stigated in detail, should be given by the change in melting point of ethylene with pressure[8] and with dilution.[10]

'ith pentane (Fig. 6), the critical locus can be followed down to the er critical end point (LCEP), or the lower critical solution temperature ST) on the vapor pressure curve, where two liquid phases and a gas se coexist.[3] This point lies at 91°C. at a pressure indistinguishable from vapor pressure of the pure solvent by the present method of measure- t. Freeman and Rowlinson[3] did not attain complete miscibility in system polyethylene–n-pentane, probably because they operated with ar polyethylene where the crystallization boundary was shifted to her temperatures, intersecting the critical locus above the LCEP.

t is clear that a LCEP of high molecular weight polyethylene exists only n-alkanes with five carbons and greater because of an increase in the EP with size of the solvent molecule and because of the increase in lting point of the polymer with pressure.

## DISCUSSION

All systems reported are characterized by a large free volume and by ge density differences between the components. There also should be a gative volume change of mixing $\Delta V$ along a critical locus of the type scribed. Every point on this locus, denoted by subscript c, may be con- dered as LCST with $(dP/dT)_c > 0$ or as UCST with $(dP/dT)_c < 0$. ertain inequalities involving the second derivatives with respect to mposition of the thermodynamic mixing functions must be satisfied ong the locus and, if there are no points of inflection, one has at an LCST $H < 0$, $\Delta S < 0$ and at an UCST $\Delta H > 0$, $\Delta S > 0$.[4] These latter con- itions have been verified near an LCST in several cases.[11,12] In addition, $P/dT)_c$ is given by

$$\frac{\partial^2 \Delta S}{\partial x_2^2} \bigg/ \frac{\partial^2 \Delta V}{\partial x_2^2}$$

here $x_2$ refers to the mole fraction of solute.

Clearly, all lattice treatments of polymer solutions seem here less satis- ying physically than under ordinary conditions and violate one or more of he inequalities which must be met along the critical locus, particularly here $(dP/dT)_c > 0$. One objection to the use of the results obtained rom lattice treatments is removed, when it is realized that expressions for the free energy of mixing formally identical to that of the Flory- Huggins equation have been obtained by considerations not requiring the lattice assumption.[13,14] In order to allow for negative, as well as positive, heats of mixing the Flory-Huggins interaction parameter $\chi$ must be con- sidered as a free energy,[11] as indeed required by the more general lattice treatments[15] and by the theory of Longuet-Huggins.[13] Patterson[11] has suggested further that $\chi$, although no longer a heat term, may still be identified with Hildebrand's solubility parameter term, which then becomes