book reviews

Polyelectrolytes — Science and Technology

Masanori Hara (Ed.)
Marcel Dekker, Inc., New York, 1993, 416 pages, $150.00
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Amongst the enormous literature on the science and technology of polymers, polyelectrolytes have been treated as an almost extinct species, despite their widespread industrial importance. This book goes some way to redressing the balance.

The book presents a number of aspects of polyelectrolyte behaviour in aqueous and non-aqueous solution, biopolymers and interactions between oppositely charged polyelectrolytes. These are presented by leading research workers in their fields and are primarily aimed at research workers rather than undergraduate students. Each of the six chapters starts from simple concepts and then gives a review of the state of the subject, including quite recent references. Each chapter is fully referenced, and thus the book fulfils the authors' aims of providing a review of polyelectrolytes for research workers in the field or for people wanting to start research on them. The book is well produced with a good number of diagrams to illustrate the points made in the text. Throughout, the English is easy to read and understand.

Polyelectrolytes can be prepared synthetically or may occur naturally as proteins or polysaccharides. With both classes, their behaviour in solution is largely, though not completely, dominated by the electrostatic interactions. There have long been simple theories for these, though multicharge interactions have been difficult to treat with simple theories. The recent development of scaling theory has proved most useful in handling some of the more difficult aspects of solution properties, especially as solutions become more concentrated. This applies particularly to synthetic random coil polyelectrolytes, though less so to proteins, where hydrophobic bonding and hydrogen bonding often play a greater role. The contrast between these two aspects is well dealt with in the two initial chapters on 'Scaling theory' and 'Biological polyelectrolytes'. Although proteins are far more subtle than synthetic polyelectrolytes, it is interesting to see how far one can get in looking at e.g. transitions in DNA, starting from a simple electrostatic point of view. The enormous subject of polysaccharides is clearly beyond the scope of this book and their omission simply highlights the paucity of recent books on polyelectrolytes.

One major issue plaguing the study of the solution behaviour of polyelectrolytes is the relative contribution of inter- and intramolecular interactions. With highly charged polymers, these interactions tend to keep the molecules unassociated, but have a strong influence on properties such as viscosity and diffusion. In particular, as the third chapter points out, there can be a number of diffusion processes, both fast and slow, occurring in polyelectrolyte solutions simultaneously, and their interpretation is an active area of debate. The third chapter correctly outlines the areas of certainty and conjecture.

We normally think about polyelectrolytes in aqueous solutions, though it is quite possible to dissolve them in polar, often hydrogen bonding non-aqueous solvents. The changes this brings to the transport and thermodynamic properties are less surprising than one might think at first, as pointed out in Chapter 4. Nevertheless association between like charged groups on polyelectrolytes of low charge density (ionomers) can occur, in contrast to behaviour in water. In water association of charged groups can occur, but are usually of opposite charge. These complexes of oppositely charged polyelectrolytes can form interesting material for membranes, drug delivery vehicles and these applications are described.

The emphasis of the early chapters tends to be on fundamental properties of polyelectrolytes, with the later chapters giving more emphasis to applications — indeed the final chapter gives a good insight into the relation between polyelectrolyte properties and their application in practical systems, especially biological/pharmaceutical ones.

In general, the book is an invaluable summary of certain features of polyelectrolyte behaviour and properties, giving up to date, well-referenced views from leaders in the fields. The inevitable omissions of certain aspects only serves to highlight the need for more such books. The excellent referencing for each chapter makes the book very good value for money.

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Cyclopolymerisation and Cyclocopolymerisation

George B. Butler
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In 1949, quite a lot was known about the polymerisation of certain difunctional vinyl monomers but it was always assumed that, after the first double bond had been incorporated into a polymer chain, the second would either remain inert or would inevitably contribute to ramification and eventually crosslinking. It never occurred to anyone that the product of complete reaction could be a soluble saturated polymer, yet this is exactly the outcome that Butler found and explained, simply but ingeniously. It was a marvellous example of how a fact can be utterly baffling until explained, and subsequently be so simple as to be unremarkable; it takes insight of an unusual kind to bridge the gap, and that is precisely what George Butler brought to the study of what became known as 'cyclopolymerisation'.

Perhaps a brief explanation would be in order at this point. It is perfectly feasible that two double bonds in a monomer molecule should enter a polymer structure independently; if they did so, the ramification mentioned above would result. What Butler found and understood was that, with the double bonds in certain relative positions, there is a high probability that they will *not* behave independently but that the first to react will attack the second intramolecularly, forming a ring which becomes part of the polymer backbone or main chain. Whether the competition is essentially kinetic or thermodynamic in nature is a fascinating question which is discussed in detail in the book but, surprisingly, neither 'kinetics' nor 'thermodynamics' is cited in the index. (Neither is 'metathesis', a type of mechanism that often incorporates rings into polymer backbones.)

The substance of the last paragraph should not be taken to imply that only a few systems engage in cyclopolymerisation: the list of cyclopolymerising monomers is extensive, embracing symmetrical and unsymmetrical varieties, as well as monomers with two different types of multiple bonds, and moreover cyclopolymerisation extends to cyclocopolymerisation, where two or more

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