

TABLE I.
POST-IRRADIATION POLYMERIZATION OF CALCIUM ACRYLATE AT 101°C

Hydrate	Form	% Yield (max.)
Dihydrate	Crystalline	52
Monohydrate	Crystalline	0
Anhydrous (ex-dihydrate)	Crystalline	53
Anhydrous (ex-monohydrate)	Crystalline	14
Anhydrous (ex-dihydrate)	"Amorphous"	90
Anhydrous (ex-monohydrate)	"Amorphous"	23

arrangements of ions and water molecules in the various forms. Apparently, only in the case of the dihydrate is there any information on the crystal structure.⁽⁸⁵⁾

The number of crystalline modifications in which a monomer can be obtained is limited, but a study of the polymerization of the acrylate ion in different crystalline arrangements can be extended to include other acrylate salts. A preliminary investigation of this type has been carried out by Morawetz and Rubin⁽⁸⁶⁾ who studied the post-irradiation polymerization of the alkali-metal acrylates. At any given temperature the rates of polymerization vary markedly with the alkali metal, usually in the order potassium > lithium > sodium; the potassium salt polymerizes more readily at room temperature than does the lithium salt at 100°C. A similar trend is observed for degrees of polymerization. The rates of polymerization of the less reactive lithium and sodium salts are the most sensitive to temperature; in the post-irradiation reaction of lithium methacrylate an increase in temperature from 101°C to 155°C increases the polymer yield from 2 per cent to 15 per cent, in the same reaction time (the increased yield is associated with a decrease in molecular weight). X-ray studies on partially polymerized potassium acrylate show that the polymer forms a separate amorphous phase within the monomer crystal.

A few results have also been reported for methacrylate salts. In the initial stages of post-irradiation polymerizations at 152°C, potassium methacrylate polymerizes more rapidly than does the sodium salt, but polymerization of the latter monomer is autocatalytic (to a limiting yield of about 6 per cent) and at conversions greater than 1 per cent it polymerizes more rapidly than the potassium salt.⁽⁸⁶⁾ No post-irradiation polymerization was observed in lithium methacrylate up to 160°C.⁽⁸⁶⁾ Barium methacrylate dihydrate, which has a crystal structure similar to calcium acrylate dihydrate, polymerizes to about 50 per cent conversion in the temperature range 50°–120°C after irradiation at -78°C.⁽⁸³⁾ At high temperatures polymerization is accompanied by dehydration to an unreactive anhydrous salt.

In discussing reactivities of the alkali acrylates, Morawetz and Rubin⁽⁸⁶⁾ suggest that "the bulk of the polymer lies in an amorphous phase, but the reactive end of the growing chains is effectively anchored in the lattice of the monomer crystal, and its reactivity is controlled by the geometry of the crystal lattice." There is, at present, no information available on molecular motions in these salts but, since polymerization in many other monomers appears to require a certain minimum mobility in the lattice, it may be suggested that the different reactivities of the acrylate and methacrylate ions in the various salts arise from different molecular motions and structures of imperfections which depend on the packing of the ions and interionic forces in the individual monomers. As reaction proceeds, with formation of amorphous polymer, there must be a rearrangement of the anions, with the development of strain in the lattice, and it may be visualized that the cations in the vicinity of the polymer molecules rearrange to some extent. Reaction may then be controlled partly by the ability of the cations to move and modify the forces maintaining other anions in their lattice positions.

Topotactic Polymerization

Considerable effort has been devoted to establishing a relation between the crystal structure of the monomer and the mechanism of polymerization. Detailed investigations of this type have largely centered on the polymerizations of cyclic monomers, which may give rise to highly crystalline polymers and were, until recently, thought to be entirely governed by the perfection of the monomer lattice. Since it has been clearly demonstrated that the polymerizations of small vinyl monomers, such as acrylamide and acrylic acid, take place in imperfections, there is a danger of completely disregarding the influence of the lattice in such polymerizations, although the lattice must control the polymerization to some extent, in that it determines the structures of the imperfections and the processes which can take place in them. The extent of this control will vary with the monomer and depend on the intermolecular forces, the packing of the molecules, the structures of the imperfections, and the geometrical rearrangements which must accompany polymerization.

Solid-state reactions in which the host lattice exercises a dominating influence over the orientation of the products are often referred to as topotactic reactions, and this phrase has been used to describe a number of solid-state polymerizations, especially those of cyclic monomers. There are at least three definitions of the term "topotactic", each of which implies a different degree of control by the host lattice in determining the orientation of the product. Lotgering⁽⁸⁷⁾ uses topotactic to describe "all solid-state reactions that lead to a material with crystal orientations which are correlated with the crystal orientations in the initial product." In a more stringent definition, Mackay⁽⁸⁸⁾