JOURNAL OF POLYMER SCIENCE: PART A VOL. 1, PP. 3217–3229 (1963)

Critical sol t.

EHRL P63 0194

Phase Equilibria of Polymer–Solvent Systems at High Pressures Near Their Critical Loci: Polyethylene with *n*-Alkanes*

PAUL EHRLICH† and JOHN J. KURPEN, *Monsanto Chemical Company, Plastics Division, Research Department, Springfield, Massachusetts*

Synopsis

Above the crystallization temperature slightly branched polyethylene and propane are miscible in all proportions above a critical pressure, defined as upper critical solution pressure (UCSP). This pressure decreases only very slightly from 110 to 150°C. At 110°C. the UCSP varies from 450 atm. for a polymer fraction of molecular weight 17,000, to 580 atm. for one of molecular weight 250,000. The critical polymer concentrations are low as in conventional polymer–solvent systems and shift with molecular weight in a similar manner. The pressures required to achieve solubility of the polymer in the gas at polymer concentrations less than critical (dew-point pressures) are nearly as high as the UCSP down to very low polymer concentrations. The data determine part of the critical locus in (P, T, composition) space. Experiments with other polyethylene–*n*-alkane systems (ethane, butane, and pentane) show that the critical locus changes gradually from a liquid–liquid to a gas–liquid boundary and might be termed a fluid-liquid locus. If crystallization of polymer does not intervene, this locus intersects the saturated vapor pressure curve at a lower critical end point (LCEP) which is the lower critical solution temperature (LCST) found only recently by Freeman and Rowlinson in many hydrocarbon polymers with hydrocarbon solvents. Incomplete miscibility extends over greater regions of temperature and pressure as the solvent molecule becomes smaller, but the critical locus would probably be closed along the pressure axis for a hypothetical amorphous polymethylene with ethane.

INTRODUCTION

We reported recently[1] that the phase equilibria of liquid high pressure polyethylene with compressed gases showed at least one of the usual characteristics of conventional polymer–solvent systems: a critical condition occurred at very low polymer concentration. This was associated with a change from negligible solubility of the polymer in the solvent to complete mutual miscibility over a small change in pressure. Polymers can therefore be completely miscible with compressed gases above a definite pressure[1,2] and the binary systems possess a gas–liquid critical locus in (P, T, composition) space.

Freeman and Rowlinson[3] found that hydrocarbon polymers heated

---

* Presented in part at the 145th Meeting of the American Chemical Society, September, 1963.

† Central Research Dept., 800 N. Lindbergh, St. Lo