

The Effect of Applied Pressure in Some Solid State Polymerizations

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Synopsis

We report some preliminary observations on the influence of applied pressures up to 90,000 psi on some gamma-initiated, solid state polymerizations. Four monomers have been studied: acrylamide and methacrylamide, both of which are believed to yield atactic polymer but show markedly different rates of reaction in the solid state, and some crystalline modifications of calcium acrylate and barium methacrylate, which can give rise to stereoregular polymer. The rate of polymerization of the former monomers is reduced by the application of pressure but this rate is substantially increased for the metal salts. These results are discussed with reference to the possible polymerization mechanisms.

INTRODUCTION

Many investigations on the solid state polymerization of crystalline monomers have been reported in recent years. The mechanism of polymerization is profoundly affected by changes in both the orientation of the monomeric units in the crystal and by the presence and distribution of impurities in the lattice. The method of initiating polymerization by radiation presents a means for investigating the mobility of a "growing" polymer chain within a solid monomer matrix in the absence of chemical impurity which must otherwise be introduced as a catalyst for the reactions. Since initiating species are distributed at random throughout the system, the course of the polymerization under given conditions is influenced by the presence of crystallographic irregularities (stresses, dislocations) either initially present or subsequently formed by the propagating chain. Otherwise propagation reactions are found to be independent of the radiation process and in general terms appear identical with those occurring in chemically initiated polymerizations.

The means by which a polymer chain is able to propagate within a crystalline solid is generally in doubt but it is possible to differentiate between monomers in which the regular arrangement of the crystal lattice favors polymerization and those in which crystallinity hinders initiation or propagation. A number of monomers of the former type give rise to *crystallizable* polymers that have a main chain conformation containing