a critical value is attained at which the polymer formation gives rise to defect multiplication leading to a high rate of polymerization. Moreover, with increase of molecular mobility as temperature is raised smaller critical values are required and consequently the onset of acceleration occurs after shorter times. The opposite effect is conceivably to be expected from pressure increase, which may lead to polymerization suppression[38, 39], though an

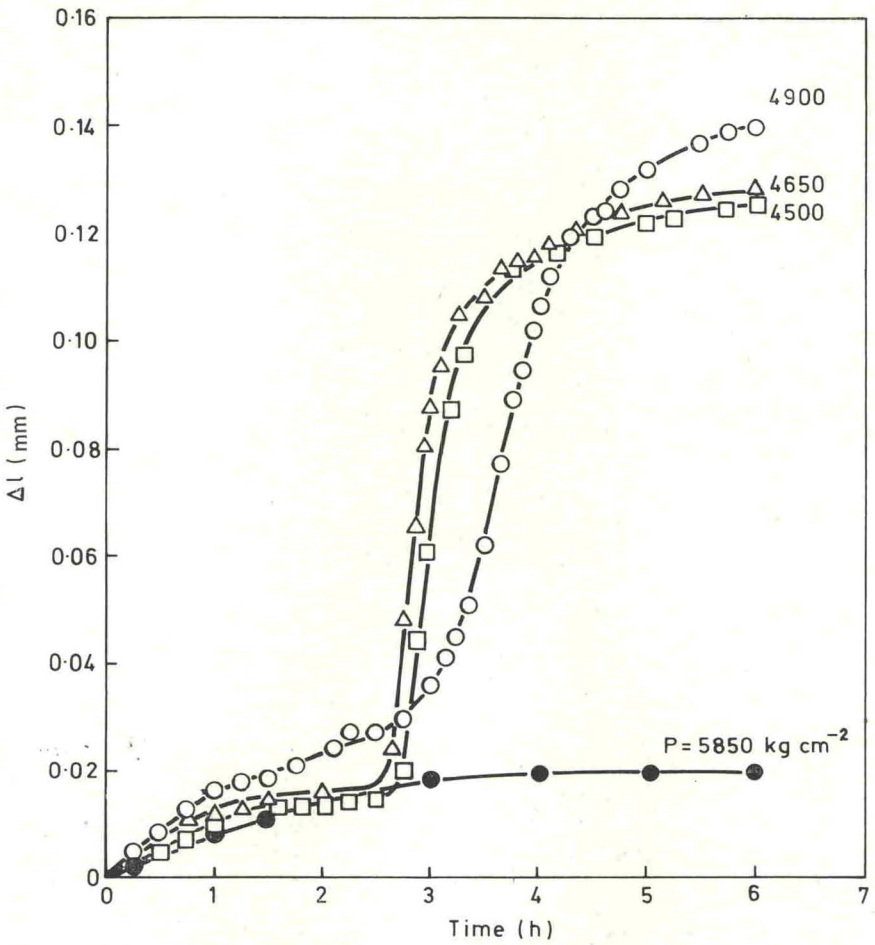

Figure 8 Pressure-dependence of the dilatometric curves for solid-state polymerization at 40·5°C

enhancement of the process is also possible, analogous to that displayed in the liquid state[40].

Several attempts have been made to describe quantitatively the kinetics of solid-state polymerization, assuming theoretical models for the propagation mechanism[37]. A treatment, based on the formation of 'hot' zones and on the 'critical' size of polymerization nuclei for thermodynamical stability[41],

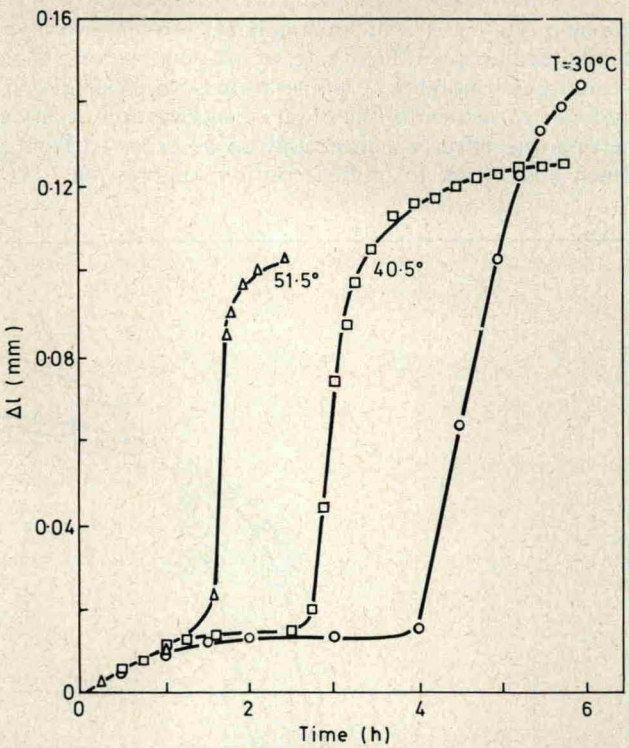

Figure 9 Temperature influence on the dilatometric curves at pressures near the melting point

leads to kinetic curves similar in shape to those of present work for an over-all process involving the successive steps: fast formation and decomposition of unstable polymer chains, annealing of unstable chains producing stable macromolecules representing 'super critical nuclei', formation and growth of 'supercritical' nuclei on crystal defects.

On this treatment, the first part of the curves represents the formation of unstable polymer which reaches a steady concentration. In the intermediate part 'supercritical' nuclei are slowly formed, and then polymerization takes place at the polymer-crystalline monomer interface with an autocatalytic character.

Istituto di Impianti Chimici e Centro di
Chimica delle Alte Temperature e
delle Alte Pressioni del CNR, Sez. I
Università di Padova;
Laboratorio di Fotochimica e Radiazioni
di Alta Energia del CNR,
Bologna, Sez. di Legnaro;
Centro di Ricerche Petrolchimiche,
Montecatini Edison,
Porto Marghera

(*Received 15 June 1970*)