book reviews

Developments in Polymer Degradation—7

N. Grassie (Ed.)
Elsevier Applied Science, Barking, 1987, x + 280 pages, £40.00
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This volume deals with aspects involving thermal mechanisms, ionizing radiations, mechanical forces, mechanochemistry, radical reactions with polymers, degradation and stabilization effects, and fire retardancy mechanisms. This field of polymer degradation is highly specialized and inevitably has a limited readership.

The polymer types and systems considered are polymethacrylate salts (PMA) and PMA salt–methylmethacrylate copolymers, condensation polymers, biological and synthetic polyesters, ligno-celluloses, general polymers and mixed phase chloroparaffin–polymer systems.

Chapter 1 considers the general thermal degradation behaviour of poly(methyl methacrylate) (PMMA) with a characterization pattern following TG, TVA, IR analysis with references throughout. The prepration and degradation of MA salts, homopolymers, initiator-type are treated in the same manner. Depolymeriation to the monomer for metal salt–polymer systems or a route to the metal carbonate, cyclic and acyclic ketones are emphasized. Important factors are the volatility of the monomer (isobutyrate) which is also formed and the thermal stability of the metal carbonate (ammonium salt is unique in formation of degradation products).

At high temperature isocyanic acid, CO and CH_4 are produced. PMA–MA copolymers with various covalently bound monomers are considered and the behaviour of MMA–ZnMA copolymer is identified.

Chapter 2 deals with an examination of the thermal degradation processes occurring in the most common condensation polymers. The inclusion of functional groups in a polymer chain lowers the importance of decomposition reactions involving free radical and multiple hydrogen-transfer processes. As a result, condensation polymers tend to decompose by a selective cleavage mode. By making a series of structural changes and then observing the corresponding variations in significant decomposition products, a consistent series of data is obtainable on the decomposition pathway of each class of polymers bearing different functional groups (polyurethanes, ureas, esters, carbonates, amides, ethers, sulphides, siloxanes and phosphazenes).

Techniques considered are flash pyrolysis, GC/MS, and slow heating, direct MS. Disadvantages are outlined, and, in relation to the latter no mention is made of the possible use of the more sophisticated computer-based pattern recognition methods now available to assist in the analysis of the composite mass spectra of pyrolysis products.

Chapter 3 considers the degradation and stabilization of polyesters of biological and synthetic origin. The routes are compared and the degradation routes are similar once catalyst residues are removed. The pure biopolymer is on the limit of melt processibility, and conventional stabilizers do not affect its random scission mode of decomposition. Control of melt viscosity is achieved by the presence of aluminium compounds or a combination of peroxides and multifunctional unsaturated compounds. Studies on copolymer and plasticized systems are reported.

Chapter 4 describes the degradation of PMMA by ionizing radiations and mechanical forces. Solution phase degradation of PMMA is examined by the novel use of an ESR–spin trapping (ST) technique using a reagent having a high trapping rate. Main chain scissions are induced in $< 1\,\mu$s. The presence of radicals with longer life times are demonstrated by ESR–ST using an alternative ST reagent. Also considered is the pulse radiolysis of PMMA in the solid phase. Cation and anion formation in a primary process is recognized from the correlation of absorption bands and possible radical identity by ESR. A reaction scheme for the radiolysis of PMMA is proposed on the basis of these results.

Other aspects involve the demonstration by ESR analysis of main chain scission of PMMA caused by milling at 77 K in vacuum. A cyclic reaction initiated by the radical is found in the process of heat treatment which results in main chain scission. Self degradation of PMMA is considered on this basis. Again, evidence of main chain scission of solution phase PMMA is provided by an ESR–ST method for ultrasonic irradiation. Other forms of agitation of PMMA leading to main chain scission are outlined.

Chapter 5 highlights the mechanochemistry of ligno-cellulose materials—wood, wood cellulose, cotton and lignin. Mechanical milling induces compression and shear forces sufficient to change topochemistry and reactivity of ligno-cellulosic polymers and cause homolytic chain scission.

Mechanoradical formation, transformation and decay reactions are envisaged to occur continuously during the processes whereby absorption of mechanical energy occurs.

Lignin because of extensive branching and crosslinking appears to absorb mechanical energy more effectively than cellulose. Stress-induced reactions in cellulose result in disaggregation of fibre bundles, shortening, loss of DP, increase in accessibility, and a decrease in crystallinity. There is more effect in this mode of mechanical stress depending on type of polymer. Furthermore, cotton fibres absorb and store mechanical energy more effectively than wood.

Chapter 6 deals with what can be described as an area of investigation of the kinetics of radical–polymer reaction in the solid state which is stated to be often neglected, particularly, with regard to the reactions and fate of small radicals.

Consideration is given to the radical production in degradation reactions, reactions of free radicals and polymers, and importance in initiating secondary reactions. Factors influencing radical reactivity are discussed and a model representing simultaneous reaction and diffusion of small radicals is introduced. Quantitative kinetic data for photochemical reactions in the solid phase involving hydrogen abstraction is obtainable and the rate data for radical–styrene polymer reactions are discussed.

Chapter 7 deals with an important feature of fire retardancy (FR) behaviour and the mechanisms for chloroparaffin (ClP, where Cl content is 70%) in isolation or in conjunction with a metal compound to impart fire retardant characteristics to polymers. Mechanisms of FR are deduced by relating the thermal degradation of polymer–fire retardant mixtures to their combustion behaviour. The effect of polymer structure on the mechanisms of FR are considered for mixtures of ClP with high density polyethylene (PE), propylene (PPP) and styrene (PS). The effect of metal compounds—Sb_2O_3 or $BiCO_3$ in mixtures with ClP–PP is described.

ClP alone or with Sb_2O_3/$BiCO_3$ generates reactive species, on heating, which are capable of modifying the thermal degradation mechanism of the polymer. A direct consequence on flammability is that the thermal volatilization of the polymer occurs at a lower rate or with production of less flammable products in the presence of FR additives. In cases where FR depends on gas phase effects, flame poisoning effectiveness of the additive may depend on reactions occurring in the condensed phase which are not predictable from the thermal behaviour of the polymer and of additives heated separately.

Considering the specialized nature of this series the cost is not beyond the reach of individuals or groups who have particular interests in this wide field and the individual style of reporting makes the articles quite readable.

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New Elastomer Synthesis for High Performance Applications

J. E. McGrath, G. L. Wilkes, T. C. Ward, A. D. Broske, B. Lee, I. Yilgor, D. J. Bradley, J. M. Hoover and T. E. Long
Noyes Data Corporation, Park Ridge, USA, 1988, x+118 pages, $36
ISBN 0-8155-1156-6

This book emanates from work carried out by the well known polymer group at Virginia Polytechnic Institute in Blacksburg, the sponsors of the research appears to have been the US Army Tank-Automotive Command. Its format is that of a technical report in that Objectives, Conclusions and Recommendations are set out in the first seven pages. The remainder of the text is headed as Discussion, and consists of five sections dealing with: (1) a laboratory scale, low pressure reactor for living polymerization; (2) hydrogenation of model elastomers; (3) investigation of organolithium initiators; (4) ion containing copolymers; (5) morphology and properties of poly(urea-urethane) elastomers. The last of these sections is the largest being some 30 pages in length.

The material is presented with a sparse style with much emphasis on the how to approach rather than what if speculations. However, the section on organolithium initiators deals with the kinetics of formation of a difunctional initiator formed by reacting sec-butyl lithium with 1,3-bis(phenylethenyl) benzene, and is a classic example of the type of work pioneered by Szwarc. The use of the initiator to prepare polymers is also briefly discussed. The section on ionomeric copolymers reviews the problems in making such materials and concentrates on development of free radical emulsion copolymerization of sodium *p*-styrene sulphonate with butyl acrylate and anionic copolymerization of styrene with isobutyl methacrylate. In the latter case, the final ionomer was prepared by subsequent partial hydrolysis using potassium superoxide. Structure–property relationships are at the heart of the section on poly(urea-urethane) elastomers. The potential difficulties in the synthesis of these materials and the means by which these are overcome are detailed. This is then followed by the full gamut of materials testing and characterization methods on the series of elastomers produced with varying urea content. The tests involve stress–strain curves, dynamic mechanical analysis, differential scanning calorimetry whilst the characterization methods are both wide-angle and small-angle X-ray scattering. Again, the material is presented in a very direct fashion and any difficulties encountered in obtaining the data or the magnitude of errors of physical quantities is not discussed. Consequently, one has to view interfacial thickness parameters of *ca.* 1–2 Å with some caution due to the sensitivity of such values to the data treatment method used.

This book certainly exemplifies the interdisciplinary nature of polymer science and is perhaps a model for putting over scientific facts cogently, lucidly and with clarity without too much of the academic speculation which often leads to serendipitous discoveries. Consequently, it should probably be necessary reading for new entrants to the polymer industry at the research and development end of the business. It is probably also true that there is little of a revolutionary nature here and therefore will not command a wide readership. Notwithstanding these comments, it is a well written publication of its type.

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Photophysics of Polymers

C. E. Hoyle and J. M. Torkleson (Eds.)
Americal Chemical Society, Washington DC, USA, 1987, xi+531 pages, USA and Canada $99.95; Export $119.95
ISBN 0-8412-1439-5

This book consists of 36 chapters arising from a symposium sponsored by the Division of Polymer Chemistry of The American Chemical Society held in Anaheim, California, in September 1986. The chapters are arranged within seven headings starting with four overviews. The first is a short chapter by Hoyle on 'Polymer Photophysics' followed by more substantial overviews by Winnik on 'Study of Complex Polymer Materials: Fluorescence Quenching Techniques', by Frank, and Zin on 'Morphology in Miscible and Immiscible Polymer Blends: Interplay of Polymer Photophysics and Polymer Physics' and by Morawetz on 'Applications of Fluorescence Techniques for the Study of Polymer Solutions'.

These overviews are followed by 10 contributions under the title 'Polymer Dynamics and Complexation' which discuss many aspects of polymer dynamics in a variety of polymers using a wide range of techniques, many involving time-dependent and steady-state luminescence measurements. Thus, Monnerie *et al.* in their paper 'Spectroscopic Investigation of Local Dynamics in Polybutadienes' use the fluorescence anisotropy decay technique and ^{13}C spin-lattice magnetic relaxation to investigate local dynamics at temperatures which are 60 K above the glass–rubber transition temperature. While Winnik reports how intramolecular fluorescence quenching processes can be used to study 'Excluded Volume Effects on Polymer Cyclization'. In the chapter 'Time-Resolved Optical Spectroscopy as a Probe of Local Polymer Motions', Waldow *et al.* use a picosecond holographic grating technique to observe the local segmental dynamics of anthracene-labelled polyisoprene in dilute solutions. Horie reviews in his article various mechanisms for non-exponential decay of phosphorescence on much longer time scales, typically milliseconds, showing how this may be related to dynamics in polymer solids. Fluorescence probes and markers feature in three chapters, namely 'Fluorescence Probes for the Study of Solvation and Diffusion of Reagents in Network Polymers' by Shea *et al.*, 'Light-Induced Conformational Changes of Polymers in Solution and Gel Phase' by Irie and 'Luminescence Studies of Molecular Motion in Poly(n-butyl acrylate)' by Toynbee and Soutar. A similar approach was reported by Hayashi *et al.* who have bonded a twisted intramolecular charge-transfer compound to poly(methyl methacrylate) and shown the luminescence to be sensitive to both the polarity and the microviscosity of the surroundings. The final two chapters in this section deal with the 'Electronic Spectroscopy of bis (4-dimethyl aminophenyl), Squaraine' and 'Specific Interactions of (+)-Catechin and (−)-Epicatechin with Polymers that contain the L-Propyl Residue' by Law and Bergmann and Marrice, respectively.

The following three articles 'Excimer Photophysics of Macromolecular Scintillators' by Birch *et al.*, 'Configurational and Conformational Aspects of Intramolecular Excimer Formation' by De Schryver *et al.* and 'Photophysics of 1,5-Naphthalene Diisocyanate-Based Polyurethanes' by Hoyle and Kim, are grouped together under the title 'Excimer Photophysics'. In the first of these articles, it is demonstrated that even good fits to fluorescence decays often still provide an incomplete description. In the