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 $[\eta] = 5·21 \times 10^{-5} M_w^{78}$ according to reference[16], an approximate value of the monomer
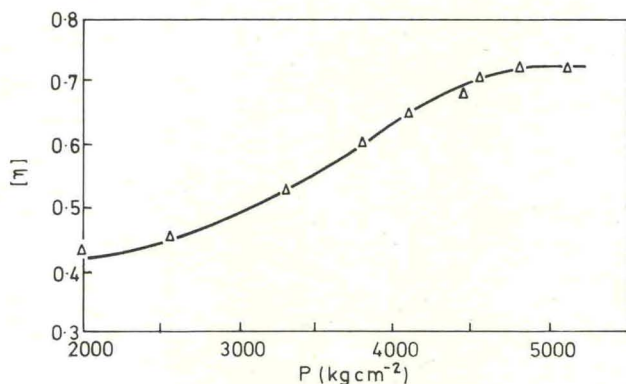

Figure 4 Intrinsic viscosity $[\eta]$ (100 cm³g⁻¹) of the polymers obtained at 40·5°C

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 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[10].

Activation energy

Figure 5 shows the Arrhenius plot of $k_p/k_t^{1/2}$ at 2550 kg cm⁻² for the liquid phase polymerization. From the plot the value of ~7 kcal mol⁻¹ is obtained, which agrees well with the value of 6·6 kcal mol⁻¹ found by Matheson *et al*[31] 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.
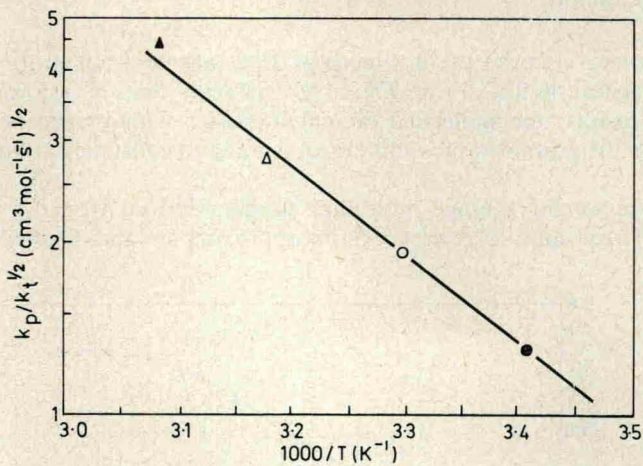
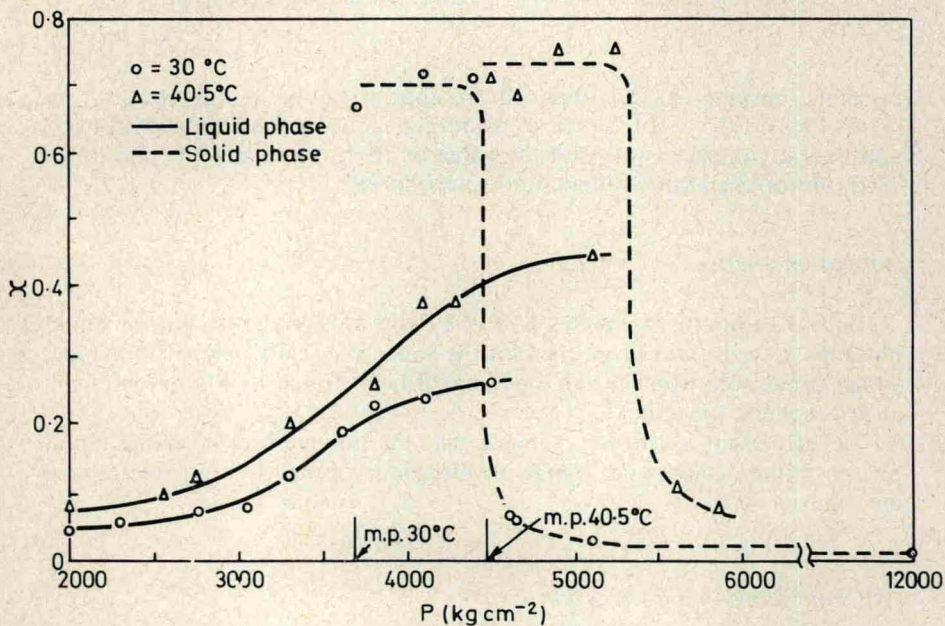Figure 5 Arrhenius plot for the ratio $k_p/k_t^{1/2}$ at 2550 kg cm^{-2}

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

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