

A limited study of the effects of lower pressures on crystalline barium methacrylate leads us to believe that this exhibits a similar behavior with a minimum lying between 14,000 and 30,000 psi.

For acrylamide the relationship between degree of pressurization and yield is complex. At low conversions (up to 10%) intermediate pressures give rise to yields intermediate between that at 90,000 psi and atmospheric pressure, but near to 70% conversion pressures as low as 14,000 psi give rise to an *increased yield* relative to the yield at atmospheric pressure. This must be contrasted with the results for 90,000 psi represented in Figure 4, showing that the mechanism alters drastically in the later stages of the propagation reaction, as the growing polymer becomes increasingly separated from neighboring monomer. Over the temperature range 19–80°C., acrylamide and methacrylamide show a high positive activation energy both with and without pressure for the in-source polymerizations, while the crystalline anhydrate of barium methacrylate and the crystalline dihydrate of calcium acrylate show no increased yield at 80°C. in the absence of pressure (see Table II).

With a pressure of 90,000 psi the calcium acrylate yield is increased by roughly 80% over the polymerization at room temperature. The increased polymer yield for irradiations at atmospheric pressure and 100°C. may be accounted for by a temperature-induced phase change above 80°C.

The polymer yields from barium methacrylate at 80 and 100°C. do not show any significant difference from the corresponding yields at room temperature.

At this time it is only possible to speculate upon the course of the reaction under applied stress. Such parameters as the density differences for the respective monomers and polymers in each class might be expected to reflect a correlation between the molecular packing fraction and magnitude of the strain energy existing in the neighborhood of a propagating chain. Our density determinations indicate that the polymer produced from crystalline or amorphous calcium acrylate is denser than the monomer, the reverse applying to the polymer from acrylamide. If this is the case, then a theory based upon strain energy would satisfactorily explain our pressure yield relationships. However our result for acrylamide contradicts those previously reported by Adler,⁹ who noted a 12% volume reduction during the course of polymerization. It is therefore necessary to repeat our work using a more refined technique in which density determinations are carried out over a range of polymer conversions. Full evaluation of our experimental results must await a detailed structural analysis of the polymers produced under different conditions of pressure and temperature, but the considerations which prompted our study appear in general terms to be substantiated.

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