

their concentration.⁽¹⁴²⁾ The increase in formyl concentration on photolysis was considered to be a consequence of ionic recombination. A similar explanation was advanced to account for the increases in radical concentration observed on warming samples after irradiation at -196°C , reaching a maximum concentration at -70°C . It was suggested that the interaction of γ -rays with trioxan causes the formation of radical ions (by loss of an electron), the loss of hydrogen atoms, and ring cleavage.⁽¹⁴²⁾ The low-temperature (-196°C) irradiation of 3,3-bis(chloromethyl)oxetane yields two radicals giving 3-line and 2-line e.s.r. spectra, respectively.⁽¹⁴¹⁾ The radical characterized by the 3-line spectrum is not thermally stable but the other radical, which gives an anisotropic e.s.r. spectrum, is stable up to about 0°C . Structures for these radicals have been proposed.⁽¹⁴¹⁾ Radicals have also been detected on irradiation of β -propiolactone and diketene.⁽¹²⁶⁾ In all cases the e.s.r. spectrum decays as the melting point is approached and molecular mobility increases.

It is generally accepted that the radiation-induced solid-state polymerization of these cyclic monomers proceeds by a cationic mechanism, partly since only cationic polymerization is known in solution,⁽³⁹⁾ and solid-state polymerization can be induced by cationic initiators. Radiolysis of the monomer presumably produces cations or radical cations, depending on the nature of the monomer and the presence of impurities; propagation occurring by addition of monomer to the cation.

Chemical Initiation

A number of papers have appeared which report the solid-state polymerization of trioxan initiated by surface catalysis using conventional cationic initiators, including borontrifluoride^(121, 143-5) and stannic chloride,⁽¹⁴⁵⁻⁶⁾ giving rise to crystalline polymers rather similar to those obtained by radiolytic initiation. The polymerization must be controlled to some extent by the diffusion of catalyst and counterion into the crystal, and it has been reported that the solvent power of the medium in which the crystals are suspended markedly affects the molecular weights of the polymers.⁽¹⁴⁴⁾ Inclusions of iodine, formed by freezing a solution of iodine in monomer, have also been used to initiate the solid-state polymerization of trioxan.⁽¹⁴⁷⁻⁸⁾ Considerable quantities of trioxan are formed during the polymerization of crystalline tetraoxan, initiated by borontrifluoride etherate at 30°C ⁽¹⁴⁹⁾ probably by the same back-biting process as occurs in the solution polymerization of this monomer; the radiation-induced polymerization at 80°C gives rise to much less trioxan.

SOLID-STATE COPOLYMERIZATIONS

In spite of obvious limitations imposed by the solid state, a number of attempts have been made to copolymerize frozen mixtures of monomers.

The results obtained from this type of study must reflect the physical nature of the frozen binary systems. Thus, if the monomers crystallize separately it is to be expected that, apart from reaction at intercrystalline boundaries, only homopolymers will be produced. Alternatively, if the monomers form solid solutions a copolymer may be formed, the composition of which will be dictated by the nature of the solid solution rather than by the reactivity ratios which control polymerizations in the liquid phase. An example of this latter situation is the copolymerization of various binary mixtures of oxetanes, when the copolymers obtained by γ -irradiation of solid solutions have compositions corresponding to reactivity ratios of unity, quite different from those observed in the liquid state.⁽¹⁵⁰⁾ Other copolymerizations of solid cyclic monomers include the incorporation of ethylene oxide,⁽¹⁴³⁾ 1,3-dioxalane, and epichlorhydrin⁽¹⁵¹⁾ into polyoxylmethylene formed by polymerization of trioxan; the presence of the latter two monomers increases the rate of polymerization.⁽¹⁵¹⁾

Tributyl phosphonium bromide and the corresponding iodide are isomorphous. The polymerization kinetics of a series of their solid solutions have been investigated in the temperature range -80°C to -60°C and in all cases sigmoid conversion-time curves leading to 100 per cent conversion were obtained. Chen and Grabar⁽¹⁵²⁾ compared the rates of reaction at various compositions from plots of the time taken to reach 50 per cent conversion against composition. On this basis both monomers and all their solid solutions reacted at the same rate at 60°C , while the rate changed monotonically with composition at -80°C . At intermediate temperatures minimum rates were observed in solid solutions containing about 4 per cent of the iodide.

Hayashi *et al.*⁽¹⁵⁰⁾ have published phase diagrams for a number of monomer mixtures and have studied their radiation induced polymerizations. In most cases eutectics were formed and the monomers polymerized independently. Maleic anhydride and acenaphthylene, which give a 1:1 copolymer in the liquid state, produce a mixture of polyacenaphthylene and 1:1 copolymer in the solid state. As in many other binary systems, the maximum rate of polymerization occurs at the eutectic composition. Maleic anhydride is probably slightly soluble in acenaphthylene crystals, since small amounts of the anhydride were detected in the homopolymer of the latter monomer.⁽¹⁵³⁾ In the initial stages of reaction the 1:1 copolymer is formed preferentially, probably in the more disordered regions of intercrystalline boundaries. As reaction proceeds the acenaphthylene homopolymerizes and finally, when there is considerable disorder in the solid, there is again a preference for 1:1 copolymer formation.⁽¹⁵³⁾

Polymerizations of acrylic acid-acrylamide mixtures have been studied in some detail by Hardy and Nagy⁽¹⁵⁴⁾ This mixture is characterized by two eutectics containing 74.5 per cent and 58.7 per cent acrylic acid, respectively, and a molecular compound with a composition 2:1 acrylic acid : acrylamide.