

## HIGH POLYMERS

AN International Conference on High Polymers was held at the University of Nottingham during July 21–24. This Conference, which was organized by a British committee under the chairmanship of Sir Harry Melville, was attended by nearly six hundred scientists, including an official delegation of twelve Russians and altogether 150 foreign specialists—from twelve nations—in the physics and chemistry of high polymers.

The Conference provided a timely opportunity for a full exchange of views between those working in the high-polymer field at universities and in industrial and government research laboratories. The main themes selected for discussion were: (a) reaction mechanisms and kinetics with special reference to heterogeneous polymerization, including trapped radicals. Production of graft and block co-polymers; (b) physical, thermodynamic and mechanical properties of high polymers. The papers, which were preprinted and circulated before the meeting, were limited to forty-four.

It is now becoming accepted practice at international polymer meetings for Prof. H. Mark of the Polytechnic Institute of Brooklyn, New York, to deliver the opening address, and on this occasion he summarized in a masterly manner recent developments in the preparation and synthesis of stereospecific polymers, and the structural importance of helical configurations in understanding the properties of these polymers.

The discovery in 1953 by Karl Ziegler that catalysts formed by interaction of a metal alkyl of groups I, II and III elements with certain transition metal compounds polymerize ethylene rapidly to a high molecular weight polyethylene at room temperature and atmospheric pressure opened up a wide and important field of the study of heterogeneous polymerization, and several papers were devoted to a study of the mechanism of the action of Ziegler catalysts. Many catalytic systems have been found to be equally effective in polymerizing ethylene and other olefins at low pressures, and one of the Russian papers dealt with the use of chromium and molybdenum oxides for this purpose. Catalysts of this type are used commercially in the United States for the synthesis of polyethylene of high molecular weight. There is much evidence that soluble complexes formed by interaction of certain titanium compounds and metal alkyls polymerize ethylene in solution at normal temperatures and pressure homogeneously, although at a rate much lower than that of typical heterogeneous catalysts. Catalysts of this kind are probably more amenable to mechanistic study, and detailed experimental kinetic results were presented on the polymerization of ethylene by homogeneous catalysts made from the interaction of aluminium triethyl and *sec*-butyl titanate, and zinc di-*n*-butyl and titanium tetrachloride in hydrocarbon solvents. Kargin and his colleagues (Moscow) reported that the mechanical properties of ethylene polymers made from catalysts formed by the interaction of organo-lithium compounds with titanium tetrachloride showed marked differences depending on the structure of the organic metallic component of the catalyst.

The most important development in the study of heterogeneous polymerization of the above type was the synthesis in 1954 by Natta and his co-workers

at the Milan Polytechnic of  $\alpha$ -olefin polymers with regular, linear, head-to-tail structures and the separation of the synthetic product into isotactic and atactic polymers. The stereospecific configuration of the former was established by X-ray methods, and a study of the nature of the catalysts enables the stereospecificity of the heterogeneous catalysts to be controlled. In this way many crystalline poly- $\alpha$ -olefins and di-olefins of definite stereochemical structure were synthesized for the first time. In the opening paper of the general discussion, Natta described his very extensive investigations on the kinetics of  $\alpha$ -olefin polymerization and co-polymerization of ethylene with  $\alpha$ -olefins. The decomposition of aliphatic diazo compounds by boron trifluoride and other boron compounds has been known for a long time to yield polymethylene of high molecular weight. From a kinetic study of this reaction Bawn and Ledwith proposed a polymerization mechanism involving boron alkyl as the true catalyst. They suggest that the polymerization is analogous to Ziegler-type polymerization of  $\alpha$ -olefins and occurs by co-ordination with the boron, and that this results in a successive series of insertions of monomeric units into a boron-alkyl bond. An interesting example of anionic polymerization was discussed by Overberger and co-workers (Brooklyn), who postulated that the initiation process of the polymerization of methacrylonitrile in liquid ammonia is a one-electron transfer from lithium to the monomer to give an anion radical.

In 1955 it was reported in the patent literature that propylene oxide could be polymerized by ferric chloride to give products of high molecular weight which were partially crystalline. C. C. Price (1956) showed that if an optically active monomer is used the activity is retained in the crystalline polymer, and the mechanism of polymerization suggested by Price is analogous to that proposed by Natta for the heterogeneous polymerization of  $\alpha$ -olefins. In a series of papers, C. C. Price and co-workers (University of Pennsylvania) and G. Gee and collaborators extend these investigations to other olefin oxides and show that a wide variety of catalyst systems—Lewis acid metal alkoxides, mixture of alkoxides and halides or metal halides—serve for the polymerization of propylene and other olefin oxides.

Many of the kinetic features of the polymerization of vinyl monomers in conditions in which the polymer formed is precipitated may be explained in terms of occlusion of precipitated free radicals of polymer chains. Bamford, Jenkins, Symons and Townsend reported results of the concentration of trapped polyacrylonitrile radicals as determined by electron resonance spectroscopy and the variation of this concentration with experimental conditions such as degree of swelling of the polymer, rate of photo-initiation and temperature. The fraction of radicals which become trapped was shown to be about 12 per cent in the bulk polymerization of acrylonitrile. Electron spin resonance measurements were also used by Atherton, Melville and Whiffen to follow radical concentrations in the co-polymerization of methyl methacrylate and glycol dimethacrylate.

F. S. Dainton and co-workers summarized their extensive and detailed studies on the polymerization of acrylonitrile in aqueous solution when initiated by: (a) Fenton's reagent, and (b) photochemically, using

various photosensitizers. By means of the rotating sector technique they have determined both  $k_p$  and  $k_t$  and also elucidated: (1) the mechanism of the termination reaction by salts of metals of variable valency; (2) the effect of coagulation on the rate of polymerization. Other interesting observations on heterophase polymerization which were reported and discussed were: (a) the increase in rate of the high-energy initiated polymerization of isobutene by the presence of metal oxides of high surface area; (b) the effect of the physical nature of the separating phase on the rate of the heterogeneous polymerization of acrylonitrile and methyl methacrylate by Palit and Guha (Calcutta); (c) the co-polymerization of water-soluble sodium methacrylate with methyl methacrylate maintained in a fine particle size with the aid of water-soluble colloids.

### Block and Graft Co-polymers

The general methods of synthesis of graft co-polymers have been fairly well worked out during the past ten years, and the group of papers presented to the discussion largely elaborated and consolidated these procedures, particularly with reference to the utilization of ionizing radiation, interaction of functional groups of macromolecules with monomeric and polymeric substances, and the initiation of monomers by macro-radicals. Various syntheses of graft and block co-polymers have been described in which polymers containing peroxides, hydroperoxides and perester groups may be used as initiators for the second-step polymerization, and Prof. G. Smets and co-workers (Louvain) presented kinetic results obtained with polymethylacrylate co-polymers containing *tert*-butyl perester groups and styrene monomer. A new method of synthesis of block co-polymers proposed involved the synthesis of polymers containing peroxide end-groups and the metal salt catalysed decomposition of the peroxide group in a second monomer. Prof. A. Berlin (Moscow) described the synthesis of graft co-polymers of branched structure by the polymerization of a number of monomers in latexes of polyvinyl chloride and synthetic rubbers. The preparation and kinetics of formation of block co-polymers from a primary polymer with amine end-groups which may be used as a macromolecular transfer agent and also the formation of graft co-polymers using a primary polymer with terminal double bond which co-polymerizes with a second monomer were described by Bamford *et al.* Wichterle and Gregor (Prague) reported the preparation of polymers of *N*-methacryloyl caprolactam. Polymer amides prepared in this way were shown to catalyse the polymerization of caprolactam, and the resulting grafted co-polymers had a three-dimensional structure. Caprolactam reacts with styrene-methyl methacrylate co-polymers to form soluble graft co-polymers, the properties of which have been studied by Chapman and Valentine. The mechanism and properties of grafts formed by polymerizing vinyl acetate monomer in the presence of polyvinyl alcohol and an alkali and a water-soluble persulphate catalyst were discussed by Hartley, and those of polymethyl methacrylate graft to natural rubber by Kobryner and Banderet (Strasbourg).

The recent interest in the use of radiation to produce new polymer hybrids has spurred a great deal of research, and four papers presented on this subject dealt mainly with grafting of vinyl monomers

to polyethylene film. In general, four methods were described for producing such co-polymers: (1) Simultaneous grafting—the film being irradiated while immersed in, or swollen by, monomer; (2) post-irradiation grafting—irradiation of dry film *in vacuo* or in air, followed by addition of monomer. These various aspects were described in the papers by Metz *et al.* (Brookhaven), Chapiro (Paris) and Hoffman (Paris). Dr. Chapiro also described the radiation grafting of styrene and methyl methacrylate on to chemically inert polytetrafluoroethylene. Cooper and co-workers compared the graft co-polymers from natural rubber latex and methyl methacrylate using visible, ultra-violet and  $\gamma$ -radiation and measured the effects of changes of monomer concentration and radiation intensity on polymerization-rates and molecular weights. The production of cross-links and of sites for grafting in solid high polymers may be achieved by hydrogen abstraction using ultra-violet light (200–300 m $\mu$ ). The rate is very much increased by the use of photosensitizers, and a comparative study of this effect with various aromatic carbonyl compounds was described by Oster (Brooklyn). Another method of grafting on to solid polymer was described by Natta (Milan) for poly- $\alpha$ -olefins. These hydrocarbons readily peroxide on heating in air, and the surface or internal hydroperoxide groupings (depending on the nature of the polymer) readily form free radical centres by thermal decomposition.

The mastication of polymers brought into a rubbery state on admixture with monomer causes polymerization of the monomer. This reaction was shown (Watson *et al.*) to have the characteristics of that expected if initiation was brought about by mechanical rupture of the polymer into free radicals. The preparation and properties of block co-polymers of polymethyl methacrylate-polystyrene were described.

### Physical, Thermodynamic and Mechanical Properties

In a theoretical paper on rubber elasticity, Flory, Hove and Ciferri (Mellon Institute) generalized the rubber elastic equation of state for the case where the chain displays change in internal energy with change in conformation, and investigated the relationship between the temperature coefficient of the mean square end-to-end chain distance  $\bar{r}_0^2$  and the elastic equation of state of the network. Gee and co-workers, developing the thesis that the effects of dynamic properties of linear polymers are closely related to intermolecular forces and chain flexibility, reported results on the measurement of the latter properties for polyisobutene. A torsion pendulum for measuring the internal friction of polytetrafluoroethylene was described by McCrum (Dupont). Results over the range 4.2° K. to the crystalline melting point at 600° K. indicated that hindered rotation occurs within the crystallites at temperatures as low as 220° K.

Several papers were concerned with the relationships between properties and structure. Meyerhoff and Canton (Mainz) discussed the molecular weights and molecular weight distribution of branched and unbranched polystyrene, and Magat *et al.* (Paris) extended the theory of the solubility of high polymers to solution of graft co-polymers. Natta discussed the dependence of the properties of  $\alpha$ -olefin polymers on their steric composition and summarized extensive results on the physical and mechanical properties of random, stereo and other kinds of block co-polymers.

The technical processes used for the manufacture of polyethylene yield a polymer which shows chain



branching, the degree of branching varying considerably with the conditions of polymerization. Methods of measurement of branching have therefore been of paramount interest in characterizing ethylene polymers, and a considerable effort has been expended on these studies. In a detailed and elegant study, Willbourn (I.C.I. Plastics) summarized the preparation of model branched polymethylenes and calibration methods which have been used for developing methods of measuring the numbers and length of branches in polythene. The effect of branching on the degree of crystallinity, crystalline melting point, density, rate of oxidation and dynamic mechanical properties were illustrated and discussed. Gubler and Kovacs (Strasbourg) presented similar physical measurements on a range of commercial polythenes and made an interesting approach to an interpretation of these properties by considering the polymer as a mixture of *n*-paraffins. The orientation of crystallites

which occurs on stretching polyethylene and its dependence on the degree of crystallinity were discussed by R. S. Stein (Amherst), and Eppe, Fischer and Stuart (Mainz) presented results obtained by electron diffraction and electron microscopic studies on the morphological structure of polyethylene, polyamides and other polymers.

The importance of crystallization under stress in fibre-making was emphasized in a paper by Thompson (I.C.I. Fibres), who proposed a model visco-elastic theory to explain the observed results, and de Vries (Amheim) discussed an empirical relationship between draw ratio of synthetic fibres and birefringence.

During the conference a number of technical visits were arranged to commercial laboratories and works. A reception was held on the opening evening, and the conference concluded with a dinner held in the Portland Building of the University.

C. E. H. BAWN

## COMPARATIVE ENDOCRINOLOGY

**D**URING May 25–29, nearly 150 scientists from many parts of the world met at the Cold Spring Harbor Biological Laboratories, Long Island, New York, to take part in the Columbia University Symposium on Comparative Endocrinology. The conference was organized by a committee headed by Prof. A. Gorbman, of the University of Columbia, and the choice of Cold Spring Harbor provided an ideal setting for its deliberations. The scientific programme was split up into a number of sections or main topics.

The first of these was concerned with endocrine factors in ecological adaptation. Prof. W. Hoar (British Columbia) reviewed the role of the endocrine system in permitting fish to survive and adapt themselves to seasonal changes, while his research associate, Miss B. Baggerman, gave neat and conclusive proof of the involvement of salinity preferences in the migratory behaviour of fish.

In his interesting account of mammalian adaptive mechanisms, Dr. J. J. Christian (Bethesda) reported on the relation between adrenal size and population growth in rodents. A gradual numerical increase in the population of mice in cages, without overcrowding, leads to a significant enlargement of the adrenal glands accompanied by lowered reproductive activity (for example, a reduction in litter size), and thus, by inference, to an adjustment of population size. Whether the two phenomena are causally connected is not clear, and it may be that the increased size of the adrenals serves merely as an indicator of population density.

The next session dealt with the endocrine basis of reproductive adaptations in the major groups of vertebrates. Prof. L. Gallien (Paris) described the unusual reproductive habits of *Nectophrenooides orientalis*, a viviparous African frog with a gestation period of nine months. Dr. M. R. Miller (Stanford), in the course of his review of reptilian reproduction, stressed the hazards of inferring endocrine function from morphological study alone. As an illustration he referred to the virtual absence of histologically demonstrable Leydig cells, apparently not associated with androgen deficiency, in certain types of lizard.

In a characteristic contribution, Prof. F. L. Hisaw (Harvard) developed a theory covering vertebrates in general, in which he stressed the ubiquitous, but

not necessarily biologically significant, occurrence of progesterone among chordates, and the gradual and independent evolution of luteal and placental function in different mammals, culminating with the largely autonomous placenta of primates.

Both the comparative morphology and physiology of the principal endocrine organs and endocrine function in developing vertebrates received considerable attention during the conference. Prof. E. Wolff (Paris) and Profs. A. Raynaud (Institut Pasteur) and L. J. Wells (Minnesota) reviewed the results of their, by now classical, experiments on somatic or endocrine growth and sexual development in mammalian embryos deprived of either the pituitary or gonads.

In the course of a comprehensive survey, Prof. A. Gorbman (Columbia) directed attention to the vagaries of thyroxine formation in lower vertebrates. Thus, certain types of fish and salamanders form thyroxine from labelled iodine administered to them only after protracted periods (lasting more than a month), while others may not do so at all. Interestingly enough, there is at least one type of frog in which the thyroid gland is completely absent but the larvæ of which none the less undergo metamorphosis.

The inadvisability of applying the results of experiments in mammals to lower animals was also emphasized by other contributors. Prof. B. Houssay (Buenos Aires) and Dr. M. R. Miller (Stanford) reviewed the effects of ablation of both the adenohypophysis and pancreas in different groups of vertebrates, and revealed the following interesting position: while the combined operation in mammals leads to the preparation universally known as the 'Houssay dog', there are important deviations from this situation in lower vertebrates. Thus, birds do not develop hyperglycaemia following removal of the pancreas. On the other hand, in the urodele amphibians (for example, *Triturus*) studied by Dr. Miller, the islet apparatus is of the purely  $\beta$ -cell type and pancreatectomy leads to severe hyperglycaemia. Hypophysectomy, however, does not cause the expected alleviation of the condition until after some months when all inter-renal tissue has atrophied. By contrast, the islets of lizards are of the  $\alpha$ -type, and removal of the pancreas induces hypoglycaemia