

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 ΔV_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 $R_T(1 \text{ atm}) = 1.27 \times 10^{-8} \text{ mol (cm}^3 \text{ s)}^{-1}$ at 80°C¹⁰; $E_T^\ddagger = 21 \text{ kcal mol}^{-1}$ ²⁶; $[M]/[M]_0 = 1.178$ at 60°C²⁷; $[M]_0 = 8.53 \times 10^{-3} \text{ mol cm}^{-3}$ at 40.5°C and

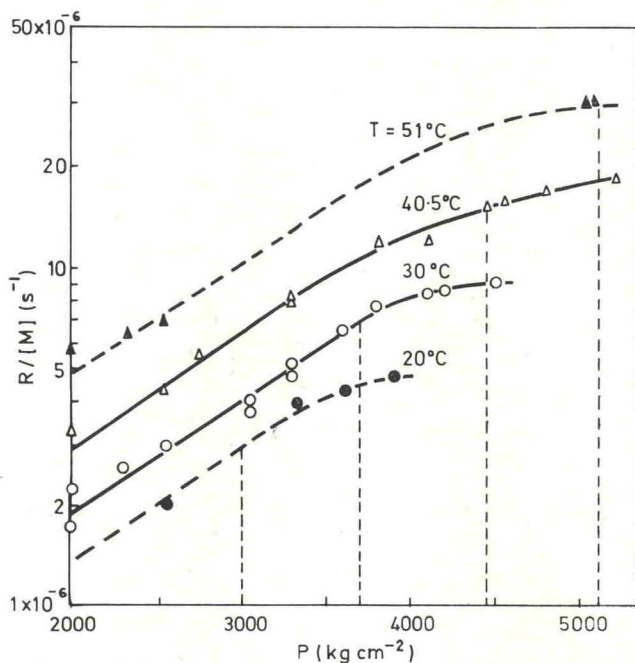


Figure 2 Pressure and temperature effects on the polymerization rate. Dashed vertical lines indicate the solidification point at the various temperatures

1 atm²⁸. 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

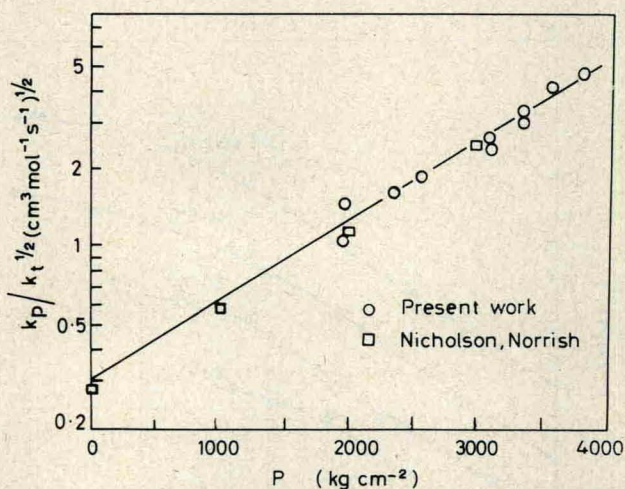


Figure 3 Comparison of $k_p/k_t^{1/2}$ values for polymerization at 30°C initiated by gamma radiation (present work) and photosensitized by benzoyl peroxide according to Nicholson and Norrish³

benzoyl peroxide³. 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 equation²⁹, with $B = 1185$ kg cm⁻², $C = 0.216$.

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 from³⁰:

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

The value $\Delta V^+ = -18$ cm³ mol⁻¹ found in this case is in agreement with the corresponding value $\Delta V^+ = -19.5$ cm³ mol⁻¹ for free-radical polymerization at 80°C in the pressure range 1–2650 atm¹⁰.