

crylate dihydrate to low conversions produces polymers in which the isotactic content is greater than the syndiotactic content.⁽⁸⁵⁾ As conversion of the latter monomer increases from about 10 per cent to 60 per cent (at 50°C) the isotactic content decreases from 37 per cent to 21 per cent and the syndiotactic content increases from 15 per cent to 33 per cent, i.e. as polymerization proceeds the microstructure of the polymer changes. Since this is a post-irradiation reaction, the microstructure must change along the polymer chain; in the later stages growth approximates to that observed in liquid phase. At 120°C there is an increase in isotactic content to 48 per cent at about 50 per cent conversion, with only about 8 per cent syndiotactic triads; at these temperatures dehydration to an unreactive anhydrous form accompanies polymerization.⁽⁸⁵⁾ Solid-state polymerization of methyl methacrylate produces a polymer containing more heterotactic and less syndiotactic triads than solution prepared polymer; the isotactic content remains approximately constant.⁽¹⁰⁵⁾

Tabata and co-workers^(77, 109) have repeatedly stated that polymers prepared from solid acrylonitrile in its various forms have different properties, e.g. thermal stability. These differences are attributed to variations in the stereoregularity of the polymers. From infra-red evidence it was shown that on heat treatment of polymers prepared at low temperatures, about -196°C, $-C \equiv N$ groups are converted to $>C = N$ -groups at a higher rate than in polymers prepared at higher temperatures. It was suggested that the preferential formation of $>C = N$ -linkages is due to increased syndiotacticity in the polymers prepared at -196°C, and similar considerations were applied in the case of polymethacrylonitrile,⁽¹¹⁰⁾ but as pointed out by Morawetz⁽¹²⁾ the intra-molecular formation of $>C = N$ -linkages is more favourable in isotactic polymer, in agreement with more recent n.m.r. studies in polymethacrylonitrile, when polymers prepared by solid-state polymerization were found to contain virtually no syndiotactic material.⁽¹¹¹⁾ Polyacrylonitrile obtained by polymerization at -196°C, initiated by vacuum u.v. radiation, was found to contain very few $-C \equiv N$ groups, and, although treatment of polyacrylonitrile in this way is expected to cause intramolecular formation of $>C = N$ -linkages, it was proposed that under these conditions polymerization through the vinyl group and the nitrile group occur simultaneously.⁽¹¹²⁾

X-ray diffraction patterns of polymer formed by polymerization of crystalline potassium acrylate show four diffuse rings which are not obtained from polymers prepared in solution.⁽⁸⁶⁾ Polyvinyl stearate prepared by polymerization in the solid phase is said to be more isotactic than that prepared in solution.⁽⁹⁰⁾ Infra-red studies indicate that polymerizations of *n*-butyl isocyanate in the liquid and solid phases give different polymers.⁽¹¹³⁾ Polymerization of solid terephthalonitrile oxide apparently produces a polymer containing oxazoxime rings, while liquid-phase polymerization produces furoxan rings; from a consideration of the monomer crystal structure it is stated that the

formation of the former ring structure could occur with a contraction of the lattice while the latter requires an expansion.⁽¹¹⁴⁾ Other changes in polymer structure have been referred to in the section dealing with topotactic processes.

More detailed studies are required to obtain an understanding of the way in which the stereoregularity of the polymer is controlled by the lattice, but it appears that this stems from a limitation of the types of molecular motion a monomer molecule can undergo, of the conformation of the propagating species or of the ways in which monomer can approach the reactive species, or some combination of these factors.

POLYMERIZATION OF CYCLIC MONOMERS

Radiation Induced

Considerable effort has been devoted to a detailed study of the polymerization of cyclic monomers since Okamura, Hayashi and their co-workers demonstrated that the radiation induced polymerization of crystalline trioxan,⁽⁶⁾ β -propiolactone,⁽¹¹⁵⁾ diketene⁽¹¹⁶⁾ and 3,3-bis(chloromethyl)oxetane⁽¹¹⁷⁾ can lead to the formation of crystalline and orientated polymers; propagation proceeds through a ring-opening mechanism.

This effort has been largely directed towards understanding the relationship between the crystal structure of the monomer and the direction of growth and the structure of the polymer. In an early paper on this subject Okamura *et al.*⁽³⁹⁾ published X-ray diffraction patterns and photomicrographs of polymers formed by polymerizing single crystals of the above monomers. These results demonstrate quite clearly that highly crystalline fibrous polymers are formed and that the fibres are aligned in specific orientations with respect to the crystallographic axes of the parent monomer crystal. Both trioxan and polyoxymethylene, formed by polymerization of this monomer, have hexagonal crystal structures and in partially polymerized crystals their *c*-axes are seen to be parallel.⁽¹¹⁸⁾ Similar observations on polymers prepared by irradiation of β -propiolactone and 3,3-bis(chloromethyl)oxetane demonstrated that the fibres are aligned at 90° and 45° to the growth directions of the monomer crystals respectively.

Various workers have carried out partial analyses of the X-ray diffraction patterns from polyoxymethylene samples prepared by polymerization of crystalline trioxan under different conditions, and have obtained slightly different results.⁽¹¹⁹⁻²¹⁾ Radiation induced polymerizations of single crystals of trioxan are usually carried out at 55°C and Carazzola *et al.* have performed a detailed X-ray analysis of the polymer formed under these conditions.⁽¹²²⁾ These latter workers found that the polyoxymethylene has a twinned structure, representing growth of the polymer along two directions in the monomer crystal (*viz.* along the *c*-axis of the monomer crystal and at an angle of 76°7' to this direction). Twinned structures have also been reported for poly-