

# Book Reviews

## Comprehensive Chemical Kinetics

### Volume 15: Non-Radial Polymerisation

Edited by C.H. Bamford and C.F.H. Tipper

Elsevier, Amsterdam, 249.00 Dfl

In reviewing this book I have looked for the ability of the writers to supply an intellectual framework to the facts. In this respect some of the chapters which make up this volume are very good. In particular, 'The Kinetics of Polymerisation Reactions', by J.H. Saunders and F Dobson, 'Polymerisation of *N*-Carboxy- $\alpha$ -Amino Anhydrides', by C.H. Bamford and H. Block, and 'Lactams', by J. Sebenda. These three chapters naturally form a distinct class with a common chemistry, namely that of the carbonyl group in its different structural environments. Probably some of the finest mechanistic studies in organic chemistry have been carried out in the polymerization studies of this type. Using modern methods for end-group analysis, molecular weight and molecular weight distribution analysis, it is possible to add a new dimension to the classical techniques of physical organic chemistry. Probably, the most important discovery relevant to condensation reactions in general is the use of metal organic compounds as catalysts for the reaction of organic acids and alcohols by transesterification. Studies of the kinetics of polyesterification have also removed many of the misconceptions in organic chemistry associated with the simple condensation reactions forming esters and amides. Reaction in thin films show that under certain conditions, when the concentration of water is very low and removed rapidly from the system, rates of reactions can be very high indeed and the process is complete in seconds rather than hours.

The chapter on lactam polymerization brings together a considerable amount of information in a very readable form. The author, has of course, made a very considerable contribution to the development of this subject. The relations between structure and polymerizability of lactam is described in detail and the thermodynamics and mechanisms classified. The anionic polymerization and the role of acetylating agents as cocatalysts is described in detail. An account is also given of the more recent observations on the polymerization of *N*-substituted lactam rings using cationic initiators in anhydrous media.

The polymerization of *N*-carbonic anhydrides of  $\alpha$ -amino-acids (NCA's) exhibit some of the chemical features shown in the polymerization of lactams. Here again a very considerable amount of information has been edited to give a concise picture of this field. Similar to lactam chemistry strong base initiators form nitrogen or carbon anions by removal of an appropriate proton from an NCA molecule which then propagates by addition to the acyl carbonyl group of an other NCA molecule. The main difference between

NCA's and lactams is that the acylcarbonyl group is active enough to react with primary and secondary amines. The latter gives a narrow molecular weight distribution whereas the former process gives a broad molecular weight distribution. Some of the more interesting observations are associated with the absorption by hydrogen bonding, of the NCA onto the propagating polypeptide chain. One is the selectivity of poly ( $\gamma$ -benzyl-L-glutamate) for the L-NCA and the other is the rate enhancement of the polymer chain on the polymerization of DL-phenylalanine NCA by poly (sarcosine dimethylamide). The latter is unusual in that the rate is dependent on the chain length of the initiating polymer for degrees of polymerization from 2 to 10.

The chapter on the kinetics of polycondensation reaction is one of the larger in the book and includes polyester, polyamide and polyurethane formation as well as the formation of aromatic polymers with ether sulphone, sulphide linkages between aromatic rings. The chapter is comprehensive and reasonably well balanced. However, there was no discussion on the very important cellular energy storage polyester, poly ( $\beta$ -hydroxybutyrate) which can also be made synthetically from the lactone. Also the organization of the division of labour between the various authors has led to the omission of the formation of polyesters from  $\alpha$ -hydroxy carboxylic acid anhydrosulphites and related cyclic compounds, which would have served to link the chemistry of this chapter with that of the NCA's. The discussion of the polymerization of carboxyl containing monomers is completed by Otto Vogls chapter on the kinetics of aldehyde polymerization.

An equally important part of the book is devoted to the polymerization of vinyl monomers, olefins and dienes by anionic, cationic and coordinated anionic initiators. Polymerizations of this type are more complex than the first group discussed but the total amount of research deployed on these studies has been very much greater. However, notwithstanding the value of the catalysts employed and the diversity of the chemistry observed, this is the least well understood region of polymerization chemistry. For example the chapter on Anionic Polymerization' by S. Bywater, which is the most readable of this group, gives an interesting review of the chemistry of the reactions involved in the simple growth reaction but comprehension ceases when stereospecificity in the propagation step is involved. This is one of the most fascinating aspects of metal-organic catalysis yet despite intensive research simple physicochemical techniques have failed to give information which enables the nature of the stereocontrol mechanism to be understood. This statement is equally true of Ziegler-Natta catalysts, comprehensively described by W. Cooper. The limitations of the present theories of stereocontrol in olefin polymerization by transition metal compounds is also discussed by W. Cooper who has succeeded in putting together a very realistic story from what is a very large group of facts. Unfortunately, the subject permits few generalizations and a systematic organization of the

subject matter along purely chemical lines is only possible in terms of the types of reactions occurring, the types of catalyst available and the structure of the monomers and their polymerizability. In my view it would have helped if the single metal systems had been discussed separately since they are able to demonstrate most of the basic reactions in unequivocal terms. An additional advantage to discussing these catalysts in this order is that it is possible to differentiate between anionic initiators, which is an extension of carbanion chemistry and the coordinated anionic type which are a feature of transition metal chemistry.

The chapter on the 'Kinetics of Homogeneous Cationic Polymerisation' by Ledwith and Sherrington covers most of the basic aspects of the subject. It overlaps to some extent with the discussion of the polymerization of cyclic ether and sulphides by P. Dreyfuss and M.P. Dreyfuss. The latter summarizes in a readable form a considerable amount of information and in particular the reaction kinetics of the polymerization of tetrahydrofuran which is reasonable well understood.

In conclusion the book is well written and expertly edited. It covers the important aspects of the subject in one volume in a way which makes comparisons between various types of non-radical polymerization processes relatively easy.

D. G. H. Ballard

## The Application of Flow Birefringence to Rheological Studies of Polymer Melts

J. L. S. Wales

Delft University Press, Delft, 1976  
111 pp. 25 Dfl

This monograph is the doctorate thesis presented by Dr Wales to the Delft University of Technology. It describes work carried out in the Central Laboratories of TNO, Delft, most of which is already reported elsewhere in the literature. The author's intention was 'to use flow birefringence to measure and characterize molten polymers of the type that are of industrial interest'. The specific materials studied are a series of narrow molecular weight distribution polystyrenes and a range of broader distribution commercial samples of polystyrene, high and low density polyethylene, poly (dimethyl siloxane), polypropylene and poly (vinyl chloride).

Following a rather brief survey of the elements of linear viscoelasticity and the theory of flow birefringence, Dr Wales goes on to describe in some detail several pieces of apparatus for determining the various components of the refractive index tensor for polymer melts in simple shear flow. There is next a chapter on molecular theories of rheology which gives a good summary of the

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physical and mathematical basis of the widely used bead-spring type models and, more importantly, some theories which attempt to describe non-linear behaviour (where, incidentally, Graessley's name is misspelt throughout).

The main experimental results are concerned with establishing the stress-optical law for polymer melts and examining the influence of molecular weight, molecular weight distribution, applied shear gradient, entrance and exit effects and sample pre-history. A great number of very useful data are presented for the shear and normal components of the refractive index and stress tensors under different conditions. Unfortunately, much of the discussion and interpretation of the results is semiquantitative and often non-rigorous. For instance, in establishing the validity of the linear stress-optical relation (pp 58-67) no estimate is ever given of experimental uncertainty. It is thus impossible to judge the significance of deviations from such a law ob-

served in some of the Figures, especially when data are presented on log-log plots which can be notoriously misleading. Again, on p 106 the claim is made that  $(n_{33} - n_{22})/(n_{11} - n_{22})$ , the optical equivalent of the ratio of second to first normal stress difference, is 'clearly independent of molecular weight and the molecular weight distribution', which is inconsistent with Figure 5.33.

The most useful study from the engineer's point of view is that made of orientation in injection moulding of polystyrenes. This showed that birefringence in moulded products can be semi-quantitatively predicted from steady shear flow studies, even for some two-phase materials. Whilst the results in themselves are interesting, it is disappointing that the heart of the processing problem is not tackled. After recognizing that 'impact strength and environmental stress resistance are considerably affected by the degree of molecular orientation determined by bire-

fringence', this relationship is discussed no further.

As with most theses published in book form, this monograph is unlikely to appeal to a very wide audience. There are certainly better and more detailed expositions of theories of rheology available, and the background treatment of flow birefringence is brief and necessarily directed to the specific problems in hand. Nevertheless, those intending to work in this field will find the experimental sections extremely useful and the potential of this technique in the study of complex flows and processing-property relationships should be of interest to the polymer engineer. Anyone with interests in these areas is at least saved a search through the literature and presented with a coherent, if somewhat expensive, account of work spread over several years.

G. C. Maitland

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