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Electron Spin Resonance
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Electron Spin Resonance

Volume 7

Foreword

Interest in Electron Spin Resonance continues unabated with new applications ranging more widely than ever, from the simplest chemical species (electrons) to the most complex of living organisms. The time horizon is also expanding, with applications to the study of processes on time-scales from sub-nanosecond to those of geological processes. The cross-fertilization resulting from the activities of workers in the many disciplines represented in this volume is clearly generating a new confidence in the information which can be gained from e.s.r. and further expansion into areas well outside those of the traditional chemist can be expected.

This diversity and interaction of topics is reflected in Volume 7 of this series of Specialist Periodical Reports by increases in the number of chapters, reporters and references. It also results, inevitably, in some overlap where several Reporters have drawn attention to papers which have significance in a number of different fields. This is as it should be, since it demonstrates the care which Reporters have taken to provide a comprehensive and balanced account of developments in their own fields.

As in the previous two volumes, the first chapter is devoted to a retrospective and critical assessment of progress in one field not covered specifically on a regular basis – in this case Polymer Chemistry. The remaining chapters, though now sub-divided to some extent, cover approximately the same range of topics as before. (It is hoped that ENDOR and ELDOR will return in Volume 8). However, the Senior Reporter is aware that there are still important areas of application of e.s.r. which do not receive adequate coverage, and would welcome suggestions for contributions to future volumes.

October 1981 P. B. Ayscough

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Applications of E.S.R in Polymer Chemistry

BY D. J. T. HILL, J. H. O'DONNELL, AND P. J. POMERY

1 General Introduction

E.s.r. has a long history of applications in polymer chemistry since the pioneering experiments of Schneider[1] on *X*-irradiated poly(methyl methacrylate) in 1951, at the time when e.s.r. was first being utilized in chemistry. For most of this period, e.s.r. studies in polymer chemistry have been confined mainly to solids in which radicals were produced by u.v. or ionizing radiation, the latter giving a more uniform distribution throughout the sample rather than at the surface. The elegant single-crystal studies used for small molecules could not be performed with polymers owing to the small size of the crystalline regions, but limited measurements were made on oriented radicals; this was achieved by tensile elongation of fibres or films.

These e.s.r. investigations of irradiated polymers had practical importance since they were relevant to the modification of the properties of polymer materials by crosslinking and scission. Industrial processes have been developed in this area and the selection of polymers for use in radiation environments is also now better understood.

The identification of trapped radicals, especially after irradiation at low temperatures, and their transformations and decay on warming were used as a basis for the proposal of mechanisms for radiation degradation. Two assumptions were usually implicit: (i) non-radical reactions were unimportant and (ii) the sequence of radical reactions during warming was the same as that occurring on a much shorter time-scale during (and following) irradiation at a higher temperature. These are undoubtedly both gross oversimplifications in many systems and continue to present great difficulties in the relationship between e.s.r. measurements and radiation chemistry of polymers. E.s.r. evidence for the production of radicals must always be taken as only one piece of evidence contributing towards the overall picture. In particular, quantitative measurements of the concentrations of individual radical species must be compared with the yields of small molecular products, chain scissions, and crosslinks, *etc.* More use of selective ionic scavengers could also be combined with e.s.r., despite dispersion and reactivity problems.

Solid-state polymerization is an area in which e.s.r. has been widely used to show the presence of radicals and to follow details of initiation, propagation, and termination reactions, inaccessible by other methods. The original

[1] E. E. Schneider, M. J. Day, and G. Stein, *Nature (London)*, 1951, **168**, 645.

interest in producing stereospecific polymers has been largely unrewarded, but recent work on diacetylenes has provided a new stimulus in this field.

E.s.r. investigations of irradiated polymers and solid monomers suffer from the poor resolution of the spectra due to the large linewidths resulting from anisotropic spin–lattice interactions. The difficulty with liquid systems is that the steady-state radical concentrations are normally below the detection limit. However, very successful liquid-phase work has been done by flowing initiator and monomer solutions, usually in water and with titanous ion–hydrogen peroxide as initiator, into a mixing chamber immediately before entry into a flow cell in the spectrometer. A wide variety of propagating radicals have been observed in this way, with narrow linewidths permitting accurate measurements of α, β, and γ hyperfine splittings.

Many studies have been made of the decay rates of radicals in polymers, but the measurements have been difficult to interpret by any consistent mechanism. Initial fast decays are usually attributed to radicals produced in close proximity to one another, *i.e.* in spurs or blobs. The actual mechanism of radical decay may involve chain movement, as at glass transition (T_g) or melting (T_m) temperatures, when decay is usually rapid and often complete, or hydrogen hopping, which has been proposed at lower temperatures. Certainly, greater mobility of radical sites, to form crosslinks for example, than of polymer chains seems to occur.

There is currently an upsurge of interest in the utilization of e.s.r. in polymer chemistry. This can be partly attributed to the availability of a new generation of e.s.r. spectrometers, which have greatly improved sensitivity, field stability, and variation of microwave power into the cavity – this last feature is very useful for selective saturation in polymers, enabling identification of the component radicals in a sample. Digital data output and interfacing to computer facilities are now standard. The advantages over the limitation to chart output are immense, particularly for immediate double integration of first-derivative spectra to measure radical concentrations, storage of spectra, and comparisons of experimental and simulated spectra. Rapid-scanning facilities enable kinetic studies using the entire spectrum and immediate observation of spectra on the oscilloscope screen to be made so that instrumental and sample conditions can be rapidly adjusted to obtain optimum spectra.

The use of spin traps for e.s.r. studies in polymer chemistry is a field which is certain to expand rapidly in the immediate future. The advantages include well resolved spectra, high concentrations of radicals from the liquid phase, and information on the early steps in polymerization or degradation reactions, depending on the reactivity of the chosen spin trap and the radicals in the system.

This is the first occasion when e.s.r. studies in polymer chemistry have appeared as a separate section in these Specialist Periodical Reports. Previously, relevant papers have appeared in different sections. The book by Ranby and Rabek[2] entitled 'E.S.R. Spectroscopy in Polymer Research'

[2] B. Ranby and J. F. Rabek, 'E.S.R. Spectroscopy in Polymer Research', Springer-Verlag, Berlin, 1977.