

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.

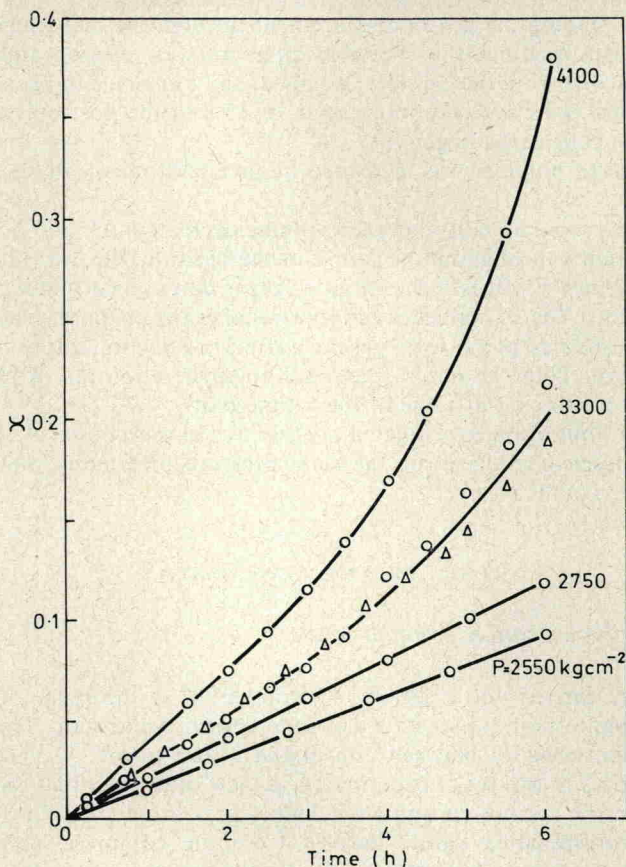


Figure 1 Rates of polymerization of styrene at  $40.5^{\circ}$  in liquid phase

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