

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

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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^{1–11} and ionic¹² 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^{13–16}. At higher temperatures, however, this is so only when the monomer is super-dry^{17–18}, and, if special care is not taken to remove moisture, the polymerization occurs by a free-radical mechanism^{14,16,19}.

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 temperature²⁰.

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^{14,21}, can be investigated at higher temperatures.

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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 described¹¹. 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 Bridgman²². 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 2×10^{-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 polymerization¹¹.

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°C), 3700 (30°C), 4450 (40.5°C) and 5100 (51°C) 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 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