Rates of polymerization of the binary mixtures, at −15°C, are higher than those of the pure monomers (at this temperature pure acrylamide does not polymerize), and the rates are a maximum at the eutectic compositions, with a minimum at the intermediate composition of the molecular compound. The resulting copolymers have compositions corresponding to those of the eutectics and the molecular compound; polyacrylic acid is formed under conditions where acrylic acid crystallizes from the monomer mixture. Chapiro and Cordier[155] obtained similar results in acrylonitrile–styrene mixtures polymerized at −94°C. Styrene does not polymerize under these conditions and the polymers obtained are pure polyacrylonitrile and a copolymer containing 10–20 per cent styrene, approximately the styrene content at the eutectic point.

Copolymers of vinyl acetate and sulphure dioxide can be formed in the solid state.[156] This mixture does not polymerize when irradiated at low temperatures in the liquid state, but in the solid state the rate of polymerization increases as the temperature is decreased from the melting point (−120°C) to −150°C. Below −150°C polymerization does not occur but samples irradiated at the lower temperatures do polymerize on warming to −140°C.

EFFECTS OF PRESSURE

So far, there is only a small number of references to the influence of pressure on the course of solid-state polymerizations, although this is one of the few variables available. The studies which have been carried out may be divided into two categories, the effects of very small pressures, of the order of 10 atm, studied by one group, and the effects of pressures of thousands of atmospheres reported by other workers. In the absence of further information, it would appear that a direct comparison of results obtained in the two pressure ranges may not be valid. Consequently, we shall discuss the effects separately.

Small Pressures

In discussing the nature of the reaction sites in the polymerization of crystalline vinyl monomers we have already described (pp. 10, 11) some of the results obtained by applying small stresses to crystals of acrylic and methacrylic acids during u.v. irradiation.[23, 24] These results have been taken to indicate that polymerization occurs in dislocations which are mobile under stresses of the order of 150 lb/in.^{2}

The magnitudes of the effects are very sensitive to experimental conditions, and a parameter referred to as the pressure effect has been defined such that if the applied stress stops the reaction it has a value of infinity and a value of zero if there is no effect.[157] An increase in reaction temperatures from 4°C to 7°C decreases the pressure effect in acrylic acid from infinity to zero.[23, 24] Reductions in the magnitude of the pressure effect are also observed as the temperature is lowered, although the change is much more gradual.[157] In a series of experiments using methacrylic acid as monomer, the effect decreased from 18·5 at 4°C to 2 at −10°C and zero at −14°C. This decrease in the pressure effect at lower temperatures is attributed to a general hardening of the crystals, so that movement of dislocations is more difficult.[157] The loss of the effect in acrylic acid at 7°C is considered to result from increased disorder in the monomer at this temperature. At 7°C there is considerable mobility in the crystals as judged by broad-line n.m.r.[62] and measurements of optical retardation, and probably represents the onset of premelting.[23] Under these conditions the general mobility is probably too high for the stress to have any effect.

Small impurity concentrations can have a dramatic effect.[157] The presence of 0·1 per cent isobutyric acid in methacrylic acid reduced the effect from 18·5 to 2 at 4°C, and with 0·3 per cent of the additive the effect fell to 0·5. It is conceivable that if absolutely pure monomer was available these small stresses could stop the polymerization of methacrylic acid. A pressure effect is observable at −14°C on addition of 0·1 per cent isobutyric acid but the effect is again reduced on increasing the additive concentration to 0·5 per cent.[157] The sensitivity of the pressure effect to such low concentrations of additive is further evidence that lattice imperfections play an important role in these polymerizations. In metals it is known that impurity atoms concentrate around dislocations in the form of Cottrell clouds[50] which may prevent the movement of dislocations under small stresses. This mechanism could account for the reduction of the pressure effect on addition of isobutyric acid at 4°C but would not explain the results at −14°C. It seems probable that the temperatures used in this work are too high for a Cottrell cloud mechanism to operate, since impurity clouds fail to pin down dislocations in metals at high temperatures. It is considered that addition of isobutyric acid produces an increase in mobility in the neighbourhood of the dislocations, equivalent to an increase in temperature. This view also explains the reappearance of the effect and its subsequent decrease on the addition of increasing amounts of additive at −14°C. The pressure effect is also very sensitive to the magnitude of the applied stress.[157] In view of the various observations it would appear unlikely that alternative explanations based on freezing of liquid-like regions, or squeezing liquid out of cracks could account for all the results.

High Pressures

There are a few reports in the literature of the influence of pressures in the range 5×10^3 to 5×10^5 lb/in.^{2} on the course of solid-state polymerizations.