An indication of the influence of the physical state of the monomer on the polymerization rate is given by plots of final conversion, determined gravimetrically, against pressure for liquid, 'supercooled' and solid states. From the examples shown in *Figure 6*, a marked increase in rate appears to take place when the monomer changes from liquid to solid, followed by an equally marked decrease when a certain excess of pressure above the solidification value is attained. On the other hand no discontinuity is observed if the monomer passes from the liquid to the 'supercooled' state. A comparison of the molecular weights of the polymers obtained in the liquid and solid phases could not be made, because in the latter conditions an insoluble gel was always obtained. Higher polymerization rates in the solid phase than in the liquid phase are encountered with a number of monomers in normal pressure conditions[32], including styrene[14, 21]. Also in cases of solidification obtained by applying high pressure a similar behaviour has been observed[33].

The obvious conclusion to be drawn is that the arrangement of monomer molecules in the solid state, near the freezing point, is more susceptible to polymerization than that in the liquid state; and, in the present case, also than that in the 'supercooled' state, under similar conditions of temperature and pressure. At the same time however, it appears that a certain mobility of the monomer molecules is needed for the polymerization to occur in the solid state, as can be inferred from the high rate in the proximity of the melting point and the drastic reduction observed with further pressure increase.

In this context it may be pointed out that the 'explosive' thermally-initiated polymerization of styrene, which sets in when pressure, rapidly applied, passes through the solidification point[11], can be explained in these terms.

A better insight into the solid-state polymerization mechanism can be obtained from the shape of the dilatometric curves, although the transformation of the dilatometric data into conversion data is less accurate than in the liquid state, because of the considerably lower volume change caused by the polymerization, e.g. at 4100 kg cm^{-2} and 30°C $\Delta V \simeq 0{\cdot}02$ cm^3 g^{-1} in solid and $\Delta V \simeq 0{\cdot}08$ in liquid.

The accuracy of the dilatometric determinations was checked by comparing polymerization conversion curves, obtained dilatometrically, with a number of gravimetrically measured conversions corresponding to runs stopped at different times. From the results shown in *Figure 7*, the dilatometric curves seem to represent the conversion curves in shape with sufficient approximation, in spite of the rather large scatter of the gravimetric data. This is further supported by the thermocouple measurement of the sample temperature changes occurring during the run, also shown in *Figure 7*. A temperature increase is found to occur in the initial period, and also when the high rate sets in, while in the intermediate period a constant temperature is recorded.

Some of the dilatometric curves obtained at 40·5°C are shown in *Figure 8*. The relevant features are: an initial period in which a slow volume decrement

---

* Units: 1 k cal mol^{-1} ≡ 4·19 kJ mol^{-1}

occurs almost linearly with time; an intermediate period characterized by nearly constant volume, and a final period in which volume rapidly decreases. The latter is not present when pressure is substantially higher than the melting point. This characteristic behaviour is also observed at the other temperatures investigated, but the length of the intermediate periods decreases as the temperature is raised (see *Figure 9*).

This form of kinetic curve has been obtained in the solid-state polymerization of other vinyl monomers[34, 35] and is in line with the general assumptions concerning the process mechanism[36, 37]. Since polymerization requires movement of monomer molecules from their lattice sites, it must be considered to occur almost exclusively at the crystal defects, where mobility is enhanced. Thus, initially, the active centres (of unidentified nature) which radiation produces homogeneously in the solid monomer, can promote polymerization only in limited portions of the crystal structure.

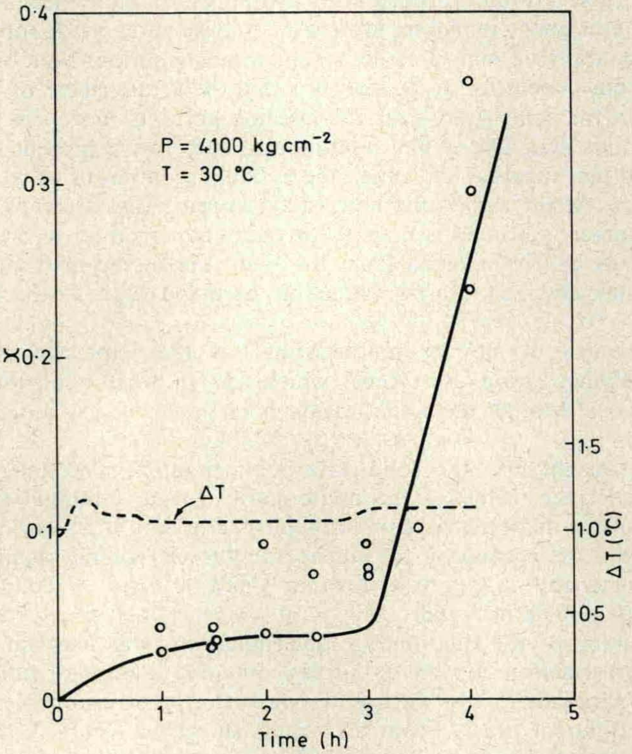

Figure 7 Polymer yield against time: continuous curve derived from the dilatometric data, assuming proportionality between piston displacement and conversion; points represents gravimetric determinations. Dashed line gives the corresponding temperature difference between sample and thermostat

As irradiation is continued, new defects are progressively developed until