

Phase Equilibrium of a Semicrystalline Polymer–Liquid System: Isotactic Polypropylene–Dibutylphthalate

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Abstract—A hypothesis proposed for semicrystalline polymers as metastable, microheterogenous, three-dimensionally structured liquids with crystallites as grid sites is developed. The phase diagram of the isotactic polypropylene (PP)–dibutyl phthalate system obtained via this approach is discussed in detail. Additional arguments for the thermodynamic nonequivalence of the liquidus line in this and similar systems, on one hand, and in the systems of low-molecular-mass crystalline–liquids, on the other hand, are given. The appearance of a boundary curve, reflecting the transition of the original two-phase system into a single phase, such as a liquid-solution in a polymer, on the phase diagram of the semicrystalline polymer–liquid system is shown to fundamentally change the technological meaning of the diagram, thereby clarifying the mechanism of microporous-membrane formation from solutions of semicrystalline polymers via thermally induced phase separation.

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INTRODUCTION

The fundamental research by Richards [1] showed (Fig. 1) that two types of phase diagrams are possible for semicrystalline polymer–liquid systems. The first contains only one phase line, similar to the liquidus line on the phase diagrams of systems of low-molecular-mass liquid–crystallines, as was considered in [2–4]. The second type includes a fragment of the liquidus line and the binodal of the liquid equilibrium in the region of compositions enriched with a low-molecular-mass component and is explained as a combination of crystalline and liquid equilibrium. At the same time, Richards supposed that the specifics of the first systems consist in that the binodal of the liquid equilibrium of a noncrystallizing analog of a semicrystalline polymer should be below the liquidus line.

The incompleteness of the phase diagrams of semicrystalline polymer–liquid systems that were obtained by Richards was first indicated in [5]. There, the necessity to supplement these diagrams with a line characterizing the temperature dependence of the solubility of the liquid in the amorphous regions of the semicrystalline polymer was verified on the basis of the thermodynamic analysis of the dissolution of these polymers. This view was further developed in [6–9].

Figure 2 shows the phase diagram of the isotactic PP–*m*-xylene system, which is a good solvent in the thermodynamic sense [9]. It, as well as the phase diagrams of the systems based on LDPE [5–8], differs by two features from those in the literature [3, 10–18]:

(i) In the region of compositions enriched with a low-molecular-mass component, the liquidus line has segment *AB* with a constant temperature of complete amorphicity of the polymer component in the absence of the binodal of liquid equilibrium.

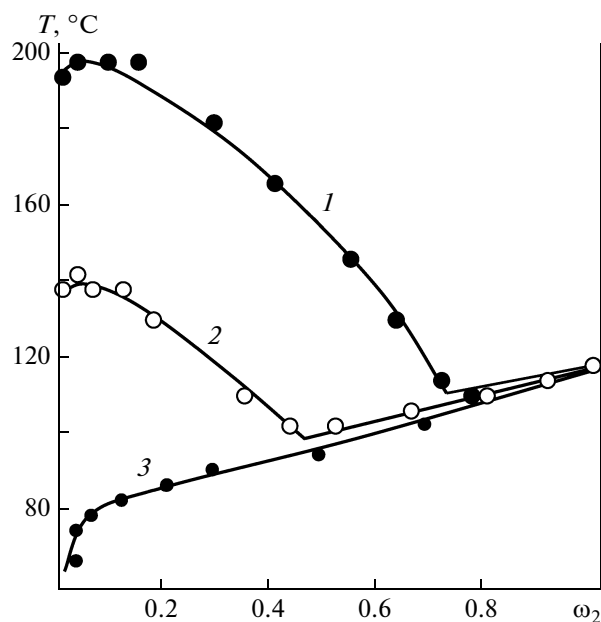


Fig. 1. Phase diagrams of (1) LDPE–nitrobenzene, (2) LDPE–amylacetate, and (3) LDPE–xylene systems; ω_2 is the mass fraction of the polymer.

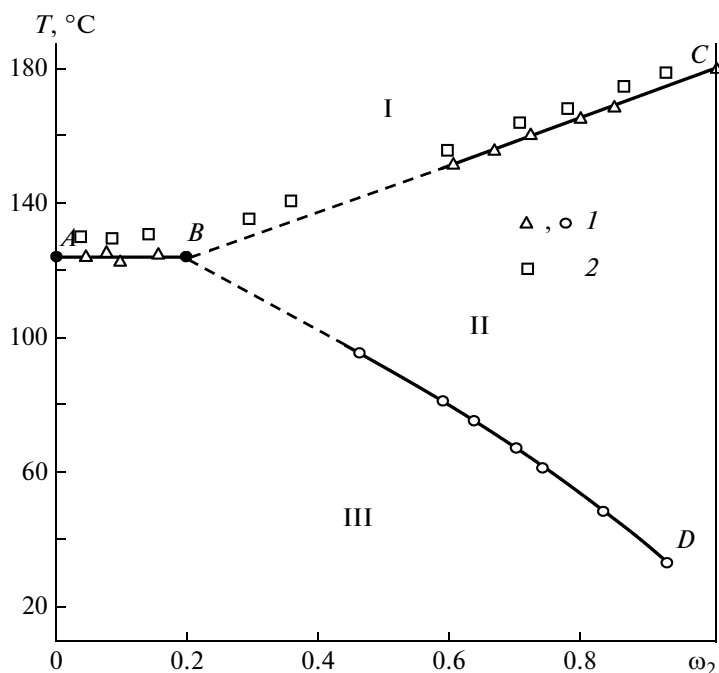


Fig. 2. Phase diagram of the PP-*m*-xylene system. Data were obtained via the (1) optical method and (2) DSC method (2). See notations in text.

(ii) The diagram contains additional boundary line *BD*, whose specificity is that it has two thermodynamic interpretations. On one hand, this line is the temperature dependence of the solubility of the liquid in the amorphous regions of the semicrystalline polymer and, hence, the osmotic equilibrium established in the system as a result of unilateral diffusion of the liquid into the polymer molecules. On the other hand, *BD* is the phase line formed by the set of temperatures of complete dissolution of a certain amount of the liquid in the amorphous regions of the polymer [8]. It separates the two-phase polymer-liquid system from the single-phase system: a liquid solution in the amorphous regions of the polymer at a ratio equal to the original ratio.

In strict thermodynamic terms, this diagram reflects the point of view [7] that the phase state of a semicrystalline polymer is a metastable (internally stressed), microheterogeneous, three-dimensionally structured liquid and fixes four specific situations arising in this case during the transition from the initial two-phase system to the final single-phase system.

(i) The liquid in the starting system has already dissolved in the polymer, but crystallites remain there (line *BD*).

(ii) All the polymer crystallites are destroyed as a result of additional heating of the emerging one-phase system (line *BC*).

(iii) Dissolution of the liquid in the initial system in the polymer is accompanied by the destruction of all the crystallites (point *B*).

(iv) The polymer crystallites have already been destroyed, and the liquid in the initial system is not yet dissolved fully (line *AB*). Depending on the thermodynamic affinity of the liquid for the polymer, either the two-phase system that appeared is transformed into a single-phase system directly on the line *AB* or the binodal of liquid equilibrium with the UCST appears over line *AB*.

Use of the term *crystallite destruction* in this case emphasizes the fact that the change in the degree of polymer crystallinity with a change in temperature is a reversible thermomechanical process both in the presence of liquid [7] and in its absence [19, 20].¹

Only the last crystallites, unbound by passage chains, are destroyed thermally, e.g., melts, [9].

With allowance for the above information, the phase diagram of the system of a semicrystalline polymer and a "good" solvent reflects the existence of its three regions: region I, a molecular mixture of high- and low-molecular-mass liquids; region II, a single-phase microheterogeneous system (a liquid solution in the amorphous regions of the polymer) that may be a fluid or solid gel with crystallites at the lattice sites with respect to the physical state; and region III, a two-phase system where the liquid solution in the amorphous regions of the polymer and the pure solution of

¹ The mechanism of thermomechanical destruction of polymer crystallites via "drawing" of the individual atoms of the main chain from it due to excess stresses in the amorphous regions was first proposed by Alfrey and Mark [21].

the liquid or its solution of polymer fractions not included in the crystallites coexist.²

A thermodynamically important characteristic of the system is the coordinates of figurative point *B*. It is obvious that a tendency should be manifested with an increase in the thermodynamic quality of the liquid, as that in the polymer solvent: $\omega_{2B} \rightarrow 0$, $T_{am}^{\min} \rightarrow T_m(L)$, where ω_2 is the polymer mass fraction, T_{am}^{\min} is the minimum temperature of complete amorphicity of the polymer in the presence of the solvent, and $T_m(L)$ is the melting point of the low-molecular-mass component of the system.

The goals of this study are to show for the example of the previously partially investigated [12] isotactic PP-dibutylphthalate (DBP) system how the complete phase diagram of the semicrystalline polymer-“bad” solvent should look and to present additional arguments in favor of the fact that, even in the absence of line *BD*, line *BC* in thermodynamic terms is not equivalent to the liquidus line in the phase diagrams of the corresponding low-molecular-mass systems.

EXPERIMENTAL

We used isotactic PP of the Kaplen 01250 brand (OOO NPO Neftekhimiya), with a melt flow rate of 1.25 ± 0.05 g/10 min at 190°C; a lading weight of 2.16 kg (DIN EN ISO 1133:2005); and a melting temperature of $T_m = 176.9 \pm 0.1^\circ\text{C}$, determined via the method of quasi-equilibrium stepwise isothermal amorphicity in the immersion-liquid medium [19] of DBP (high-purity grade) with a refractive index and density corresponding to the reference data [22].

Before the experiment, pellets of isotactic PP were stirred in DBP for 5 h at a polymer-solvent volume ratio of 1 : 7 and at a temperature of 160°C to remove macromolecules fractions not participating in the formation of crystallites. The proportion of these fractions was ~2 wt % in a sample of isotactic PP.

During plotting of the phase diagram, the main instrument was an optical method [8] involving observation of the state of the polymer-liquid binary system placed in a glass vial with an inner diameter of 3 mm and a total volume of ~0.3 cm³ to measure the temperature with a horizontal microscope. Additional information was obtained via DSC. The optical method is based on the difference in the refractive indexes of coexisting phases in the system.

At least two vials of the polymer-liquid system with the same composition were used to perform the experiment. A preweighed tube was loaded with a portion of granules with a precisely known mass, and a thin neck of the tube was formed with a gas burner in such a way

that, after sealing, the bottom of the tube became an ampoule of 0.2–0.3 mL volume. Dosing of the liquid was performed through the neck with a microsyringe with a long needle. After sealing of the neck, the tube was reweighed on a Sartorius MF 215S electronic balance with a measuring error of $\pm 3 \times 10^{-5}$ g to establish the exact mass of the entered liquid.

In our experiments, it was assumed that the ratio of the volume of the current ampoules to the mass of the used liquid has to satisfy the condition that the mass of the liquid vapor at the experimental temperature should not exceed 1–2% of the mass of the used liquid.

One of the vials prepared via the described method and containing the binary system of a given composition was placed in a glass thermostat, and the temperature of the liquid was found to be $25.0 \pm 0.1^\circ\text{C}$. After 1 h, the number of phases in the system and its phase state were estimated from the presence or absence of the liquid meniscus. The conversion of the system into a single-phase system (an opalescent liquid solution in the amorphous regions of the polymer) meant that, at this ratio of the starting components, the transformation temperature of the two-phase polymer-liquid system into a single-phase system was $T_{LP} < 25^\circ\text{C}$.

If a system remained two-phase, it was subjected to stepwise heating at 5°C increments and standing at each temperature for 1 h until the liquid meniscus disappeared and the system turned into a single-phase system. This temperature was taken as an indicative value of T_{LP} .

Further heating according this procedure was continued until the conversion of the opalescent (microheterogeneous) single-phase system into an optically transparent (homogeneous) system, thereby making it possible to roughly estimate the temperature of this transformation, T_{mL} .

After obtaining the approximate values of T_{LP} and T_{mL} , the thermostat was cooled to a temperature ~5°C below the found value of T_{LP} , and a second vial with the given binary mixture was placed inside. Then, stepwise heating with steps of 0.5°C and holding at each temperature for 30 minutes were performed to provide an average temperature-rise rate of ~1°C/h. First T_{LP} and then T_{mL} were determined at this heating rate with a precision of 0.5°C. Lines *BC* and *BD* are plotted with the use of the set of values T_{LP} and T_{mL} obtained in this way for systems of different compositions (Fig. 3).

During plotting of segment *AB*, the temperature that was used corresponded to the disappearance of opalescence in the two-phase system of excess DBP (transparent component) and a DBP solution in isotactic PP (opalescent component). Figurative point *B* is obtained through a graphical extrapolation of the dependences $T_{LP} = f(\omega_2)$ and $T_{mL} = f(\omega_2)$ until their intersection with segment *AB*, corresponding to the condition $T_{mL} = \text{const} = T_{am}^{\min}$.

² We can say that, in the first case, the diagram reflects the existence of osmotic equilibrium in region III, while in the second case, the diagram reflects the existence of osmotic and extraction equilibria.

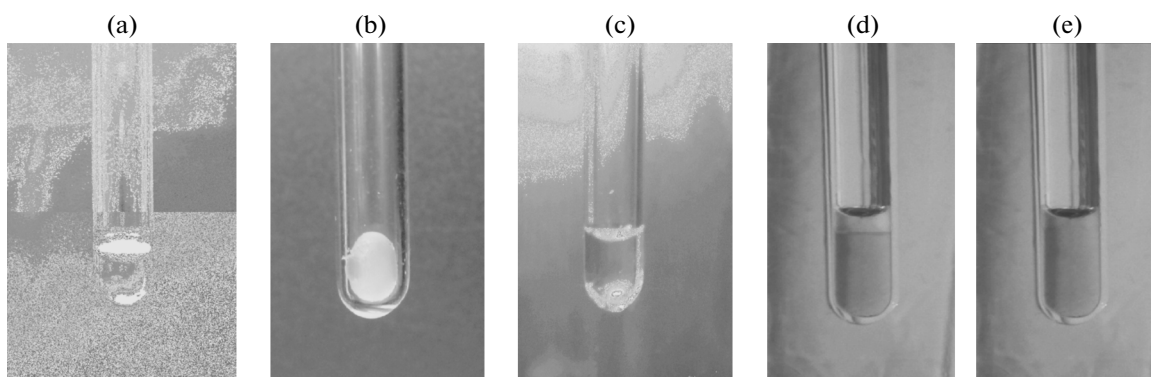


Fig. 4. Photographs of the PP–DBP system at (a) 25°C, (b) T_{Lp} , (c) T_{mL} , (d) T_{am}^{\min} , and (e) T_{LL} .

Note that, during the transition from point K to point K_1 , an increase in the quantity of the opalescent polymer phase is visually registered, and at $T \geq 140^\circ\text{C}$, a decrease in the amount of the clear component (DBP) is found.

At higher temperatures (in the path from point K_1 to point K_2) and a constant ratio of the components in the single-phase system, the opalescence intensity decreases and disappears completely at point K_2 at T_{mL} . At this temperature, the binary mixture loses its form of swollen granules and transforms into a flowable homogenous liquid–DBP solution in the polymer melt (Fig. 4c).

A system containing 25 wt % PP in the initial mixture (point K') has two phases at room temperature, and its state is similar to the one given in Fig. 4a.

As the temperature increases stepwise, the quantity of the opalescent polymer phase increases in this two-phase system, while its opalescence intensity decreases. At point K'_1 at T_{am}^{\min} , the phase enriched with the polymer becomes optically transparent (the upper layer in Fig. 4d), but differs from the second liquid phase (DBP) in the refractive index and a lower density.

This two-phase system is maintained to a temperature corresponding to T_{LL} (point K'_2), at which the mutual mixing of the two coexisting liquid phases results in the formation of an optically clear one-phase system (Fig. 4d).

Comparison of the diagrams given in Fig. 2 and 3 shows that substitution of a “good” solvent for a “bad” one in the isotactic PP–liquid system leads not only to occurrence of the binodal in the liquid equilibrium (Fig. 3, region IV) but also to the expected change in position of figurative point B in the temperature–concentration field.

In the first case, it corresponds to the coordinates $\omega_2 = 0.22$, $T_{am}^{\min} = 124^\circ\text{C}$, and in the second case, it corresponds to the coordinates $\omega_2 = 0.48$, $T_{am}^{\min} = 169^\circ\text{C}$.

DSC method is widely used during plotting of the phase diagrams of semicrystalline polymer–liquids [13–18] under the assumption that the endotherm maximum corresponds to the temperature of polymer melting, regardless of whether the endotherm corresponds to the melting of the pure polymer [23] or the melting of the polymer in the presence of liquid.

In general, this is incorrect in any case because, in physical terms, the endotherm reflecting the process of amorphicity of the semicrystalline polymer due to its heating both in the absence and in the presence of a liquid is related to a combination of two processes: (i) the thermomechanical failure of crystallites bound to each other through passage chains and (ii) purely thermal destruction (melting) of crystallites not mechanically connected to each other. Only in the latter process is $T_m = \text{constant}$.

As an illustration, Fig. 5 shows the DSC thermograms of melting of LDPE and isotactic PP obtained at a scanning rate of 10 K/min. The endotherms indicate the true temperatures of polymer melting, which were found through the method of stepwise isothermal amorphicity in an immersion liquid medium [20].

It is evident that, if the true value of T_m of LDPE is close to T_{max} , then for isotactic PP, the true value of T_m is close to the end of the endotherm, T_f .

Physically, this means that the proportion of crystallites that degrade only thermally at $T_m = \text{const}$ (the hatched part of the endotherm) is $\sim 18\%$ in the case of LDPE and $\sim 0.4\%$ in the case of isotactic PP. Figure 6 is evidence of the correctness of such an interpretation of the endotherms of melting of semicrystalline polymers and shows the results of X-ray determination of the degree of crystallinity of LDPE as a temperature function obtained on a Bruker D8 ADVANCE diffractometer [24].

It is logical to assume that the presence of liquid does not affect the proportion of crystallites that degrade thermomechanically; therefore, DSC can be guided by T_{max} during the analysis of LDPE–liquid systems and by T_f during the analysis isotactic PP–liq-

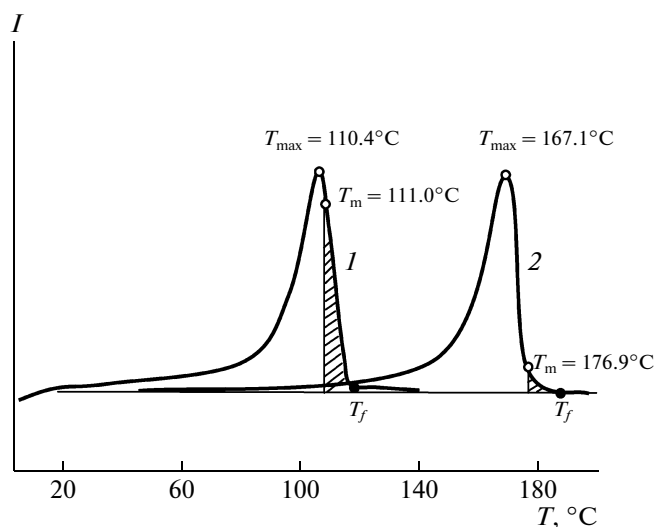


Fig. 5. DSC thermograms of melting of (1) LDPE and (2) isotactic PP.

uid systems (Fig. 2). Indeed, Fig. 2 shows that the values of T_{mL} for isotactic PP taken equal to T_f are in reasonable agreement with the values obtained through an optical method. The situation occurring in the LDPE–liquid systems is illustrated by the diagram given in Fig. 7 [8].

However, it is necessary to consider another factor: At the normal scan rate of 10 K/min, there is no guarantee that, until the moment of complete amorphicity of the polymer, all liquid initially taken is going to dissolve in it.

DSC thermograms of the mixtures of isotactic PP and DBP with different ratios of the components are shown in Fig. 8. They demonstrate that the exotherm, reflecting the thermal effect of the mixing of the melted i-PP with excess liquid excess, becomes apparent not only in the composition region $\omega_2 < \omega_{2B}$, where it has to be a priori but also in the field of $\omega_2 > \omega_{2B}$, where it should not be.

This means that the thermograms in the region of $\omega_2 > \omega_{2B}$ are related to the composition of a system different from the initial system. Therefore, their use is inappropriate for the plotting of line *BC*.

At the compositions corresponding to the inequality $\omega_2 < \omega_{2B}$, the exotherms characterize the temperature range of transformation of the resultant two-phase liquid system into a single-phase system.

It may be assumed that, in this case, we should focus on the temperature corresponding to the output of the right exotherm branch to the baseline and expect that the T_{LL} values obtained in this way, even after repeated melting, as is commonly done, are higher than those obtained via the optical method.

Now we should pay attention to the fact that the interpretation of the DSC thermograms given in

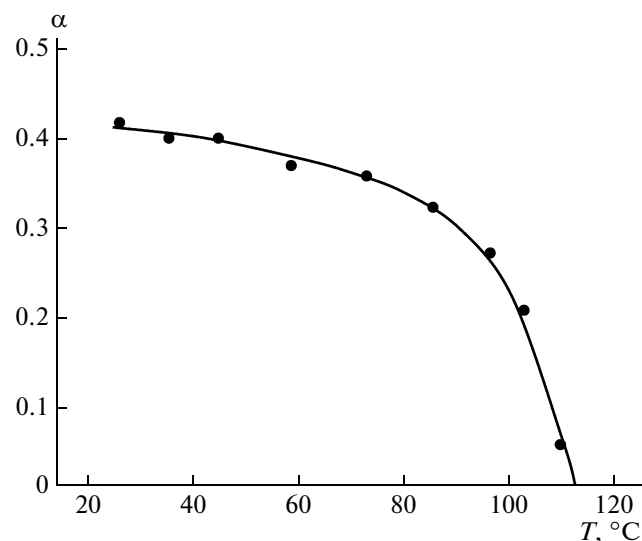


Fig. 6. Temperature dependence of the degree of crystallinity, α , of LDPE [24].

Fig. 8, like the melting endotherms of isotactic PP in the presence of a liquid, is undoubted because there are also exotherms of additional dissolution of DBP in liquid isotactic PP.

In our interpretation, as mentioned above, they appeared in the region to the right of point *B* because DBP had no time to dissolve completely in the polymer in the way from line *BD* to line *BC* at the temperature-scanning rate used in the DSC experiment.³

However, if you remove line *BD*, returning to the liquidus line shown in Fig. 1 in LDPE–xylene, reflecting, as commonly considered, the existence of only crystalline equilibrium in the system, it should be admitted that there is no thermal effect of additional dissolution of the liquid in the polymer: In this case, the DSC thermogram should reflect the thermal effect of *dissolution of crystals* of the polymer in the liquid in a wide temperature range.

To illustrate this thesis, Fig. 9 presents the phase diagram of Sn–Bi [25], while Fig. 10 shows the DSC thermogram of heating at a rate of 10 K/min of an alloy containing 57 at % Bi. It follows from the diagram that, during heating of the alloy of this composition, a sharp melting peak of the eutectic should appear on the thermal image. Its beginning corresponds to 139°C, and a broad peak reflecting the process of dissolving the excess Bi in the liquid eutectics lies in the range 139–187°C.

Figure 10 shows that the DSC thermogram almost corresponds to the expected result.

³ We intentionally present thermograms obtained via the first heating of the mixtures to illustrate the processes occurring during the DSC experiment, in systems with a known phase separated completely. These diagrams should not be used to plot the state diagrams.

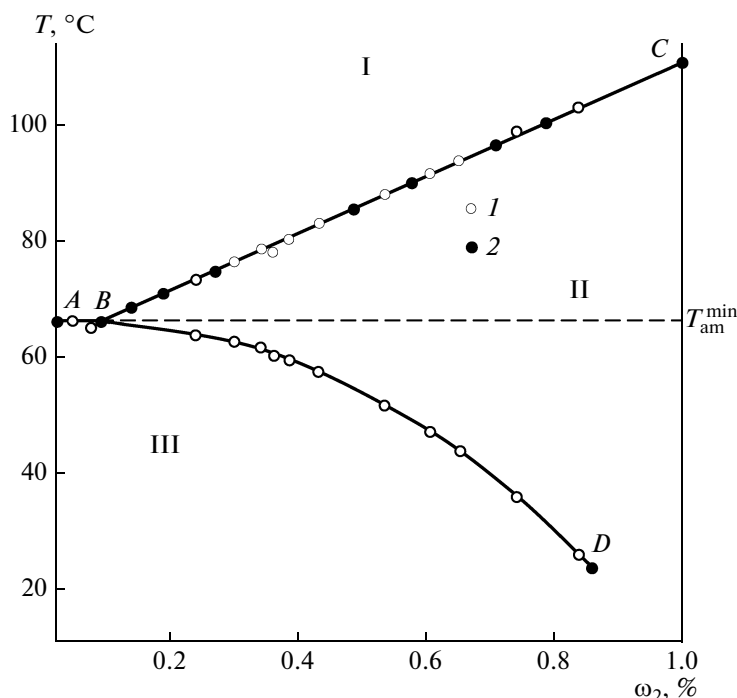


Fig. 7. Phase diagram of the LDPE-toluene system [8]. Data were obtained via (1) an optical method and (2) the DSC method.

Consequently, if the boundary curve of the system of LDPE-xylene truly reflects the existence of the crystalline equilibrium characteristic for low-molecular-mass systems of liquid-crystalline substances, DSC thermograms, in spite of their shape, are interpreted as endotherms of the dissolution of the polymer in the liquid in the temperature range from T_b to T_r .

The DSC thermograms in Fig. 8 relieve this problem and serve as a basis for the formulation of the true thermodynamic sense of line BC (Figs. 2, 3).

The thermodynamic feature of line BC consists in that the transition through it and during heating and cooling of the system is accompanied by a first-order transition not leading to a change in the number of phases and that the system is single-phase on both sides of the line BC .

This conflict is due to the fact that the first-order transition (melting-crystallization) occurs not relative to the macromolecules but to their elementary chains.

In physical terms, this is the process of the beginning of the formation or completion of destruction of the supramolecular structure of one of the components of a two-phase system. The development of the first process, expressed in the conversion of the polymer component into a macromolecular grid with crystallites as the sites, causes the appearance of a second phase (a pure liquid or solution of the low-molecular-mass polymer fractions) only during cooling to a temperature below T_{LP} (line BD).

In essence, passage through line BC is accompanied by the disappearance and appearance of microheterogeneity in a single-phase system because of the presence of microregions with three-dimensional order in the spatial arrangement of some of the elementary units of macromolecules in the polymer component.

It follows that, for any semicrystalline polymer, there is temperature $T_{m\infty}$ at which microcrystallites, either connected by passage chains or not yet connected, and statistically distributed elemental chains and kinetic segments of most of the macromolecules coexist in the volume of the semicrystalline polymer at equilibrium.

Because the situation is related only to elementary units of macromolecules, it is possible to arrive at this temperature through both cooling of the liquid polymer and heating of the solid polymer, regardless of the presence of the molecules of other substances, which however affect the absolute value of $T_{m\infty}$.

Therefore, with respect to the semicrystalline polymers, as opposed to low-molecular-mass substances, it is correct to talk about depression of both the crystallization temperature and the melting temperature in the case of the presence of molecules of impurities.

Consequently, in the thermodynamic sense, line BC characterizes the dependence of $T_{m\infty}$, which appears in the famous Flory equation [26] as T_m^0 , on the content of molecules of these substances in the polymer.

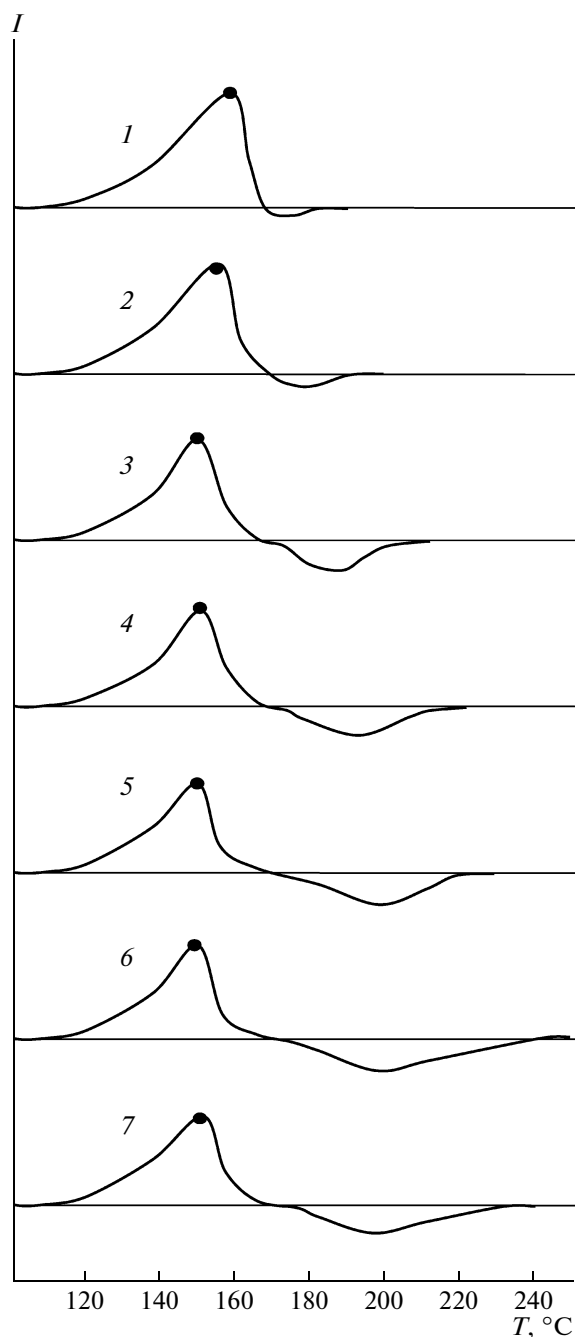


Fig. 8. Thermograms of the mixtures of isotactic PP-DBP containing (1) 17, (2) 27, (3) 53, (4) 63, (5) 71, (6) 81, and (7) 91 wt % of the liquid.

As applied to the real experiment, line *BC* is the dependence of the temperature of either the appearance of the first crystallite or the disappearance of the last crystallite on the amount of impurities in the polymer. Obviously, the first is almost always smaller, while the second, in contrast, is greater than $T_{m\infty}$.

The results of the study of the systems of LDPE and alkyl benzenes [27] and LDPE and *n*-alkanes [28] are consistent with this conclusion and show that the dif-

ference between these temperatures increases with an increase in the low-molecular-mass component in the system.

Let us return to line *BD*, which changes not only in the thermodynamic sense but also in the engineering sense of the phase diagram of a semicrystalline polymer-liquid.

The appearance of this line facilitates the understanding of the formation of microporous membranes from solutions of semicrystalline polymers via thermally induced phase separation [11, 13, 15, 18, 29-35].

In fact, regardless of whether the solvent is "good" or "bad" for a semicrystalline polymer, a rapid transition from region I to region III, where clean liquid and its solution in the polymer (gel) at a concentration equal to or less than $1 - \omega_{2B}$ coexist in equilibrium, should be accompanied by microphase separation and the spontaneous formation of a capillary-porous body with internal structuring (the size and nature of the distribution of the pure liquid in the pore volume of the gel phase) and rheological (stress-deformation) parameters depending on the ratio of components in the starting mixture, the cooling rate of the homogeneous melt, and the temperature of transformation of a two-phase microheterogeneous system into a single-phase one during the removal of the low-molecular-mass component of the system from the gel pores.

CONCLUSIONS

The results listed in this study of the isotactic PP-DBP system clearly show again that the semicrystalline polymer-liquid system and the low-molecular-mass crystalline compound-liquid system are nonequivalent from the thermodynamic point of view. At the heart of this nonequivalence is the fact that the semicrystalline polymer is a specific liquid in terms of its phase state (metastable, microheterogeneous three-dimensionally structured).

Exactly this circumstance allows the situation where the first liquid (polymer) acts as an osmotic cell with a variable capacity for the second one, while the second liquid, being dissolved in the first, increases this capacity owing to the destruction of the sites there in the form of a three-dimensional grid of crystallites.

In such a binary mixture, there is always a critical ratio of the two liquids at which complete dissolution of the latter in the former destroys all its crystallites.

At ratios smaller than critical, additional heating of the single-phase system (a solution of the second liquid in the first liquid) is required for complete amorphicity of the polymer liquid.

When the concentrations of the second liquid are greater than the critical value, the resulting two liquid phases with different concentrations of the polymer component are mixed spontaneously either at a tem-

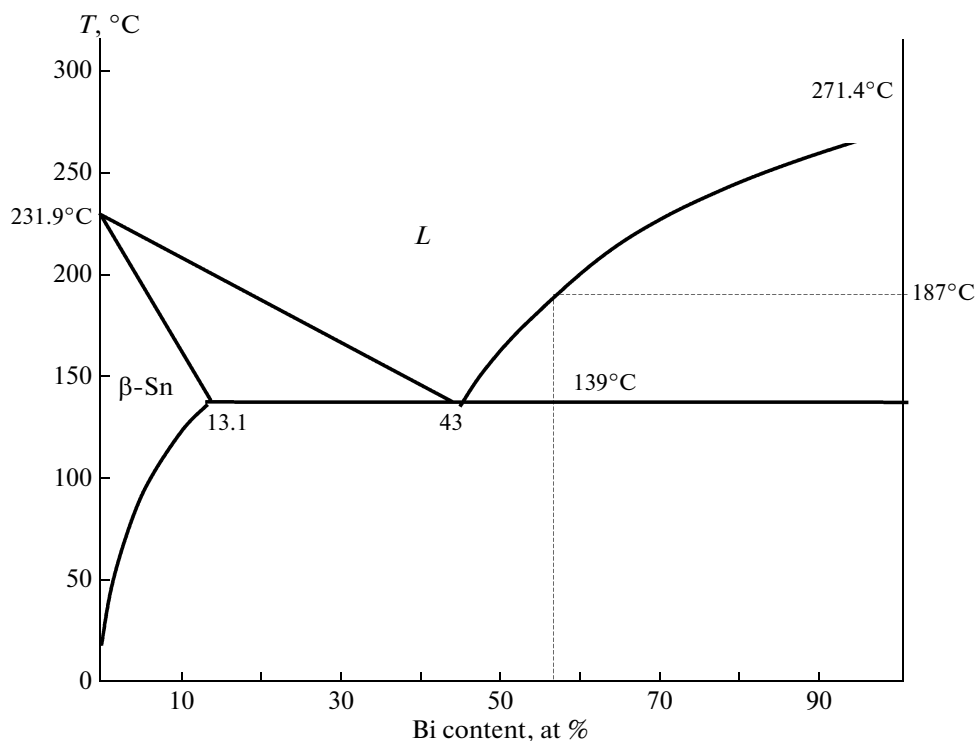


Fig. 9. Phase diagram of the Sn-Bi system [25].

perature corresponding to the critical composition or at a higher temperature.

At the same time, there is another conflict that requires separate discussion and is related to the fact that macromolecules act as a component of the polymer phase themselves during consideration of the pro-

cesses of dissolution of polymers in a liquid [36] or its mixing with another polymer [37,38].

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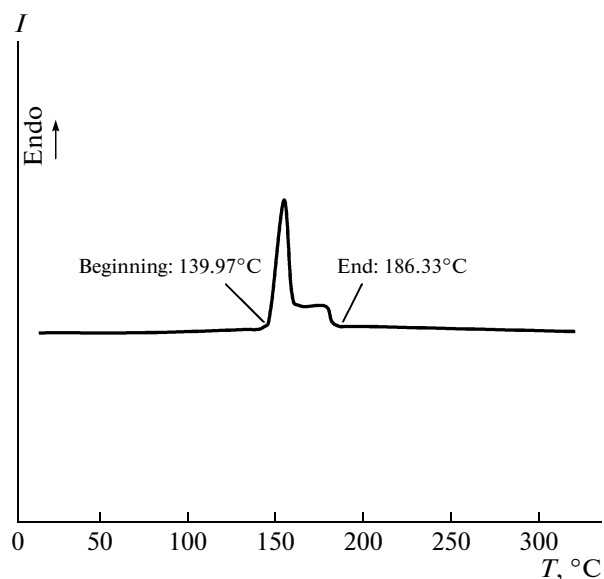


Fig. 10. Thermogram of Sn-Bi containing 57 at % Bi.

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