

the latter group tend to

between the two classes if it is a polymer, it is necessary to retain its crystalline structure here the unit cell of the polymer. If these monomer units must be disrupted or by disruption of the polymer dependent on whether the extension than that of the

monomer of the latter type, incorporation of the non-polymer, or addition of small amounts of polymerization. In each case or loosening the crystalline structure is reduced. This is a local stress, at least in the early stages considered to determine the mechanism of polymerization.

occur at some unique location subsequent to nucleation and arising from the incorporation giving rise to "regulate" propagate by rotation and energy from such a transition to activate the next monomer with energy and high rate for those monomers in our observation of an interphase

it would be expected to favoring the propagation formed along a preferred direction it tends to oppose the energy available to, the grow-

up to 90,000 psi (6500 atm) state polymerizations. Observations for four monomers which are believed to affect rates of reaction in the calcium acrylate and barium methacrylate extensively studied the effects of acrylic and acrylic acid

salts including these two.<sup>3</sup> In the later work<sup>4</sup> they also studied the anisotropy of the free radicals on the end of the growing barium methacrylate chain and suggested that an orientation in a preferred crystallographic plane exists at least in the early stages of propagation for this polymerization.

Comparison of the effect of pressure upon these four monomers might be expected to define further the very different reaction kinetics previously noted. Polymerization rates are high for both acrylamide and the crystalline form of calcium acrylate prepared from the dihydrate, the former monomer exhibiting relatively large activation energies for both the in-source and postpolymerization reactions.<sup>5,6</sup> Methacrylamide and the crystalline anhydrate of barium methacrylate have appreciably lower rates than either of the above solid state polymerizations but represent examples of reactions that have in the one case a positive activation energy and in the other either a very low or zero temperature dependency.<sup>3</sup> During the course of our work we have attempted to substantiate these results for the effects of pressure applied to the monomers at temperatures up to 100°C.

Since our investigations were started, Tabata<sup>7</sup> has published some results on the effect of pressure on the polymerization of acrylamide, but with this exception the only previous study has been by Bamford et al.,<sup>8</sup> who reported upon the effects of low pressures (50 psi) on the ultraviolet-initiated polymerization of solid acrylic and methacrylic acid.

### Experimental

Commercial samples of acrylamide and methacrylamide were purified by repeated crystallization from chloroform solution and finally vacuum dried at 50°C. over 48 hr.

Barium methacrylate and calcium acrylate were prepared as the crystalline dihydrates by addition of the solid hydroxide to a 3*N* water solution of freshly distilled acid with phenolphthalein as indicator. After filtration the salts were crystallized by slow evaporation at room temperature. The crystalline anhydrides were prepared by dehydration over anhydrous calcium chloride. Amorphous calcium acrylate was produced by rapid dehydration of the dihydrate over P<sub>2</sub>O<sub>5</sub>. Preparations were characterized by both an x-ray diffractometer with monochromatized CuK $\alpha$  radiation and by infrared spectroscopy.

For the greater part of the work reported, the particle size of the dry monomers was reduced to 0.25 mm. or less by grinding in an agate pestle and mortar to pass a B.S.S. sieve. After grinding, the acrylamide was found to contain a small but significant proportion of polymer. The presence of this preformed polymer was subsequently taken into consideration when assessing the yield of radiation-induced product.

In-source polymerization both with and without applied pressure were conducted in air at room temperature (18°C.) with the solid monomers contained in a modified stainless steel pressure vessel (Fig. 1) manufactured by Research and Industrial Instruments as a halide disk press. This was