Book Reviews

Chemical Microstructure of Polymer Chains

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The value of polymeric materials derives not just from their high molecular weight, nor from the number of atoms of which the molecules are constituted though a large number is necessary of course, but from the identity of the elements concerned and from the way in which they are arranged relative to each other. A simple illustration of this is the organization of DNA, in which five elements (H, C, N, O and P) are arranged to form an extensive backbone and side chain system, whose function is to encode the information describing life at the chemical and biological level. The interrelation between the microstructure of a particular strand of RNA and the proteins derived from it is so well understood that to have the sequence of either is to have a full description of the sequences of both. The reproducibility of the structure of DNA during cell division and the variations which occur during meiosis concern us all, and have done so for some time, though this was little appreciated by our ancestors. Our present understanding of the structure and function of such biological molecules has developed in recent years simultaneously with the design and industrial production of plastic materials. The dichotomy between natural polymers such as wood and wool and products such as polythene may soon cease to be recognized if we can discover other living systems like that whose vital force, enshrined in its DNA microstructure, converts carbohydrate feed into poly(3-hydroxybutyrate). This product might be more useful if it had not a completely perfect tacticity.

For even a simple monomer such as vinyl chloride, the predominant head to tail addition reaction of propagation is supplemented by processes such as reverse addition and side chain production. Whereas in preparative organic chemistry the products of side reactions can be removed, when polymers are produced there is no such possibility: the irregularities are entrained in the polymer chain. The family of catalytic systems discovered by Zeigler and Natta create highly ordered structures and have been a most significant development in this respect. However irregularities in chemical placement and in stereochemistry are not necessarily regarded as imperfections in an ideal structure. They may be tolerated or even desired. What is required is that we can easily recognize them, that we understand their origin so that their prevalence can perhaps be controlled at the preparation stage, and that the link between their presence and the processability and properties of the bulk materials is understood. Koenig's book is devoted to the first and essentially more basic part of such developments in understanding polymeric materials.

The value of ^{13}C n.m.r. spectroscopy and of high field ^{1}H n.m.r. spectroscopy for characterizing the microstructure of polymers in solution has been well established in recent years. Hetero atoms in either the main chain or in pendant groups influence chemical shifts in recognizable ways. In purely hydrocarbon polymers, the Grant and Paul parameter set or similar schemes may be applied to the shifts of C atoms in the neighbourhood of crosslinks or branch points to characterize the connectivity of the molecular framework. Provided that side chains are not too remote from each other, stereochemical effects may also be recognized in solution spectra. It is the relative placement of side chains, known well as taciticity, which controls the conformation of the main chain in the solid state and ultimately such bulk properties as the extent of crystallization. Most of the above microstructural features can also be detected in the solid state itself by Raman and infra-red spectroscopy which have also their more straightforward uses as an analytical tool. Moreover, the vibrational spectroscopy of polymers, to which this author has made a major contribution, is sensitive to long range order within one macromolecule shuch as is found in helical or other extended conformations, to intramolecular packing effects and to features at and on each side of the crystalline–amorphous interface. As well as these two spectroscopic methods, whose experimental techniques and power of discrimination are well illustrated, Koenig indicates the possibilities of e.s.c.a., u.v./visible spectroscopy and mass spectroscopy among others. Certain aspects of chain structure may also be revealed by chemical reactions concerning the polymer.

The structure of a macromolecule is determined by the conditions which prevailed during its preparation. The microstructure records in space what happened in time at the reaction site, and indeed some chemists value this feature alone for the information it provides them about their catalytic species. As we turn our attention from a one-dimensional to a three-dimensional macromolecule, the record of the order of events of preparation becomes less certain, the structural elements become more difficult to define and detect and the statistical apparatus required for analysis becomes more elaborate. The kineticist would wish to describe a preparation in terms of stoichiometry, mechanism and have values for the rate constants, but even for a linear molecule the business is complex enough. For the simplest case, a binary copolymerization to which Bernouillian statistics apply, the author describes the inherent difficulty, which arises from the structure of the errors, in finding the reactivity ratios from feed and copolymer compositions, and he provides the solutions of Tidwell and Mortimer and others. For such a copolymerization reaction, however, monomer sequence information obtained at different feed ratios is more sensitive than rate or polymer composition data obtained under similar conditions for distinguishing between the various possible models. Accounts of the theory of stochastic processes and of the statistical relations between the various possible sequences of repeat units are thus given prior to the treatment of Bernouillian and Markovian models of instantaneous binary copolymerizations. Subsequently he examines the consequences of the drift of feed composition with conversion for binary copolymerizations, several special cases of multicomponent polymerizations and the influence of extra possibilities such as the formation of charge–transfer complexes between monomers and the occurrence of depropagation reactions near the ceiling temperature appropriate for the addition of one monomer. In a separate chapter the related but simpler topic of side chain stereo configuration is described. The tacticity of both homopolymers and copolymers may be produced by a simple terminal model, or may justify the development of penultimate, penepenultimate or two stage (Coleman–Fox) models.

We have here a well organized guide to three aspects of polymer microstructure: its definition and statistical description, its characterization by experimental methods and its use for elucidating the polymerization process. There are many, both old hands and newcomers who will find in this book succour and stimulus.

A. H. Fawcett

Developments in Polymer Stabilisation Volume 2

Editor G. Scott

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The papers in this volume deal with the function of organotin compounds and metal soaps as thermal stabilizers in PVC. Ayrey and Pollar summarize the synthesis of alkyl tin stabilizers and describe the sporadic attempts which have been made to produce polymeric stabilizers. Their review of the toxicity of organotin derivatives should prove a useful introduction to this important subject. Like Ayrey and Pollar, Cooray and Scott consider in depth the stabilizing roles of organotin compounds. The latter authors point out that in mixing in the presence of small amounts of oxygen mechanochemical scission can give rise to the products, HCl, unsaturation and hydroperoxides, which decrease the thermal stability of PVC. How various stabilizers are effective in nullifying the catalytic effect of one or more of these products is a major topic of this paper.

After a brief review of the literature Guyot and Michel give a comprehensive account of work in their laboratory on the stabilization of PVC. From kinetic studies of the effects of metal chlorides, carboxylates and secondary stabilizers on the thermal dehydrochlorination of the model compound 4-chloro-2-ene an explanation of the stabilizing mechanism of each of these systems is proposed. For the more practical reader examples are given where colour, torque, infra-red, g.p.c. and coulometric techniques have been usefully employed to study PVC stabilization processes.