

In-source polymerizations of crystalline acrylamide have been studied by Tabata and Suzuki⁽¹⁵⁸⁾ and by Fydelor and Charlesby⁽¹⁵⁹⁾ using pressures of 5000 and about 6500 atm, respectively. At temperatures below 30°C both groups report that the application of pressure has virtually no effect on initial rates. According to the former group,⁽¹⁵⁸⁾ pressures of 5000 atm reduce the rates of polymerization at 28°C up to conversions of at least 20 per cent. At higher temperatures, up to 70°C, rates are reduced initially but increased after some finite conversion which decreases with increasing temperature from about 5 per cent at 50°C to about 1 per cent at 70°C. Using the slightly higher pressure at 18°C, Fydelor and Charlesby report that the maximum reduction in rate occurs at approximately 8 per cent conversion and that above about 60 per cent conversion rates are increased.⁽¹⁵⁹⁾ These latter workers have also reported that the applied pressure does not affect the initial rate of polymerization of methacrylamide, but after about 0.5 per cent conversion reaction virtually ceases.⁽¹⁵⁹⁾

Prince and Hornyak have investigated the influence of high pressures (36,000 atm) on the post-irradiation polymerization of acrylamide, initiated by high-energy electrons⁽¹⁶⁰⁾ and γ -rays.⁽¹⁶¹⁾ In all cases these pressures increased conversion to polymer, usually by a factor of about 2, but by considerably more at low irradiation doses. It was suggested that these pressures release trapped radicals by producing dislocations, although this presumably implies that some radicals are initially produced in the more perfect regions of the crystal. Fydelor and Charlesby found that pressures of 6500 atm did not affect the post-irradiation reaction of this monomer.⁽¹⁵⁹⁾

Pressures of 6500 atm accelerate the rates of polymerization of crystalline and amorphous anhydrous calcium acrylate and crystalline anhydrous barium methacrylate at 18°C.⁽¹⁵⁹⁾ With crystalline anhydrous calcium acrylate the rate is increased markedly up to conversions of 50 per cent after which it decreases rapidly, while with the amorphous salt conversions approaching 100 per cent are readily achieved at low radiation doses. At low conversions (< 8 per cent) the rates of polymerization of the barium salt are increased by these pressures, the acceleration increasing with conversion.

Fydelor and Charlesby have also reported some interesting preliminary results on the effects of different pressures,⁽¹⁵⁹⁾ and further results of this type must assist the interpretation of the results at present available. These workers conclude that, in all the monomers they have studied, the main influence of pressure is on propagation. It was suggested that in acrylamide the lower rates in the early stages are due to the pressure opposing disruptive stresses produced in the lattice by polymerization, but that at higher conversions the pressure reduces the free volume produced on polymerization and hence increases the rate. On the other hand, the accelerations produced in the crystalline salts are attributed to the removal of defects, which would be consistent with polymerization occurring preferentially in the perfect lattice,

in agreement with a previous suggestion that the lattice exercises a dominating influence on these polymerizations.⁽¹⁸⁵⁾

Other reports of the effects of high pressures on the solid-state polymerizations of vinyl monomers include the in-source polymerization of methacrylonitrile (m.p. -35.8°C) in the temperature range -196° to -43°C , the rates of which are reduced by pressures of 5000 atm.⁽¹⁶²⁾ The polymerizations of certain fluorocarbons,⁽¹⁶³⁾ styrene,⁽¹⁶⁴⁾ and methyl methacrylate⁽¹⁶⁴⁾ have been studied under pressures sufficiently high to solidify the monomers at relatively high temperatures; under suitable conditions, using benzoylperoxide as initiator, styrene, and methyl methacrylate polymerized explosively.⁽¹⁶⁴⁾

There appears to be only one reference to the effects of pressure on the polymerization of crystalline cyclic monomers. According to Rao and Ballantine,⁽¹³²⁾ application of pressures of about 36,000 atm. prior to irradiation increases the polymer yields obtained from both the in-source and post-irradiation polymerizations of trioxan. Smaller pressures applied after irradiation either reduced the extent of the post-irradiation reaction, or removed it altogether. It was proposed that the application of pressure prior to irradiation aligned the monomer molecules into positions favourable for reaction (possibly with a simultaneous reduction in rate of initiation) and that application of the pressure after irradiation caused a recombination of primary species, possibly associated with the occurrence of a phase change in the monomer.

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