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DSC INVESTIGATION OF NON-LINEAR POLYETHYLENE CRYSTALLIZATION FROM THE SOLUTIONS IN ALKYLBENZENE

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Abstract

The example of polyethylene of low density (PELD) crystallization in ethylbenzene and some other alkylbenzenes presence demonstrates the unsufficiency of formal liquidus curve knowledge for the description of phase equilibrium in amorphous-crystalline polymer–liquid system. Experimental data affirming polymorphous structure of PELD crystalline phase and influence of the solvent on the order of various regular structures formation in it are being reported.

Keywords: alkylbenzene, melting curves, phase equilibrium DSC, polyethylene of low density

Introduction

The crystallization of polymers from the solutions is always accompanied by the formation of irregular (amorphous) areas [1] which are able to absorb the solvent and thus to influence on the total quantity of crystalline phase and its characteristic parameters [2]. Therefore to carry out phase analysis of amorphous-crystalline polymer–liquid systems the formal liquidus curve as well as data on polymer crystalline phase melting peculiarities at various composition of systems are to be available.

The present study illustrates this statement by polyethylene of low density (PELD) crystallization in the presence of ethylbenzene and other alkylbenzenes.

Experimental

PELD with melting index of 26.5±3.0 g·min^{-1}, density of 911.2 kg/m^3 at 298 K, branching degree of ~2.6 CH$_3$-groups for 100 carbon atoms of the main chain and specific melting heat of 69.0±2.0 J/g (calculated for one gramm of polymer) was used.

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The purity degree of alkylbenzene corresponded to ‘chemically pure’ and ‘analytically pure’ classification.

The measurements have been carried out on the differential scanning calorimeter (DSC) of DSM-2M type at heating rate of 8 deg·min^{-1}. Heat contact of the sample with the calorimetric capsule was reached by premelting of the sample and its further cooling just in this capsule. Naphthalene was used as a standard sample, the polymer weight in samples analyzed was about 5–10 mg.

Results and discussion

Two experimental sets have been carried out in the present study. In the first set melting curves for PELD – alkylbenzene systems obtained by rapid (8–16 deg·min^{-1}) cooling from 385 to 295 K of PELD melt containing different quantities of alkylbenzene were registered.

In the second set melting curves for the same systems were registered but the above systems were undertaken to heat treatment as follows: 10 days at 353 K and 10 days at 333 K, and then were rapidly cooled.

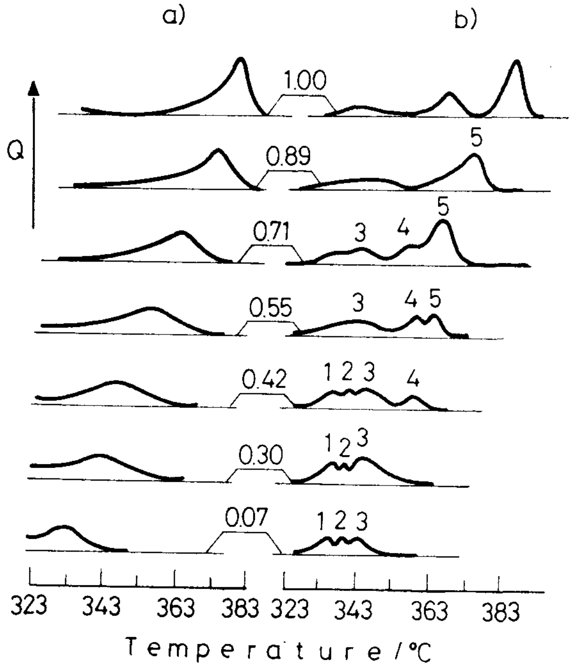

Fig. 1 Melting curve for hardened (a) and heat treated (b) systems being formed from the mixture of PELD melt and ethylbenzene. Numbers next to the curves denote the polymer content in mixture (weight fraction)

Figure 1 shows melting curve for PELD – ethylbenzene system containing from 0.07 to 1.0 weight fraction of polymer. The examination of the system with ethylbenzene replaced for *p*-butyltoluene, tertiary-butylbenzene and 1,3,5-triethylbenzene gives the same picture.

Unimodality of melting curves observed in this case is considered to be the argument for the factual uniphase character (in the sense of free liquid absence) of PELD – alkylbenzene system appeared during the rapid cooling of polymer melt containing solvent, and for ceasing of phase decomposition in the system at the start of its separation. Under this condition only the composition of coexisting phase is the same and identical to the composition of the initial mixture that is resulted in the appearance of the only melting peak.

In other words during the rapid cooling of PELD melt containing even 0.93 weight fraction of alkylbenzene crystallization of polymer in the presence of low-molecular component takes place but not phase decomposition of the system crystallizing polymer–liquid itself.

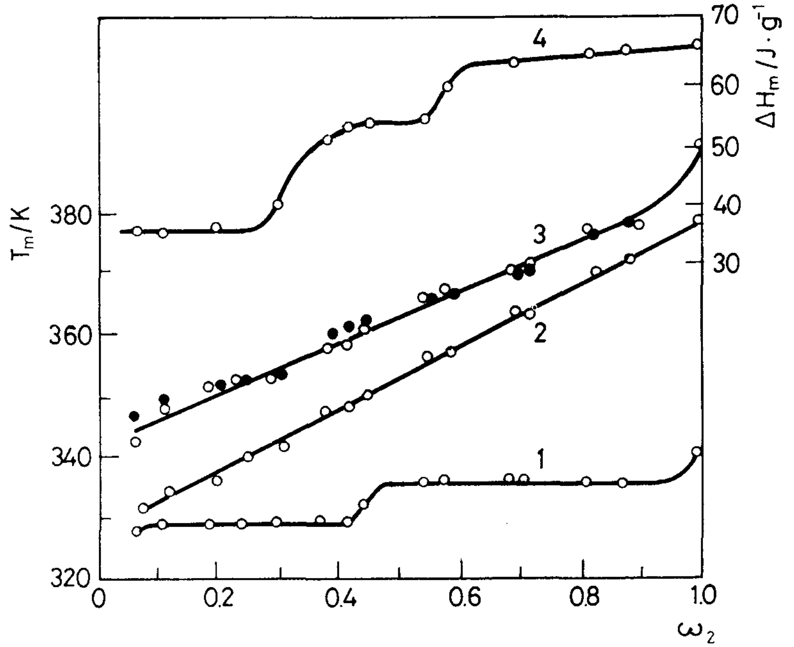

Fig. 2 Temperature of the start (1), maximum (2) and the end (3) of melting peak, and specific melting heat (4) of hardened samples as a function of PELD weight fraction in the initial mixture. Dark points on the line (3) correspond to heat treated samples

Analysis of melting curves shows (Fig. 2) that temperatures of the start, maximum and the end of melting peak are changed with the composition of system change in accordance with different laws, and the temperature interval for melting constantly increases with the increase of weight fraction of polymer (w_2).

Asymmetry of melting peak in the range within $w_2<0.3$ is caused by high temperature and in the range within $w_2>0.3$, vice versa, low temperature, shoulder.

Specific melting enthalpy of polymer crystal phase changes originally (Fig. 2) with the composition of the system change. Two critical values of w_2 at which change of ΔH_{melt} for PELD in the presence of alkylbenzene proceeds jumpwise are observed, and the one after which practically linear increase of ΔH_{melt} is noted.

Such kind of ΔH_{melt} on w_2 dependence leads to a conclusion that presumably three types of crystallites different in their resistance to stretching tensile forces appeared during swelling of polymer amorphous areas in solvent could exist.

DSC investigation of PELD undertaken to the long gradual (2 days at 373 K, 10 days at 353 K, 10 days at 333 K) heat treatment confirms our suggestion and registrates the existence of regular structures with melting point at 343, 368, 385 K in PELD (Fig. 1b).

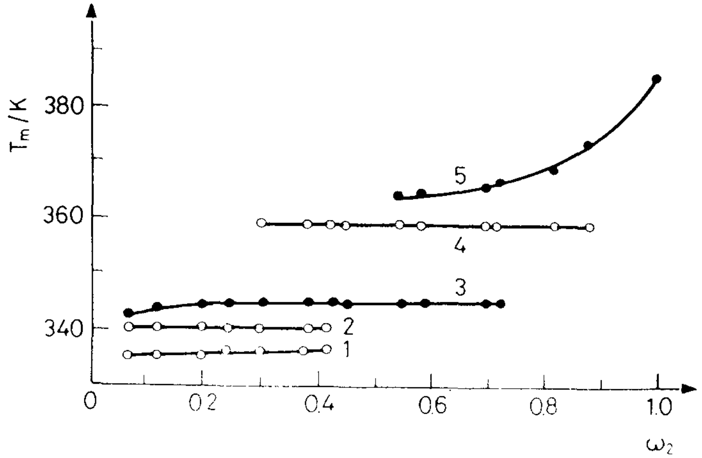

Fig. 3 Number of peaks and of their maximum temperatures on melting curves for heat treated samples as a function of PELD weight fraction in the initial mixture. Numbers next to the curves correspond to the peak items on melting curves (Fig. 1b) in the order of T_{melt} increase

Now, the results of the second experimental set will be discussed taking into account the fact of polymorphous structure of PELD crystalline phase and the suggestion of $T_{melt}(\max)=f(w_2)$ dependence (Fig. 2) being the liquidus curve in an ordinary sense of this term. In case the last suggestion provided the long heat treatment of any systems PELD – ethylbenzene examined in this study first at 353 K and then at 333 K will result in two phases formation: polymer solution in alkylbenzene with w_2>0.07 and polymer crystals with three different melting points. Rapid cooling of such system would be followed by crystallization of PELD from this solution according to mechanism described above and by appearance of polymodal melting curve with temperatures for maximum about 333, 343, 368 and 385 K. Actually the picture (Fig. 1b, Fig. 3) is essentially different.

Melting curve in the range within 0.07<w_2<0.38 has three peaks with maximum at 336, 340 and 345 K; in the range within 0.30<w_2<0.42 – four peaks at 336, 340, 345 and 359 K; in the range within 0.43<w_2<0.72 – two peaks at 345 and 359 K. At w_2<0.55 a peak with the place maximum of dependent on the composition of the initial system is observed. This peak becomes the only and strongly asymmetrical at w_2>0.9.

These results could be interpreted as follows.

Stage heat treatment of systems depleted with polymer (w_2<0.3) leads to the formation of, first, areas being actually the solution of PELD in ethylbenzene containing ~0.16 and 0.25 weight fraction of polymer and giving at rapid cooling crystallites with melting point at 336 and 340 K, and, second, of amorphous-crystalline areas formed from crystallites melting at 343–345 K. Starting with w_2=0.3 the formation of additional phase of crystallites with T_{melt}=368 K proceeds. This phase however contains irregular areas plasticized by alkylbenzene and thus they are being melted at 359 K. Finally, at w_2>0.55 phase of crystallites with T_{melt}=385 K strongly sensitive to the presence of solvent in irregular areas is formed.

It is to be emphasized that heat treatment of PELD in the presence of different quantities of alkylbenzene does not influence on the temperature of the melting peak end (Fig. 2) which in its physical sense, evidently, corresponds to the melting point of last crystal and, at fixed sample weight and constant heat supply conditions, does not depend essentially on the degree of crystallite perfection.

It is of importance that a phase identified as a solution of polymer in liquid disappears practically at w_2>0.42 and alkylbenzene placed into the system is found to be dissolved in amorphous areas of polymer crystallized.

It means formally that such system does not submit to the phase rule any more but follows the mechanism of liquid dissolving in polymer in which three-dimensional network of intermolecular bonds is formed by crystallites able to be decomposed under stretching tensile forces caused by swelling of polymer irregular areas in liquid.

In conclusion it is to be noted that alkylbenzene presence in PELD melt promotes (Fig. 1b) the formation of polymer regular structures different in their melting points when melt is enriched with low-molecular liquid and, vice versa, blocks this process when the content of low-molecular liquid is under 0.1 weight fraction, and alkylbenzene structure also influences essentially on the effectiveness of different regular structures separation in PELD. It was stated, in particular, that PELD weight fraction at which crystallites with maximum melting point being to form is being decreased in the row ethylbenzene>toluene>*p*-xylene ~ *o*-xylene>tertiary-butylbenzene>*m*-xylene>*p*-butyltoluene>triethylbenzene from 0.55 to 0.10 that reflects, evidently, in the described graduation the reduction of values for the thermodynamic affinity of examined alkylbenzenes to PELD.

Conclusion

The present investigation demonstrates actually two principal moments.

The first states that availability of $T_{\text{melt}}=f(w_2)$ curve is not sufficient for identification of phase composition forming during rapid cooling of homogeneous crystallizing polymer–liquid system since due to the specific structure of polymer this dependence may not be a liquidus curve in an ordinary sense of the term.

The second concerns the obtaining of experimental data affirming polymorphous character of non-linear polyethylene crystalline phase and solvent influence on the graduation of different regular structures formation in the above phase.

References

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Zusammenfassung — Das Beispiel der Kristallisation von Polyethylen niedriger Dichte (PELD) in Ethylbenzol und in Gegenwart einiger anderer Alkylbenzole zeigt die Unzulänglichkeit der Kenntnisse über die formale Liquiduskurve zur Beschreibung des Phasengleichgewichtes in amorphen-kristallinen Polymer – Flüssigkeitssystemen. Die experimentellen Daten bestätigen die polymorphe Struktur von PELD Kristallphasen und den Einfluß des Lösungsmittels auf die Art verschiedener regulärer Strukturbildung.