

# Macromolecules

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## Paolo Corradini



On October 19th, 2000, Professor Paolo Corradini celebrated his 70th birthday with his family, friends, students, and colleagues. A one-day meeting was held on October 23rd at the University of Naples to celebrate this event. Professor Corradini's former and recent students attended the meeting to recognize his fundamental contributions to the field of polymer science. Paolo Corradini has been passionately involved in teaching chemistry and polymer science and in building our understanding of the organization of macromolecules in polymer crystals and the mechanisms of stereospecific polymerization.

Corradini was the pioneer in the establishment of the structures of stereoregular polymers. He is recognized internationally as one of the leading polymer scientists of the past half-century, having introduced the basic principles of polymer crystallography. The influence of

his studies on polymer science has been profound, as he contributed to the determination of the structure of almost all the isotactic polyolefins prepared in the 1950s with Ziegler–Natta catalysts. The contributions of Corradini started with fundamental studies, in collaboration with Giulio Natta, on the synthesis and structural analysis of stereoregular crystalline polyolefins. He solved the structure of isotactic polypropylene and established the chain conformation to be a 3/1 helix.<sup>1</sup> This was the third major determination of polymer structures with chains in helical conformations, after the  $\alpha$ -helix of poly( $\alpha$ -amino acids) and the double helix of nucleic acids, and the first of a helical synthetic polymer.

Paolo Corradini was born in Rome, Italy, on October 19, 1930. He studied Chemistry at the University of Rome and graduated in 1951. His graduate research was related to the determination of the crystal structure by X-ray diffraction of 1,1'-cyclobutane–dicarbonylurea.

In 1952, Paolo Corradini joined Professor Giulio Natta's research group at the Institute of Industrial Chemistry of the Polytechnic of Milan. During the same year collaboration started between Natta and Ziegler on the synthesis of linear ethylene oligomers with aluminum alkyl catalysts (the "Aufbaureaktion") to obtain higher molecular weight ethylene oligomers and the corresponding linear carboxylic acids, which were used to produce soaps. At the end of 1953, Ziegler's group used a catalytic combination of aluminum alkyls and titanium tetrachloride to produce high molecular weight polymers. The titanium catalysts were then used in the Natta laboratories for the polymerization of propylene in order to obtain elastomeric polymers through the copolymerization of ethylene and propylene. On March 11, 1954, a solid material was obtained using the titanium catalyst with the propylene alone. Corradini examined the material by X-ray diffraction and found that it was crystalline. A new class of crystalline polymers, stereoregular polymers, was discovered. This was the starting point of fundamental structural studies. The terms isotactic, syndiotactic, and atactic were invented to describe the microstructure of vinyl polymer chains and are now basic concepts of macromolecular chemistry.

Within a few months, Corradini solved the crystal structure of polypropylene and found that the polymer chains were characterized by regular configurational sequences and a regular helical conformation. This

discovery was the basis of the structure determination of many new synthetic crystalline polymers. Within a few years, Corradini solved the crystal structures of almost all the new stereoregular polymers produced in the Natta laboratories using the new catalyst: isotactic polystyrene,<sup>2</sup> substituted polystyrenes,<sup>3</sup> isotactic polybutene,<sup>4</sup> syndiotactic polypropylene,<sup>5</sup> *cis*- and *trans*-1,4-polybutadiene,<sup>6,7</sup> isotactic and syndiotactic 1,2-polybutadiene,<sup>8,9</sup> and so forth. Natta and Ziegler shared the Nobel Prize for the discovery of stereospecific polymerization in 1963, in recognition of the fact that nature's monopoly on building macromolecules with ordered steric helical units had been broken. Corradini played a key role in Natta's work.

In 1960, Corradini left Natta's group and was appointed Full Professor of Inorganic Chemistry at the University of Cagliari. In 1961, he was called to the University of Naples "Federico II" as Professor of Inorganic Chemistry. Professor Corradini has been at the University of Naples since that time and, since 1991, has held the Chair of Industrial Chemistry.

In addition to the determination of the crystal structures of most of the stereoregular polymers, Corradini established the basic principles which define the conformation assumed by polymer chains in the crystalline state and general rules concerning the mode of packing of polymers in crystals.<sup>10</sup> Corradini has shown that most of the known crystal structures of polymers can be easily rationalized in terms of these principles.

In 1968, Corradini spent one year as Visiting Professor at the Polytechnic Institute of Brooklyn. For many years, from 1968 to 1979, he was Member of the Macromolecular Division of IUPAC, and from 1989 to 1990, he was the President of the European Polymer Federation. Corradini has also served as Director of the Chemical Institute in Naples and as President of the Scientific Council of the CNR Laboratory for the Technology of Polymers in Naples.

Paolo Corradini has received many honors and awards, including those from the Italian Ministries of Education (1982) and Culture (1985). Among other notable prizes is the Giulio Natta medal of the Italian Chemical Society. In 1987, Paolo Corradini was elected Corresponding Member of the "Accademia Nazionale dei Lincei", the most important Italian Academy, of which Galileo Galilei was a founding member, and since 1993 he is Full Member.

Most of the polymers studied by Corradini in the early 1960s have achieved a very large industrial importance, and their emergence as plastic materials has changed our life. For instance, isotactic polypropylene, from its birth in 1954, has achieved an annual world production by 2000 in excess of 30 million tons. In the field of elastomers, *cis*-1,4-polybutadiene has achieved a similar importance. After the discovery of stereoselective homogeneous metallocene catalysts for the polymerization of olefins in 1984, many new crystalline polymers have been produced in recent years. Once again Corradini and his collaborators in Naples have solved the crystal structures and clarified the polymorphic behaviors of most of the novel syndiotactic polymers, such as syndiotactic polybutene,<sup>11</sup> poly(4-methyl-1-pentene),<sup>12</sup> polystyrene,<sup>13</sup> or alternating isotactic and syndiotactic copolymers of styrene and carbon oxide.<sup>14,15</sup>

More recently, Corradini has investigated the mechanism of stereospecific Ziegler-Natta polymerization of olefins. On the basis of the evaluation of the interactions

between nonbonded atoms at the catalytic sites, he has given a unifying model which explains the stereoselectivity of the polymerization reaction on TiCl<sub>3</sub>-based and on high yield MgCl<sub>2</sub>-supported heterogeneous catalysts as well as on homogeneous metallocene catalysts.<sup>16</sup>

The extensive scientific research of Paolo Corradini has resulted in more than 400 scientific papers. Those of us who have had the privilege to collaborate with Paolo Corradini have found enthusiasm and inspiration. His passion for research has always been an example that has stimulated many young researchers to start studying polymer science. His never-failing desire to share his knowledge has been our immense fortune. He keeps teaching his unique vision of macromolecules and polymer crystals and how to see, "with the eyes of the mind", the spatial arrangement of polymer chains and macromolecular crystals. We are sure that Paolo Corradini will continue to contribute significantly to the field of polymer science with his characteristic passion.

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