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PHASE EQUILIBRIUM IN LOW-DENSITY POLYETHYLENE—NORMAL ALKANES SYSTEMS

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The crystalline equilibrium diagrams were obtained for eight LDPE—n-alkane systems with the cloud point method. A point of view was formulated in which there is a major difference between crystal separation in low-molecular-weight systems and systems containing flexible macromolecules, and it derives from differences in the essence of the phase transitions that take place in these systems.

Investigating the phase state of low-density polyethylene (LDPE)—normal alkane systems is of dual interest. First, these systems are important in a purely practical aspect due to the development of technology for fibrillization of a new generation of synthetic leather bases by the method of selective extraction, and second, they are an example of systems whose crystalline separation diagrams are not reported in the literature.

The experiments were conducted by the cloud point method. The average cooling (heating) rate of 5 $K \cdot h^{-1}$ was ensured by a stepwise decrease (increase) in the temperature of the system by 1 K every 12 min. The accuracy of maintaining the temperature in the isothermal step was a minimum of ±0.1 K. The temperature of the disappearance of visually identified opalescence in the system was set as the melting point (T_m) and the temperature of its appearance was set as the crystallization point (T_{cr}).

We investigated brand 12203-320 LDPE with T_m of 381.5±0.5 K (determined microscopically for a heating rate of 4 $K \cdot min^{-1}$), with intrinsic viscosity in *p*-xylene at 348 K of 0.77, density at 298 K of 911.2 kg/m^3, and degree of branching of ~2.6 CH_3 groups per main chain 100 carbon atoms, as well as normal alkanes — heptane, decane, tridecane, tetradecane, pentadecane, hexadecane, octadecane, and nonadecane.

The solvents were distilled before use and the degree of purity was monitored with the values of the density determined by the oscillator densimetry method in [1].

The results of determining T_m and T_{cr} for these systems are summarized in Table 1, and as an example, the crystal separation diagram of the LDPE—heptane system is shown in Fig. 1. This and all of the other LDPE—alkylbenzene diagrams obtained in the present study and described previously [2] have two special features:

– up to a concentration of the low-molecular-weight component of 0.8-0.9 mass fraction, T_m (T_{cr}) of LDPE decreases almost rigorously linearly, and a sharp decrease is only observed for a degree of dilution exceeding these figures;

– the boundary curves obtained in cooling of a homogeneous solution and heating of the heterogeneous system that arises do not coincide and the difference between them increases as the polymer melt is diluted by the low-molecular-weight component.

In the indicated region of compositions, the curves for these systems are satisfactorily linearized (Table 2) in the coordinates of the equation

$$T_m^{-1} = (T_m^0)^{-1} + \frac{R}{\Delta H_{fus}^0 M_1}\omega_1 = (T_m^0)^{-1} + \beta\omega_1 , \tag{1}$$

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TABLE 1. Melting and Crystallization Points of LDPE—*n*-Alkane Systems

Concentration of *n*-alkanes, wt. %	Heptane		Decane		Tridecane		Tetradecane		Pentadecane		Hexadecane		Octadecane		Nonadecane	
	T_m, K	T_{cr}, K	T_m, K	T_{cr}, K	T_m, K	T_{cr}, K	T_m, K	T_{cr}, K	T_m, K	T_{cr}, K	T_m, K	T_{cr}, K	T_m, K	T_{cr}, K	T_m, K	T_{cr}, K
99.5	—	—	353.0	342.0	355.5	346.0	356.0	348.0	358.0	349.0	358.0	349.5	359.5	350.5	359.0	351.0
99.0	351.0	341.0	353.0	344.5	356.0	348.0	357.0	350.0	359.0	352.0	359.0	350.5	360.0	352.0	360.0	353.0
98.0	352.0	345.0	355.0	346.5	357.0	350.5	359.0	352.0	360.0	353.0	360.0	352.0	361.0	353.0	362.0	355.0
96.0	354.0	347.0	357.0	349.0	359.0	352.5	360.0	354.0	361.0	355.0	361.5	354.0	362.0	355.0	363.0	357.5
94.0	356.0	348.0	358.0	352.0	360.0	353.0	361.0	355.0	362.0	356.5	363.0	356.0	364.0	357.0	364.0	359.0
92.0	356.5	349.0	359.0	354.0	361.0	354.5	362.0	356.5	363.0	357.5	363.5	358.0	365.0	359.0	365.0	360.0
90.0	357.0	351.0	360.0	355.5	362.0	356.0	363.0	358.0	364.0	359.0	364.0	360.0	366.0	361.0	366.0	361.0
85.0	358.0	353.0	361.5	359.0	363.0	358.5	364.0	360.0	365.0	361.0	365.5	361.5	367.0	363.0	367.0	363.0
80.0	359.0	355.5	363.0	361.0	365.0	360.0	365.5	362.0	366.0	362.0	367.0	363.5	368.0	365.5	368.0	365.0
75.0	360.0	356.0	364.0	362.0	366.0	362.0	366.5	364.0	367.0	365.0	368.0	365.0	369.0	367.5	—	—
70.0	362.0	358.0	366.0	364.0	367.0	364.0	368.0	365.0	368.0	366.0	369.0	366.5	370.0	369.0	—	—
65.0	—	—	367.0	365.0	368.0	365.0	369.0	367.0	369.0	367.0	370.0	367.5	371.0	370.0	—	—
60.0	365.0	362.0	368.0	366.0	369.0	367.0	370.0	368.5	370.0	368.0	371.0	369.0	372.0	371.0	—	—
50.0	367.0	365.0	371.0	369.0	371.0	370.0	372.0	371.0	372.0	370.0	373.0	372.0	373.0	372.0	—	—
40.0	370.0	367.0	373.0	372.0	373.0	372.0	374.0	373.0	374.0	373.0	375.0	374.0	375.0	374.0	—	—
30.0	—	—	376.0	375.0	375.0	374.0	376.0	375.0	376.0	375.0	377.0	376.0	377.0	376.0	—	—
20.0	376.0	373.0	378.0	377.0	378.0	377.0	378.0	377.0	379.0	378.0	379.0	378.0	379.0	378.0	—	—
10.0	379.0	376.0	380.0	379.0	380.0	379.0	380.0	379.0	381.0	380.0	381.0	380.0	381.0	380.0	—	—

TABLE 2. Results of Processing the Experimental Data with Eq. (1)

Solvent	$\beta \cdot 10^{1.5}$, K^{-1}		ΔH^0_{fus}, J/g	
	for T_m	for T_{cr}	for T_m	for T_{cr}
Heptane	1.99 ± 0.10	2.33 ± 0.16	417 ± 21	356 ± 24
Decane	1.53 ± 0.20	1.94 ± 0.10	383 ± 50	302 ± 16
Tridecane	1.46 ± 0.17	1.91 ± 0.18	309 ± 35	236 ± 22
Tetradecane	1.34 ± 0.15	1.76 ± 0.18	313 ± 35	238 ± 24
Pentadecane	1.31 ± 0.11	1.74 ± 0.11	299 ± 25	225 ± 14
Hexadecane	1.24 ± 0.19	1.71 ± 0.16	296 ± 45	215 ± 20
Octadecane	1.14 ± 0.19	1.47 ± 0.14	286 ± 48	227 ± 21
Nonadecane	1.11 ± 0.20	1.52 ± 0.38	279 ± 50	204 ± 51

Note. In all cases, it was assumed that $T^0_{cr} = T^0_m = 381.5$ K.

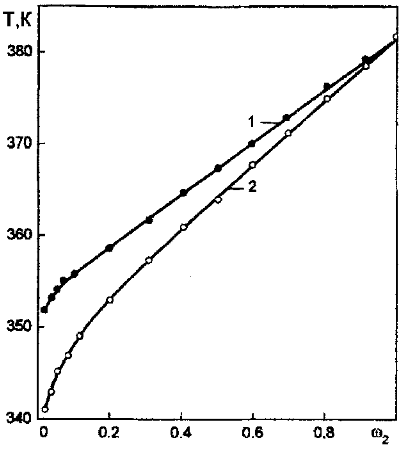

Fig. 1. Melting (1) and crystallization curves (2) of LDPE in the presence of heptane.

obtained in [2] from the well-known Flory equation [3] in the assumption that the Flory—Huggins parameter for a polymer—liquid system is negligibly different from zero and the correlation between the volume φ_l and weight ω_l fractions of the liquid in the system is described by the equation

$$\varphi_l = \omega_l \rho_2 \rho_l^{-1}. \quad (2)$$

Table 2 shows that parameter β is constant regardless of whether it is calculated with the values of T_m or T_{cr}, but in the second case, its absolute value is always higher than in the first case.

Note also that the melting heat of 1 g of LDPE crystals calculated with Eq. (1) is clearly a function of the nature of the solvent. This contradicts the physical meaning of this quantity and suggests that the interpretation of coefficient β deriving from Eq. (1) is not completely rigorous.

The second distinctive feature of the LDPE—*n*-alkane and LDPE—alkylbenzene system (noncoincidence of the boundary curves obtained in conditions of cooling of homogeneous and heating of heterogeneous systems) from our point of view is major in character and reflects the specific features of the polymer melt—partially crystalline polymer phase transition which takes place in the presence of a low-molecular-weight component which is thermodynamically active with respect to the polymer.

The essence of this feature can be comprehended if we consider that with respect to the partially crystalline polymer—liquid system, the expression

$$\Delta G_{\mathrm{s}} = \Delta G_{\mathrm{el}} + \Delta G_{\mathrm{m}} + \Delta G_{\mathrm{mi}} , \tag{3}$$

which correlates the change in the Gibbs energy (ΔG_{s}) in formation of a solution of the polymer in the liquid with the changes in this quantity in devitrification of unordered regions of the polymer (ΔG_{el}), melting of crystallites (ΔG_{m}), and mixing of a solution of the liquid in the viscous-flow or highly elastic polymer formed as a result of the last two processes, with the residual volume of the liquid (ΔG_{mi}) is, in contrast to the equation

$$\Delta G_{\mathrm{s}} = \Delta G_{\mathrm{subl}} + \Delta G_{\mathrm{sol}} , \tag{4}$$

(where ΔG_{subl} and ΔG_{sol} are the changes in the free energy in sublimation of a crystal of the low-molecular-weight substance and solvation of its molecules in their migration into the solvent, respectively), a reflection not of hypothetical but of real, successively occurring processes.

In heating of a heterogeneous partially crystalline polymer—liquid system, melting of crystallites, established either calorimetrically or optically, obviously precedes formation of a solution, i.e., a homogeneous bicomponent liquid system, as a result of dilution of the polymer gel arising at the time of its total amorphization by the remaining volume of solvent not contained in the polymer. For this reason, the boundary phase equilibrium curve obtained in heating a mixture of polymer and liquid (melting curve) reflects the transition from one heterogeneous system (partially crystalline polymer—liquid) to another heterogeneous, but already liquid system (totally amorphized polymer gel—liquid), and the composition of the gel at this time is not identical to the composition of the initial mixture.

In movement in the opposite direction (from a homogeneous to a heterogeneous system), conversion of the homogeneous solution into a heterogeneous system precedes crystallization and requires some perhaps important supercooling of the system which, superimposed on the temperature lag of the crystallization process itself, results in experimentally perceptible differences in the temperatures of "melting of the last" and "appearance of the first" crystals.

Dilution of a crystallizable polymer by a low-molecular-weight component should increase the degree of supercooling of the system required for realization of a phase transition in its liquid state and consequently increase the difference between the experimentally established values of T_{m} and T_{cr}.

A phenomenologically important conclusion follows from the above: there is a major difference between crystal separation processes in low-molecular-weight systems and in systems containing flexible macromolecules; it consists of the fact that in the first case, a crystal—homogeneous liquid—mixture (true solution) of molecules of crystalline substance and liquid takes place in the presence of a liquid (solvent), and in the second case, the transition crystal—heterogeneous liquid system (totally amorphized polymer gel—pure liquid or solution of low-molecular-weight fractions of the polymer in this liquid) takes place. Such a system can either exist in an experimentally perceptible temperature range and then a set of such systems arising from the initial mixtures of different composition is identified as amorphous equilibrium in the region of $T > T_{\mathrm{m}}$, or in a temperature range difficult to perceive experimentally, passes into a liquid one-phase system — a true solution of the polymer in the liquid or the liquid in the polymer whose composition is identical to the composition of the initial mixture. This case is classified in [4] as purely crystalline equilibrium in a polymer—liquid system.

Two particular conclusions derive from this general conclusion:

– the melting and crystallization curves of partially crystalline polymer—liquid systems experimentally identified by traditional methods do not reflect the real dependence between the phase transition temperature and composition of the polymer—liquid system at this time and consequently cannot be used in the thermodynamic analysis of these systems;

– the chemical potential of the solvent in a totally amorphized polymer gel in contact with a pure liquid or a solution of low-molecular-weight fractions of the polymer in it is not equal to the chemical potential in a solution identical in composition to the initial liquid or heterogeneous mixture and consequently the well-known Flory equation, including in the form of Eq. (1), is fundamentally inaccurate.

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