

following irradiation at atmospheric pressure and  $-50^{\circ}\text{C}$ ., from which it is evident that the major influence of an applied stress, be it retardation or acceleration, is to act upon the propagation reaction.

We have also studied the in-source polymerization of the amorphous anhydrate of calcium acrylate prepared from the dihydrate (Fig. 7), a monomer reported to exhibit a high rate at  $50^{\circ}\text{C}$ .<sup>3</sup> At room temperature ( $18^{\circ}\text{C}$ .) this monomer polymerizes only to a very low conversion (2-3%); application of pressure however accelerates the reaction to complete conversion. The simplest explanation of this effect would be that applied stress so compresses the amorphous mass as to simulate the conditions existing in the crystalline monomer by elastic removal of defects. Such an explanation might account for the results for the crystalline monomers

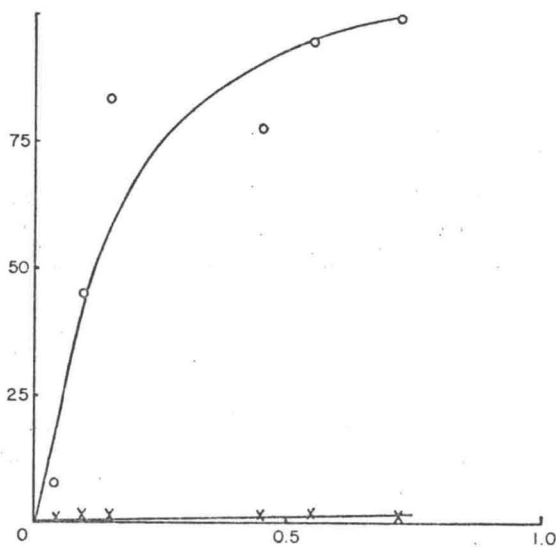


Figure 7.

studied in this work by presuming that acrylamide and methacrylamide polymerize preferentially at defects, while the acid salts propagate only in the perfect crystal. Bamford<sup>8</sup> assumed that polymerization of acrylic acid and methacrylic acid occurred in regions containing discontinuities, and attributed the reduced yields under pressure to the movement of dislocations away from the polymerizing front. While this might be a feasible explanation of the pressure effect for monomers polymerized just below their crystal melting points, it is doubtful that the same explanation can apply to monomers at least  $65^{\circ}\text{C}$ . below their melting points, even at the high pressures employed in our work. The increased rate for the amorphous calcium salt would be expected on the basis of our introductory theory in that the monomer represents an extreme case of a randomly polymerizing solid in many ways analogous to the liquid phase. The fact that an efficient, presumably free radical, propagation reaction only exists