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# *Polymerization induced by gamma radiation of styrene under pressure\**

G. B. GUARISE, G. PALMA, E. SIVIERO AND G. TALAMINI

The radiation-induced polymerization of styrene in both liquid and solid states has been investigated at high pressure in the temperature range 20–50°C. In the liquid phase pressure increases the polymerization rate as well as the molecular weight of the polymer in agreement with the results for chemically-initiated polymerization. In particular, activation volume and energy are consistent with literature values. When the monomer has undergone the liquid–solid transition a sudden increase in the polymerization rate takes place. However the latter falls again to negligible values for a comparatively small pressure excess above the solidification point. The mechanism of the solid-state polymerization in the high-rate region is considered in the light of existing theories.

## INTRODUCTION

THE EFFECTS of high pressures on the liquid phase polymerization of styrene, proceeding both via free-radical<sup>1–11</sup> and ionic<sup>12</sup> processes have been extensively investigated. In these studies, in order to establish the pressure dependence of the propagation and termination rate constants, it was necessary to know the pressure-dependence of the rate of formation of the active centres.

The radiation-induced polymerization of styrene has been studied at ordinary pressure over a large temperature range, both below and above the melting point, in bulk and in solution. At low temperatures the liquid monomer, especially when dissolved in halogenated solvents, undergoes polymerization by an ionic mechanism<sup>13–16</sup>. At higher temperatures, however, this is so only when the monomer is super-dry<sup>17–18</sup>, and, if special care is not taken to remove moisture, the polymerization occurs by a free-radical mechanism<sup>14,16,19</sup>.

With high energy radiation used to initiate free-radical polymerization, at these temperatures, the pressure effect on the propagation and termination rate constants can be profitably investigated, as the rate of initiation is independent of pressure as well as of temperature<sup>20</sup>.

At the same time, if the pressure is increased beyond the solidification point, the solid-phase polymerization, for which data are available at temperatures up to the normal melting point<sup>14,21</sup>, can be investigated at higher temperatures.

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\* Some preliminary results of this work were presented at the X Congresso Nazionale della Società Chimica Italiana, Padova, June 1968

## EXPERIMENTAL

*Materials*

Styrene, supplied by Montecatini Edison SPA, was washed with 10% sodium thiosulphate solution, 10% sodium hydroxide solution and distilled water, dried with anhydrous magnesium sulphate and finally distilled three times under reduced nitrogen pressure.

Benzene, toluene and methanol, supplied by C. Erba, were distilled before use.

*Apparatus*

A 1/4 in diameter PTFE capsule, fitted with a conical PTFE lid, contained the monomer; it was inserted into a tungsten-carbide piston-cylinder apparatus as previously described<sup>11</sup>. Pressure was applied by means of a hydraulic press designed to minimise radiation attenuation.

A jacket, in which water from a thermostat circulated, surrounded the pressure cylinder; the temperature, measured with a thermocouple in close proximity to the sample, was controlled within  $\pm 0.1^\circ\text{C}$ .

Pressure calibration of the system was performed utilizing the liquid-solid transitions of carbon tetrachloride, aniline, chloroform, and carbon disulphide as given by Bridgman<sup>22</sup>. Uncertainty in the cell pressure value was checked to be less than 100 atm by repeated calibrations.

Volume change of the sample were measured with  $2 \times 10^{-3}$  mm sensitivity dial gauges symmetrically arranged with respect to the cylinder axis. The average of the two readings was taken as the piston displacement. Gauge indications were read during irradiation by means of a closed circuit television system.

*Procedure*

The cell which was already inserted in the pressure cylinder and brought up to the chosen temperature, was filled with monomer under nitrogen and then quickly pressurized to make it airtight. Then pressure was increased to the required value slowly, to avoid overheating which could lead to thermal polymerization<sup>11</sup>.

If pressure is increased above the liquid-solid equilibrium value the liquid state, ('supercooled' liquid state), continues to exist till a certain excess pressure is reached. At this point a sudden pressure decrease to the equilibrium value is detected, followed by an isobaric volume change denoting the liquid-solid transition. Equilibrium pressures 3000 ( $20^\circ\text{C}$ ), 3700 ( $30^\circ\text{C}$ ), 4450 ( $40.5^\circ\text{C}$ ) and 5100 ( $51^\circ\text{C}$ )  $\text{kg cm}^{-2}$  were obtained with this procedure.

Exposure to gamma rays of Co-60 was carried out at a dose rate of  $3.2 \text{ rad s}^{-1}$ , which was determined by means of the FRICKE solution inserted in the pressure cylinder in the radiation position. Owing to the small volume of the cylinder, several samples for each irradiation time were needed to allow the spectrophotometric determination (radiation yield  $G(\text{Fe}^{3+}) = 15.6$ ).

In the course of the irradiation the volume decrease of the sample was

followed by reading the piston displacement through the dial gauges. At the end of the run as quickly as possible, pressure was released and the PTFE cell was removed from the cylinder, weighed, and immersed in benzene. Since this procedure does not take more than 10–15 min the post-polymerization effect can be considered negligible.

The dissolved polymer was recovered by precipitation with large excess of methanol.

Assuming proportionality between volume decrement  $\Delta V$  and polymerization conversion  $x$  throughout the course of the reaction, the  $\Delta V$  values can be transformed into  $x$  values if the ratio  $x_f/\Delta V_f$  is determined (index  $f$  refers to the final point). The  $\Delta V$  values are proportional to the piston displacement  $\Delta l$  as in the investigated pressure ranges the piston cross section can be considered to be constant. Thus the initial fractional polymerization rate  $R/[M]$  can be evaluated from the initial slope of the  $x$  time plot.

The lower limit of the investigated pressure range was chosen at about 2000 kg cm<sup>-2</sup> in order to reduce error due to the pressure uncertainty, and to assure good tightness in the PTFE cell.

## RESULTS AND DISCUSSION

### (A) Bulk polymerization in liquid phase

Runs were carried out at 20, 30, 40.5 and 51°C in the range of pressure corresponding to both liquid state and supercooled liquid state. The assumption of proportionality between conversion  $x$  and piston displacement  $\Delta l$  can be accepted in this set of experiments in view of the fact that the ratio  $x_f/\Delta l_f$  found in the various runs is only slightly pressure-dependent and agrees with the corresponding values derived from the compressibility data of monomer and polymer<sup>23</sup>. Therefore the results can be reported in terms of conversion against time as shown in *Figure 1* for some of the runs at 40.5°C.

The characteristic autocatalytic behaviour is evident for  $x > 0.1$ ; the linearity of the curves for  $x < 0.1$  allows a sufficiently accurate value of the initial rate to be derived. In order to indicate the reproducibility two different runs at 3300 kg cm<sup>-2</sup> are reported. The difference is negligible in the initial period and it can be ascribed to the uncertainty in the pressure value; and in the gravimetric determination of  $x_f$ , (0.2 g samples were used).

### Thermal polymerization

By extending the well known scheme for the chemically initiated free-radical process<sup>24</sup> to the polymerization induced by radiation, the following correlation can be derived for the overall rate:

$$R = (R_\gamma^2 + R_T^2)^{1/2} \quad (1)$$

$R$  = polymerization rate; subscripts  $\gamma$  and  $T$  refer to radiation- and thermally-initiated polymerization respectively.

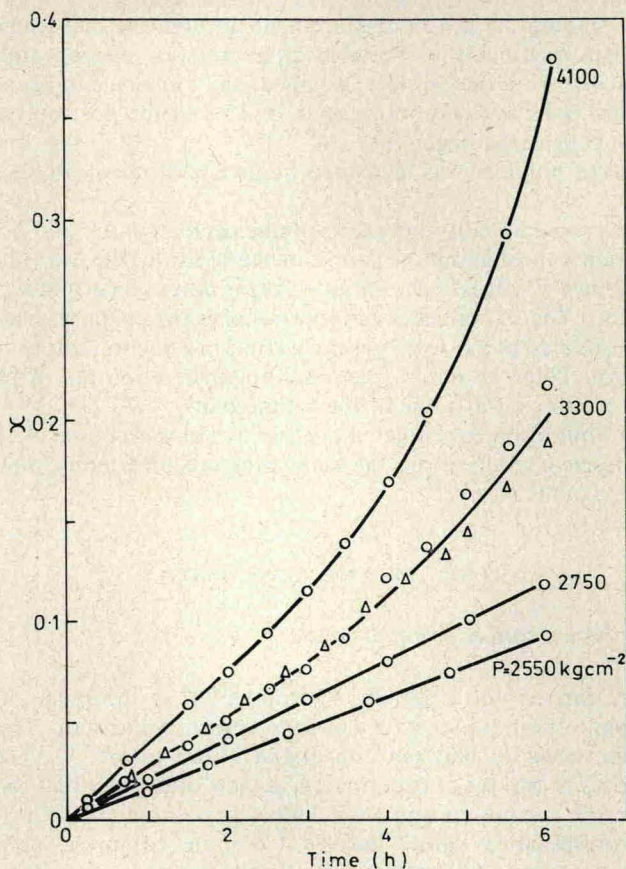


Figure 1 Rates of polymerization of styrene at 40.5° in liquid phase

In equation (1) the terms  $R_\gamma$  and  $R_T$  are of the form:

$$R_\gamma = k_p[M](R_{i,\gamma}/k_t)^{1/2} \quad (2)$$

$$R_T = k_p(k_{i,T}/k_t)^{1/2} [M]^2 \quad (3)$$

$k$  = rate constant; subscripts  $p$ ,  $t$ ,  $i$  refer to propagation, termination and initiation reactions respectively,  $[M]$  = monomer concentration.

In turn, the rate of initiation induced by radiation is given by:

$$R_{i,\gamma} = 1.03 \times 10^{-12} IdG_R \quad (4)$$

$R_{i,\gamma}$  = initiation rate induced by radiation ( $\text{mol cm}^{-3}\text{s}^{-1}$ );  $d$  = monomer density ( $\text{g cm}^{-3}$ );  $I$  = dose rate ( $\text{rad s}^{-1}$ );  $G_R$  = radiolytic yield. For styrene  $G_R = 0.69^{25}$ .

Considering the above formulation it is evident that to obtain  $R_\gamma$  from  $R$  requires a knowledge of the contribution due to the thermal polymerization, as in equation (1). For this purpose runs were carried out without irradiation

of the sample. The results showed that thermal polymerization can be ignored in the explored temperature and pressure ranges. Conversions less than 3% were found at 4000 atm and 40.5°C for the usual reaction time of 6h. This conclusion was checked by evaluation of  $R_T$  from the known values of activation volume  $\Delta V_T^\ddagger$  and energy  $E_T^\ddagger$ , using the following correlations:

$$\text{isothermal } \Delta \ln R_T = -\Delta V_T^\ddagger \Delta P/RT + 2 \Delta \ln[M] \quad (5)$$

$$\text{isobaric } \Delta \ln R_T = -(E_T^\ddagger/R) \Delta(1/T) + 2 \Delta \ln[M] \quad (6)$$

The following values were utilized:  $\Delta V_T^\ddagger = -25.8 \text{ cm}^3 \text{ mol}^{-1}$  and  $R_T$  (1 atm) =  $1.27 \times 10^{-8} \text{ mol (cm}^3 \text{ s)}^{-1}$  at 80°C<sup>10</sup>;  $E_T^\ddagger = 21 \text{ kcal mol}^{-1}$ <sup>26</sup>;  $[M]/[M]_0 = 1.178$  at 60°C<sup>27</sup>;  $[M]_0 = 8.53 \times 10^{-3} \text{ mol cm}^{-3}$  at 40.5°C and

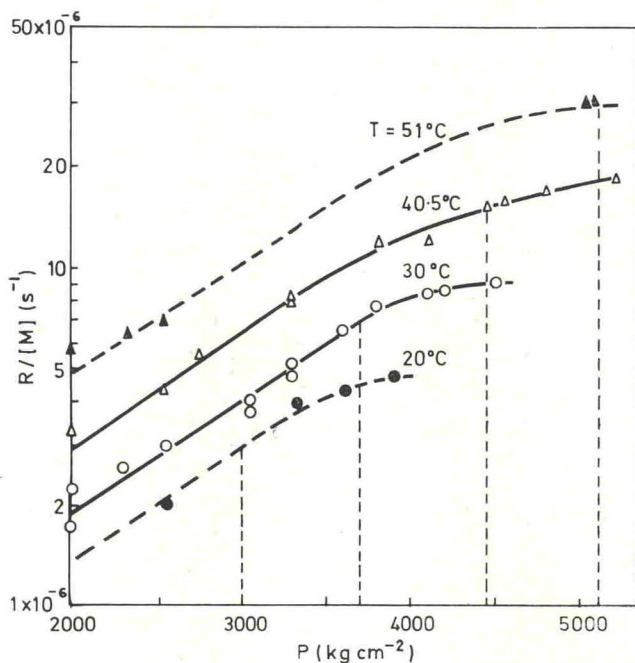


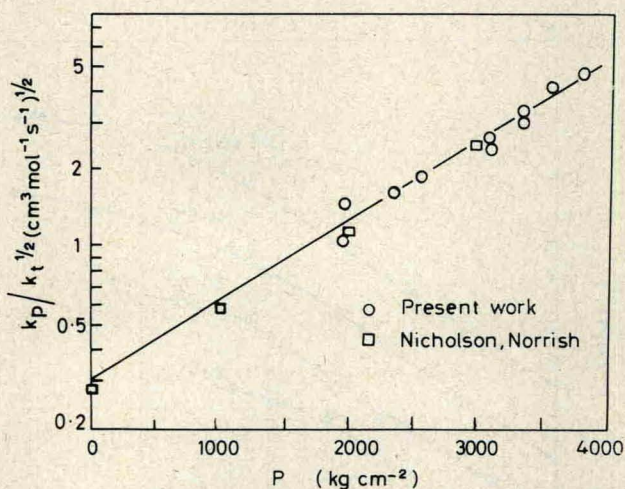
Figure 2 Pressure and temperature effects on the polymerization rate. Dashed vertical lines indicate the solidification point at the various temperatures

1 atm<sup>28</sup>. Then from equations (5) and (6) the value of  $R_T$  is  $2.78 \times 10^{-8} \text{ mol (cm}^3 \text{ s)}^{-1}$  at 4000 atm and 40.5°C. Interpolation at the same pressure, of the experimental results at 40.5°C (Figure 2) gives  $R = 1.35 \times 10^{-7}$  and from equation (1) the value  $R_\gamma = 1.32 \times 10^{-7} \text{ mol (cm}^3 \text{ s)}^{-1}$  is obtained. The comparison of these values indicates that at least up 4000 atm and 40.5°C the thermal polymerization can be neglected, so that  $R_\gamma = R$ .

*Effect of pressure on polymerization rate*

The results of the liquid phase runs are shown in *Figure 2* as plots of  $R/[M]$  against  $P$ . Most of them refer to the isotherms 30 and 40.5°C; a few values at 20 and 51°C are also reported for comparison. The plots indicate that the polymerization rate is an exponential function of pressure for most of the liquid region, whereas a tendency of the slope to decrease is observed at higher pressures, including the 'supercooled liquid region'. In this respect it is worth noting that no discontinuity is apparent between the two regions.

In *Figure 3* the results obtained at 30°C are compared with Nicholson and Norrish's values for the polymerization of styrene photosensitized by



*Figure 3* Comparison of  $k_p/k_t^{1/2}$  values for polymerization at 30°C initiated by gamma radiation (present work) and photosensitized by benzoyl peroxide according to Nicholson and Norrish<sup>3</sup>

benzoyl peroxide<sup>3</sup>. The ratio  $k_p/k_t^{1/2}$  was evaluated from the corresponding value of  $R_p/[M]$  and from equation (4); using density values derived from the data of the above Authors by means of the Tait equation<sup>29</sup>, with  $B = 1185$  kg cm<sup>-2</sup>,  $C = 0.216$ .

The good agreement with Nicholson and Norrish's values supports the assumption of the same reaction mechanism in both cases. In addition, it gives *a posteriori* evidence for the negligible effect of pressure on the initiation reaction induced by gamma radiation.

The activation volume of the rate constant  $k_p/k_t^{1/2}$  can be derived from<sup>30</sup>:

$$[\partial \ln(k_p/k_t^{1/2})/\partial P]_T = -\Delta V^+/RT \quad (7)$$

The value  $\Delta V^+ = -18$  cm<sup>3</sup> mol<sup>-1</sup> found in this case is in agreement with the corresponding value  $\Delta V^+ = -19.5$  cm<sup>3</sup> mol<sup>-1</sup> for free-radical polymerization at 80°C in the pressure range 1–2650 atm<sup>10</sup>.



### Molecular weight

The intrinsic viscosity  $[\eta]$  in toluene at 25°C was determined for the polymer obtained at 40.5°C. From Figure 4, it appears that, in accordance with literature results, the molecular weight increases with increasing pressure for most of the examined pressure range, tending to constancy at higher pressure.

From the weight average molecular weight, derived from  $[\eta] = 5.21 \times 10^{-5} M_w^{0.78}$  according to reference<sup>16</sup>, an approximate value of the monomer

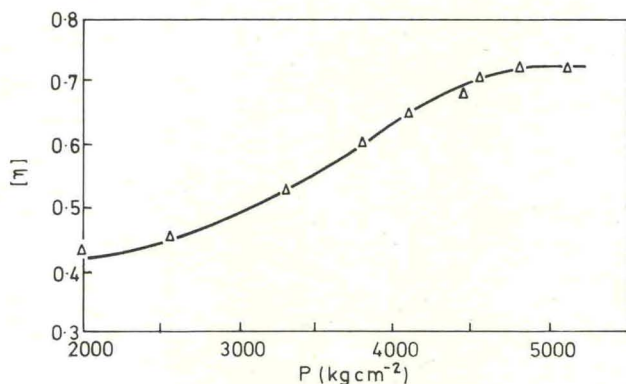


Figure 4 Intrinsic viscosity  $[\eta]$  ( $100 \text{ cm}^3 \text{g}^{-1}$ ) of the polymers obtained at 40.5°C

transfer constant can be obtained. It appears to lie in the range from  $0.7 \times 10^{-4}$  to  $0.5 \times 10^{-4}$  with pressure change from 2000 to 4600  $\text{kg cm}^{-2}$  and thus it compares well with the value of  $10^{-4}$ , found at 80°C and up to 2650 atm for chemically-initiated polymerization<sup>10</sup>.

### Activation energy

Figure 5 shows the Arrhenius plot of  $k_p/k_t^{1/2}$  at 2550  $\text{kg cm}^{-2}$  for the liquid phase polymerization. From the plot the value of  $\sim 7 \text{ kcal mol}^{-1}$  is obtained, which agrees well with the value of  $6.6 \text{ kcal mol}^{-1}$  found by Matheson *et al*<sup>31</sup> at atmospheric pressure.

The agreement is further evidence that the polymerization in the liquid phase in the temperature range investigated, occurs by the free-radical mechanism.

### (B) Solid phase polymerization

Runs with samples, which had passed through the liquid–solid transition, were followed dilatometrically, and were usually stopped after 6h.

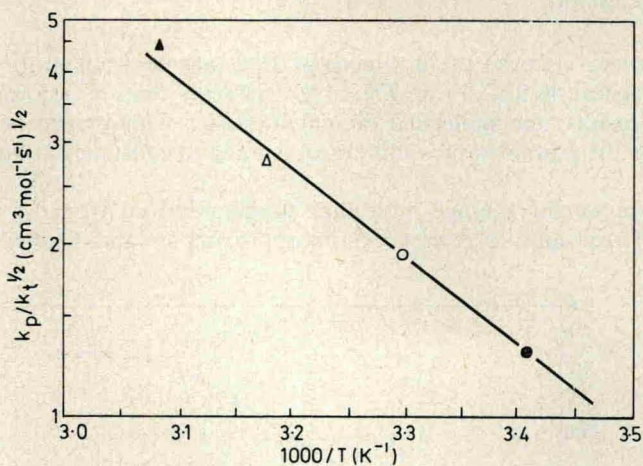


Figure 5 Arrhenius plot for the ratio  $k_p/k_t^{1/2}$  at  $2550 \text{ kg cm}^{-2}$

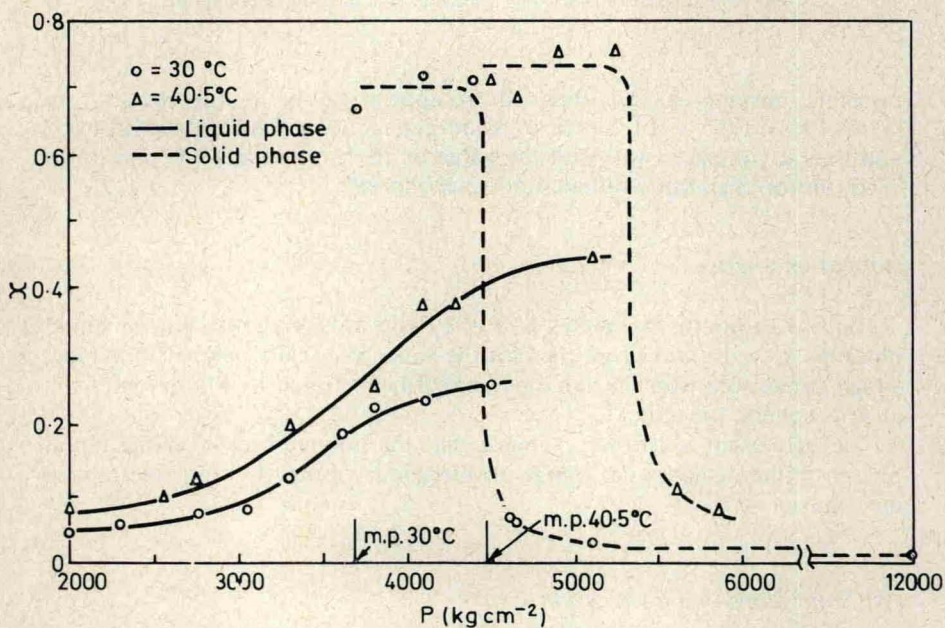


Figure 6 Pressure-dependence of polymerization conversion after 6 h irradiation at 30 and  $40^\circ\text{C}$ . The value at  $12000 \text{ kg cm}^{-2}$  refers to a 24 h irradiation

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<sup>32</sup>, including styrene<sup>14, 21</sup>. Also in cases of solidification obtained by applying high pressure a similar behaviour has been observed<sup>33</sup>.

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<sup>11</sup>, 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  $4100 \text{ kg cm}^{-2}$  and  $30^\circ\text{C}$   $\Delta V \simeq 0.02 \text{ cm}^3 \text{ g}^{-1}$  in solid and  $\Delta V \simeq 0.08$  in liquid.

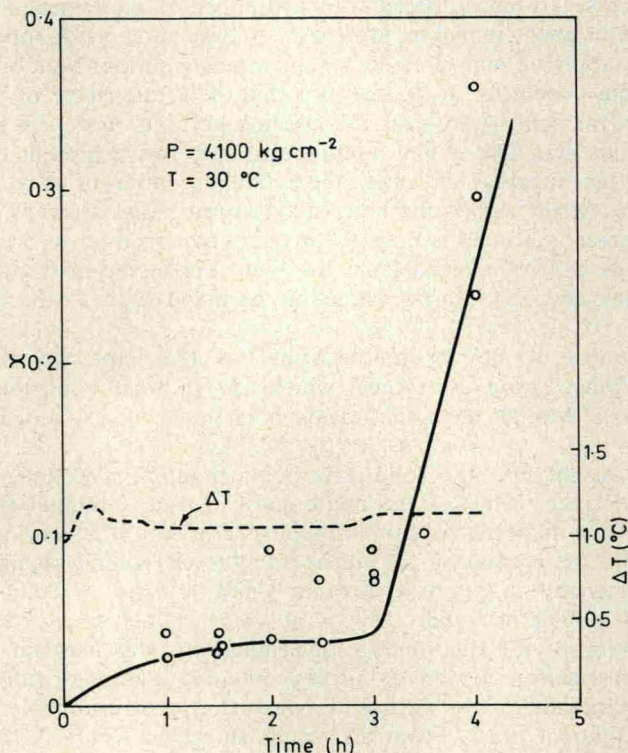
The accuracy of the dilatometric determinations was checked by comparing polymerization conversion curves, obtained dilatometrically, with a number of gravimetrically measured conversions corresponding to runs stopped at different times. From the results shown in *Figure 7*, the dilatometric curves seem 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  $40.5^\circ\text{C}$  are shown in *Figure 8*. The relevant features are: an initial period in which a slow volume decrement

\* Units:  $1 \text{ k cal mol}^{-1} \equiv 4.19 \text{ kJ mol}^{-1}$

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<sup>34, 35</sup> and is in line with the general assumptions concerning the process mechanism<sup>36, 37</sup>. Since polymerization requires movement of monomer molecules from their lattice sites, it must be con-



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

sidered 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.

As irradiation is continued, new defects are progressively developed until

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<sup>38, 39</sup>, though an

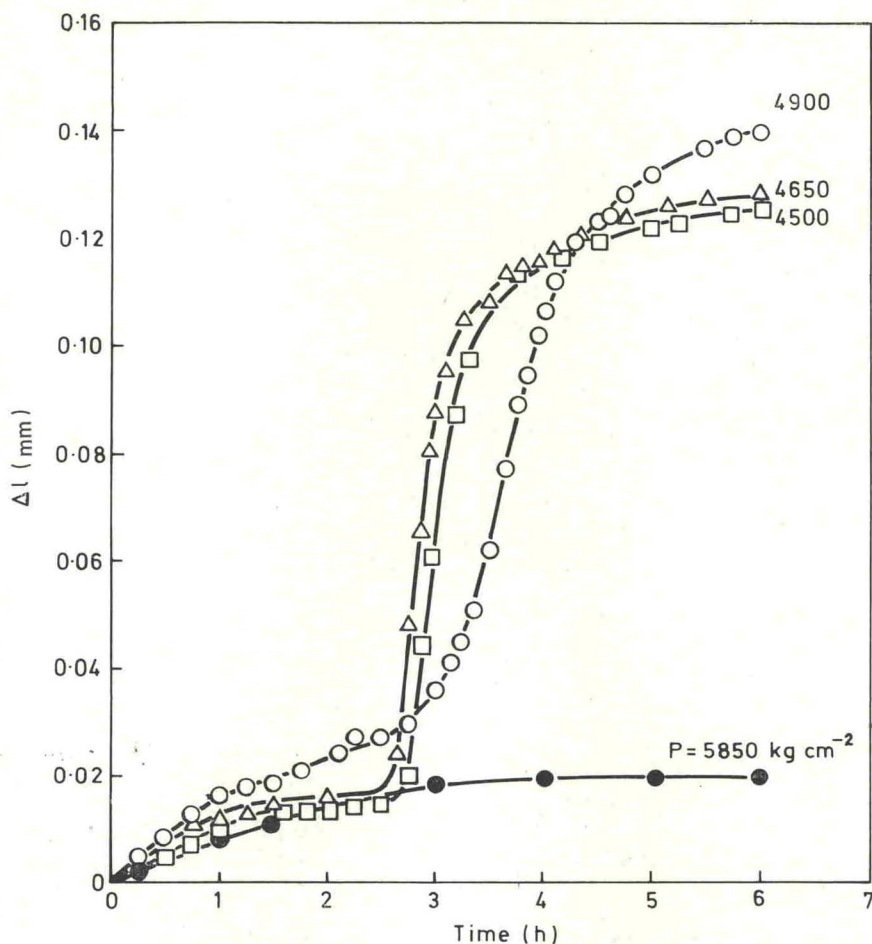


Figure 8 Pressure-dependence of the dilatometric curves for solid-state polymerization at 40-50°C

enhancement of the process is also possible, analogous to that displayed in the liquid state<sup>40</sup>.

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

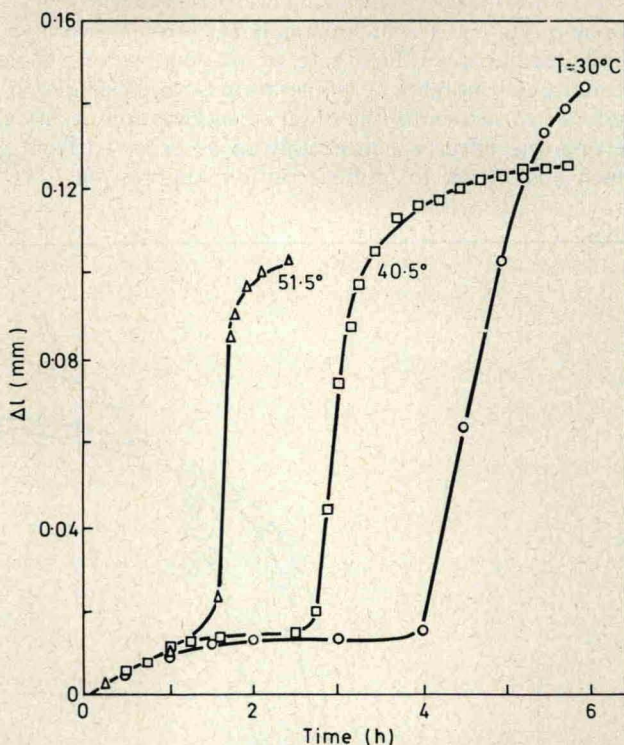


Figure 9 Temperature influence on the dilatometric curves at pressures near the melting point

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.

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- Preparation and purification of biological macromolecules
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- The interactions of biopolymers with ions and small molecules

In a rapidly growing field such as polymer science, a list such as this cannot be exhaustive. The editors welcome contributions on topics which are not listed but which fall within the scope of polymer and biopolymer science and technology.



