CLOUD-POINT BEHAVIOR OF POLYETHYLENE-BUTENE COPOLYMER IN PENTANE ISOMERS

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Hydrocarbons are conventional solvents. Solvent quality as well as all other hydrocarbon properties depends on number of carbon atoms in molecular backbone. For hydrocarbon isomers this number is fixed and molecular structure becomes a primary factor for their properties variation. We study the effect of solvent molecular structure on solvent quality for pentane isomers, namely, *n*-pentane, isopentane, neopentane, and cyclopentane. Competition of molecular interaction forces between solvent molecules and between solvent and solute molecules determines conditions for dissolution. Elevated pressure helps to dissolve some polymers even if they are not soluble at ambient conditions. In four pentanes we dissolved statistically random deuterated poly(ethylene-*co*-20,2 mol %-1-butene) (d-PEB10), which is important for related neutron scattering experiments. At ambient conditions this polymer is dissolved in cyclopentane. For dissolution of this polymer in *n*-pentane, isopentane, and neopentane elevated pressure is necessary. It is expected that their various molecular structure is important for packing around polymer chain. By comparison of cloud-point curves for solutions of a polymer in various solvents we are able to characterize their solvent quality.

Cloud-point curves have been obtained at high-pressure apparatus with variable-volume view cell. Some improvements are implemented in our apparatus [1]. Intermediate vessel containing pure solvent is installed in high-pressure line between the view cell with polymer-solvent mixture and high-pressure generator operating with tap water. The vessel almost eliminates risk of minimal contamination of the mixture by tap water with possible seal leakage at the floating piston in the view cell. Also, observation of sharp laser beam in the sample makes registration of the cloud point more convenient and accurate as compared with usage of conventional light source. The turbidity of the d-PEB10-pentane mixture in the view cell is determined by monitoring the transmitted intensity, and the scattered intensity of a narrowly-focused He–Ne laser beam.

The polymer solution is compressed to a single phase, and the pressure is then slowly decreased until a cloud point is detected when strong multiple scattering appears at the phase transition point. The *P–T* phase diagram for pentane isomers is presented in the Fig. 1.
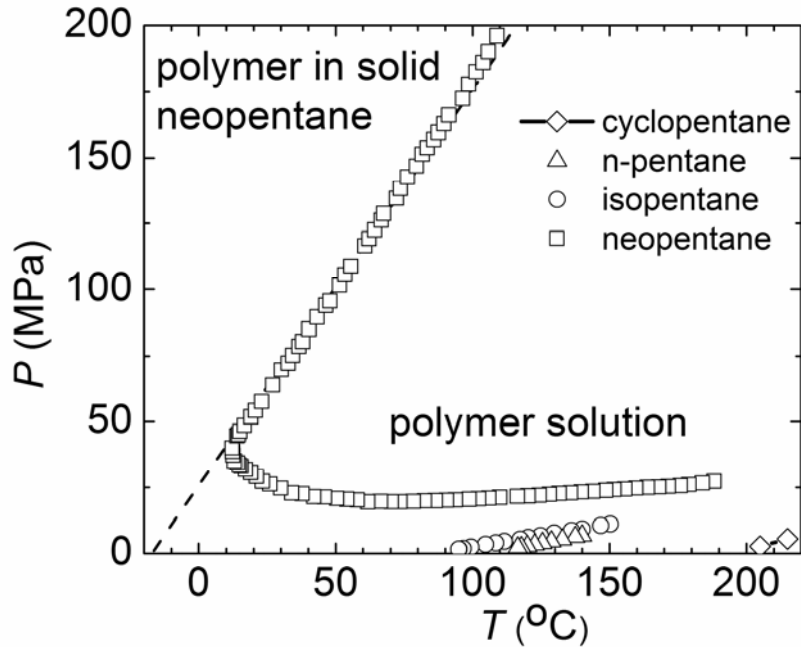

Fig. 1. Phase behavior of 0,3 wt % d-PEB10 in pentane isomers.
The dashed line is the melting curve for neopentane [2]

Neopentane data at high pressure represent the boundary branch where solidification of neopentane occurs [2]. The branch of the cloud-point curve at lower pressure is virtually flat at a fixed pressure of about 20 MPa from 200 °C to about 30 °C. The cloud-point curves for other three pentanes are located at lower pressure and exhibit the following ordering in solvent quality increase: neopentane being the poorest quality solvent, isopentane, *n*-pentane, and cyclopentane being the highest quality solvent. The solvent quality increase follows the same ordering as the magnitude of the critical temperatures with cyclopentane ($T_c = 238,5$ °C), *n*-pentane ($T_c = 196,5$ °C), isopentane ($T_c = 187,3$ °C), and neopentane ($T_c = 160,6$ °C).

We have estimated the Hildebrand solubility parameter δ for pentane isomers. More complicated Hansen solubility parameter (being an extension of Hildebrand solubility parameter for polar and hydrogen-bonding liquids) appears to have the same value for non-polar pentanes. Hildebrand solubility parameter δ is commonly estimated from [3]:

$$\delta = \sqrt{\frac{\Delta_v H - RT}{V_m}} \; , \qquad (1)$$

where $\Delta_v H$ – vaporization enthalpy, R – gas constant, T – temperature, and V_m – molar volume. Hildebrand solubility parameter δ for solvent and for solute at dissolution conditions is expected to have close values, so that their difference is small at the dissolution phase transition boundary. The values of δ shown in the Table correspond to temperature of 120 °C, where we have the cloud-point pressure data for three pentane isomers. Vaporization enthalpy and molar volume for calculations have been obtained from [4]. Cloud-point pressure $P_{cl.}$ at 120 °C is also shown in the Table 1.

Table 1

Hildebrand solubility parameters and cloud-point pressure at 120 °C

	cyclopentane	*n*-pentane	isopentane	neopentane
$\Delta_v H$ (kJ/mol)	23,3	19,4	18,6	14,6
V_m (l/mol)	93,4	116,2	117,1	123,1
δ (MPa$^{1/2}$)	14,9	12,1	11,7	9,9
$P_{cl.}$ (bar)	–	2,75	6,00	21,60

Hildebrand solubility parameters for pentane isomers in the Table exhibit the same ordering of solvent quality as the cloud-point pressures shown in the Figure. Applied pressure improves solvent quality and brings increase in solvent solubility parameter. At dissolution pressure the value of Hildebrand solubility parameter for all pentanes is expected to reach the value for cyclopentane, which is a good solvent at ambient pressure. Rough estimate shows that increase in Hildebrand solubility parameter correlates with pressure increase. The difference between δ values for isopentane and δ values for neopentane is higher than the difference between δ values for isopentane and δ values for *n*-pentane. The ratio of these differences is 5,3. The distances between cloud-point curves are similar. Analogous ratio of the differences for cloud-point pressures is 4,8. These ratios for Hildebrand solubility parameters and for cloud-point pressures appear to have close values. Hence, variation of pressure at dissolution phase transition for pentane isomers is mainly governed by the energy based factor, provided in (1). No additional effect of molecular structure on solvent quality is detected in our experiment.

We conclude that the main effect of molecular structure on solvent quality for hydrocarbons appears to be already included in their thermophysical parameters.

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