and he did not discuss it theoretically in detail either. Therefore, equation (1) should be named 'Sakurada–Houwink–Mark relation' or 'Kuhn–Sakurada–Houwink relation'.

(by K. Kaji)

PAPER ON THE MIXED POLYMERIZATION, ENTITLED 'MIXED POLYMERIZATION'

The copolymerization theory by Sakurada was first reported as a lecture (I. Sakurada, *Proceedings of the First Polymer Training Course*, sponsored by Kobunshi Tomonokai, 20 September 1944). This was later reproduced in a book chapter (Chapter 8) of '*High Polymerization Reaction [Kojugo Hanno]*' by I. Sakurada, published by Polymer Chemistry Association [Kobunshi Kagaku Kyokai] (the forerunner of the Society of Polymer Science, Japan), Tokyo, 1946. This translation was made from the book chapter.

In this work, Sakurada developed a theory of copolymerization in chain reactions, which included the pioneering achievements mentioned below.

In a standard model of copolymerization of monomers X and Y, the two monomers as well as the two propagating chains with active terminal units X and Y, respectively, are kinetically distinguished. This 'terminal model' is therefore characterized by four propagation rate constants k_{ij} , with i and j ($=X$ or Y) denoting the terminal unit and the adding monomer, respectively. In earlier days, this model had contributed rather little to a comprehensive understanding of actual copolymerizations, until the assumption of steady state, effectively used in homopolymerization kinetics, was extended to copolymerization. This assumption was equivalent to compositionally neglecting the initiating and terminating chain ends, and hence dramatically simplified the otherwise complicated copolymerization kinetics, urging several researchers to reach a common equation of copolymer vs feed-monomer compositions, approximately around 1944 (T. Alfrey, Jr. & G. Golfinger, *J. Chem. Phys.* **12**, 205 (1944); F. R. Mayo & F. M. Lewis, *J. Am. Chem. Soc.* **66**, 1594 (1944); F. T. Wall, *J. Am. Chem. Soc.* **66**, 2050 (1944). Independently of these studies, Sakurada also derived the same composition equation (equation (45) in the text) using the same assumption. As is well known, the terminal-model composition equation is characterized only by the two parameters $r_X = k_{XX}/k_{XY}$ and $r_Y = k_{YY}/k_{YX}$, which were termed the 'monomer reactivity ratios' by Mayo and Lewis. Today, there is a huge accumulation of radical copolymerization data that have been organized in terms of these ratios, and the composition equation is often called the Mayo–Lewis equation, perhaps largely after the godfathers of the ratios.

Another distinguished achievement of Sakurada may be that regarding the method for experimentally determining monomer reactivity ratios. He rearranged his composition equation to a linear function of these ratios (equation (48) in the text). This equation is equivalent to the Fineman–Ross plot, which was developed later and is used by many researchers as one of the standard methods to determine the ratios (M. Fineman & S. D. Ross, *J. Polym. Sci.* **5**, 259 (1950)). In fact, the equivalence of the two equations was quickly pointed out by Sakurada and his coworkers themselves in a Japanese journal (I. Sakurada & M. Yoshida, *Kobunshi Kagaku* **7**, 334 (1950)).

(by T. Fukuda)

To this special issue, 13 papers by distinguished Japanese polymer scientists are contributed, from which some aspects of recent developments in the fields of syntheses, and structure and physical properties of polymers in Japan can be found. The editors would like to express their sincere thanks to these authors.

This special issue was planned more than ten years ago by the Editorial Committee of *Polymer Journal*. The Editor-in-Chief at that time was Prof. Yotaro Morishima, now Emeritus Professor of Osaka University. Prof. Toshikazu Takata, Tokyo Institute of Technology, Japan, who is the present Editor-in-Chief of this

journal, has reconfirmed this plan. The present guest editors of the special issue wish to thank them and their editorial staff for this beautiful policy. However, such a long period until the publication shows how difficult the translation of these scientific papers written in old Japanese is. We have been very lucky in that Dr Yutaka Sakurada accepted this translation. The editors deeply acknowledge him for his great efforts towards these translations. He graduated from Kyoto University (Doctor of Engineering) and worked in Kuraray Co. Ltd. and Kuraray Medical Inc., Japan. Now, he is at Consultant of Cerus Inc., CA, USA. Special thanks are also due to Professor Emeritus Takeshi Fukuda, Kyoto University, for his foreword to the copolymerization part and his efforts to improve the text.

We are also indebted to publishing and production team at NPG for their cooperation to publish this issue. The editors appreciate Ms

Hanako Ishida at the Institute for Chemical Research, Kyoto University, for preparing figures in the text and the cover image for this issue.

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