

SOLID-STATE POLYMERIZATION

G. C. EASTMOND

The Donnan Laboratories, University of Liverpool, Liverpool 7

INTRODUCTION

The polymerization of crystalline monomers, at first sight, appears to offer intriguing possibilities for the production of polymers with structures different from those obtained by liquid-phase polymerizations. In particular, it may be visualized that the ordered arrangement of molecules in the crystal lattice may give rise to highly crystalline or stereoregular polymers. Indeed, in the 1930s Kohlschütter and Sprengel⁽¹⁾ observed that, in the presence of formaldehyde vapour, a crystalline polymer formed on the surface of trioxan crystals, and that this polymer was orientated along the *c*-axis of the monomer crystal. These and other⁽²⁻⁴⁾ early references to polymerizations occurring in solid monomers were "lost" in the literature until after 1954, when Mesrobian *et al.*⁽⁵⁾ described the radiation-induced polymerization of crystalline acrylamide and the present development of this topic started. One reason for the upsurge in interest in this topic at that particular time was, no doubt, the possibility of using this technique as an alternative to the then new Ziegler-Natta catalysts. In the circumstances it seems strange that the early observations of Kohlschütter and Sprengel were forgotten, but it was not until 1960 that Okamura *et al.*⁽⁶⁾ "rediscovered" the formation of crystalline polyoxymethylene during the solid-state polymerization of trioxan; in this case reaction was induced by high-energy radiation.

A detailed understanding of solid-state polymerization mechanisms requires consideration of factors peculiar to the solid state, including the effect of the crystal lattice, the importance of lattice imperfections, phase transitions, and molecular mobility. In order to elucidate the importance of these factors, polymerization processes in a wide range of monomers have been studied by a variety of techniques. Although this has been an active field of research for 10 years, a difficulty is still a lack of knowledge of the crystal structures of most monomers. There is also little understanding of the detailed nature of imperfections in the organic solid state. In spite of these difficulties we now have a better appreciation of the factors controlling the reactions.

An important outcome of the investigations is the information provided on the behaviour of reactive species in molecular crystals. Since most of the monomers studied are organic materials the understanding of polymerization

processes in solid monomers must inevitably have application in the general fields of organic solid-state chemistry and physics, of which this research now constitutes a large part.

During the last decade this subject has been reviewed a number of times,⁽⁷⁻¹⁸⁾ and through these reviews changes in emphasis, as the subject has developed, can be traced. Most reviews have discussed the polymerization of cyclic monomers separately since they may produce highly crystalline polymers. They are also treated separately in this review, although it now appears that the sharp distinction drawn between the polymerization of these and other monomers is breaking down. The present review does not claim to be comprehensive in the sense of referring to all monomers which have been polymerized in the solid state (a recent list is given by Marans⁽¹⁷⁾) but discusses some important aspects of polymerizations in solids which were described by about the end of 1967 and, in combination, are leading to a better understanding of the principles involved in the reaction mechanisms. The results of studies on the solid-state polymerizations of aldehydes are not presented here, but have been discussed elsewhere recently.⁽¹⁴⁾ Solid-state polycondensations and increases in molecular weight in polyamides and polyesters, in which diffusion of a reaction product through the lattice must play a large part, are not considered.

METHODS OF INITIATION

A consequence of using solid monomers is that restrictions are imposed on the methods of initiation which can be used, especially if the monomers are crystalline rather than in the form of a glass. Most workers in this field have made use of high-energy radiation, e.g. γ -rays, X-rays, and high-energy electrons, either by irradiating monomers at the polymerization temperature or by introducing reactive centres at low temperatures and subsequently warming the sample to obtain a post-irradiation reaction. For mechanistic investigations the latter type of study has the advantage of avoiding radiation damage to the reaction product. Further advantages of using high-energy radiation are that a range of active species may be produced so that the chances of successfully inducing a polymerization reaction are enhanced and, secondly, active centres may be produced throughout a large sample of monomer, which may not be possible with other techniques. A disadvantage is that, since both ions and radicals can be produced, there may be considerable uncertainty as to the nature of the products of radiolysis and of the propagating species. Some pure monomers undergo spontaneous thermal initiation in the solid state,⁽¹⁹⁾ while others require the presence of an additive, e.g. solid vinyl carbazole polymerizes spontaneously in the presence of carbon tetrachloride.⁽²⁰⁾ In a number of cases cationic polymerizations have been induced by surface catalysis or freezing monomers in the presence of a catalyst; these reactions are referred to later. Various photolytic processes have been