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# DSC AND X-RAY STUDY OF STRUCTURE AND PHASE TRANSITIONS OF LOW MOLECULAR COMPOUNDS INCORPORATED INTO CRAZES

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Orientation, phase composition and phase transitions of a series of long chain low molecular weight compounds (LMC), such as heneicosane, cetyl alcohol, normal fatty acids, introduced into porous structure (crazes) of polymeric matrices oriented in liquid medium have been studied by means of DSC and SAXS techniques. Different types of LMC crystallites orientation in crazes of polymeric matrices have been observed. LMC phase state in crazes is shown to be characterized by higher stability of high-temperature polymer midifications. LMC melting temperature in crazes usually decreases as well as melting enthalpy (heat) and entropy. The origin of LMC properties changes observed is high dispersity (40–100nm) of LMC particles in crazes resulting in a marked growth of polymer/LMC interface influence on principal thermodynamic parameters of the systems studied.

**Keywords:** DSC, low molecolar compounds, phase transitions, polymers, X- ray

## Introduction

The preparation and study of compositions comprising a polymeric matrix and low molecular weight compounds (LMCs) are still of vital importance to obtain novel materials with useful properties. It has been shown that the cold drawing of glassy and semicrystalline polymers in adsorptionally active media (AAM) can be considered a universal procedure of preparation of such compositions [1]. Polymer drawing in AAM is known to proceed via crazing, or the formation of a highly dispersed porous structure (pore sizes ~10 nm) of crazes. It has been found that if polymer stretching is carried out in those liquids which can be crystallized in crazes or in which the required LMCs can be dissolved [1–3], appreciable amounts of various low molecular additives (even incompatible with the polymer) can be effectively incorporated into the polymeric matrix. The properties of LMCs immobilized in a polymeric matrix are mainly controlled by their specific state in the micropores, which depends on the interaction between the

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polymer chains and the LMC molecules at the interface, as well as on the parameters of the porous structure of the crazes. The aim of the present work was to study both the LMC specific state (orientation, phase composition, phase transition) in the micropores of various polymers, and the structure of a composite system as a whole.

The structure of LMCs incorporated into polymers is known to be characterized by layers in which LMC molecules aligned parallel to each other are arranged in a definite manner with respect to the layer plane [4, 5].

In HE crystals and in the α- and β–modifications of CA in the micropores of polymeric matrices, the LMC molecules are arranged normal to the layer plane. In the crystals of *n*–carbonic acids and in the γ–modification of CA, their molecules are aligned at a certain angle to it. The end-groups of the LMC molecules ($CH_3$ in HE, $CH_3$ and OH in CA, $CH_3$ and COOH in carbonic acids) lie in the layer planes (001).

## Experimental and discussion

### *LMC orientation*

It follows from the X-ray scattering data that all the LMCs crystallize in highly ordered textures in the micropores of the polymers studied (Fig. 1). Analysis of the X-ray patterns reveals that a sequence of spot reflections located on meridian, equator or diagonal could be attributed to X-ray scattering from the oriented layer planes [5]. It is worth mentioning that such a sequence of reflections is due to different reflection orders. When the orientation of layer plane determined by the orientation of the crystallites changes, the arrangement of the corresponding reflections changes, too. The correlation between the spot reflections and the layer planes is proved by a comparison of the interplanar spacings calculated from the relevant X-ray patterns with those of the LMCs in the free state (Table 1).

Normal and parallel orientations of LMC layer planes with respect to the drawing direction are denoted as ⊥ and ||, respectively. An off-angle arrangement of *n*-carbonic acids layer planes is denoted as ^.

It follows form Table 1 that all the LMCs studied are found to be oriented in PC, PVC and PMMA matrices in such a manner that their layer planes are aligned parallel to the drawing direction (Fig. 2b, d). In HDPE, PP, PTFE,Nylon-6 and PET oriented matrices, the layer planes of HE and CA are perpendicular to this direction (Fig. 2a).

**Table 1** Orientation and phase composition of LMC in crazes of oriented polymeric matrices and in free state

| LMC | Polymeric matrix | Orientation | Interlayer spacing d·10 nm | |
|---|---|---|---|---|
| | | | in polymer* | in free state [5]** |
| HE | HDPE | ⊥ | 28.8 | |
| | PTFE | ⊥ | 28.6 | |
| | PP | ⊥ | 28.7 | |
| | PET | ⊥ | 28.8 | 28.65(A) |
| | Nylon–6 | ⊥ | 28.8 | 28.92(R) |
| | PC | ‖ | 28.5 | |
| | PVC | ‖ | 28.6 | |
| CA | HDPE | ⊥ | 45.5 | |
| | PTFE | ⊥ | 45.4 | 37.37(γ) |
| | PET | ⊥ | 45.4 | 43.83(α) |
| | Nylon–6 | ⊥ | 4.54 | 44.9 (β) |
| | PC | ‖ | 4.54 | |
| UDA | HDPE | ∧ | 26.1 | 25.68(C')<br>30.16(A') |
| | PTFE | ‖ | 25.9 | |
| | PC | ‖ | 26.1 | |
| DDA | HDPE | ∧ | 27.7 | |
| | PP | ∧, ‖ | 27.7 | 32.1 (A) |
| | PET | ∧, ‖ | 27.7 | 27.42(C) |
| | PC | ‖ | 27.7 | |
| TDA | HDPE | ∧ | 30.1 | |
| | PTFE | ∧ | 29.8 | |
| | PP | ∧, ‖ | 30.0 | |
| | PET | ∧, ‖ | 30.1 | 35.35(A') |
| | Nylon–6 | ∧ | 29.7 | 30.0 (C') |
| | PC | ‖ | 29.7 | |
| | PVC | ‖ | 29.8 | |
| | PMMA | ‖ | 29.8 | |

**Table 1** Continued

| LMC | Polymeric matrix | Orientation | Interlayer spacing d·10 nm | |
|---|---|---|---|---|
| | | | in polymer* | in free state [5]** |
| PDA | HDPE | ∧ | 35.5 | 40.2(A') |
| | PP | ∧, ∥ | 35.7 | 35.8(B') |
| | PET | ∧, ∥ | 35.6 | 34.4(C') |
| | PC | ∥ | 35.8 | |
| DDA | PC | ∥ | — | — |

* Interlayer spacings were measured with accuracy of (± 1%)

** Polymorphic modifications of LMC are denoted in brackets

In PTFE and HDPE systems containing *n*-carbonic acids, in addition to the parallel orientation one can observe an off-angle orientation of the LMC layer plane (Fig. 2c). In the case of PP and PET oriented matrices (except for the PET-UDA system), the layer planes of the *n*-carbonic acids are arranged both parallel to and at a certain angle to the drawing direction. This is proved by the diagonal and equatorial spot reflections corresponding to the similar interplanar spacings.

The LMC orientation accompanying its crystallization in narrow (~ 10 nm) asymmetric pores of oriented polymeric matrices is mainly determined by the thermodynamic stability of the ordered state relative to the random one. When the arrangement of LMC crystallites in crazes is ordered, the value of the intercrystallite surface energy is minimal. The character of the LMC orientation in a polymeric matrix is determined by the minimal value of the free energy surface component at the polymeric matrix-LMC interface, since each type of interacting crystal face depending on the orientation is characterized by its own value of the interfacial energy.

It has been shown that in polymeric matrices in which only a weak interaction exists between the polymer and the incorporated substance, the following type of orientation is realized. In this case, the basal face, whose surface energy for the free-state LMC is less than that of the lateral face, is the one interacting with the polymer fibrils (Fig. 2b, d). This type of orientation takes place in amorphous or low crystalline polymers such as PC, PMMA and PVC. When the interaction between the components studied is strong enough, the lateral face is the one which comes into contact with the polymer (Fig. 2a, c), since the work of adhesion between the polymer and the lateral face is higher relative to the basal one. This type of orientation takes place in crystalline polymers such as HDPE, PTFE,

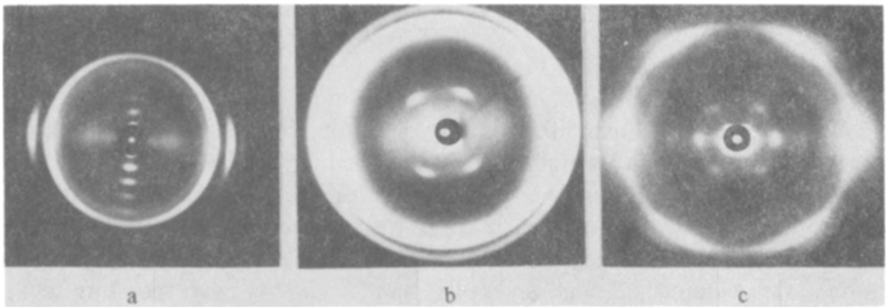

**Fig 1** WAXS patterns of the oriented systems composed of PTFE–HE(a), HDPE–TDA(b), and PET–TDA(c)

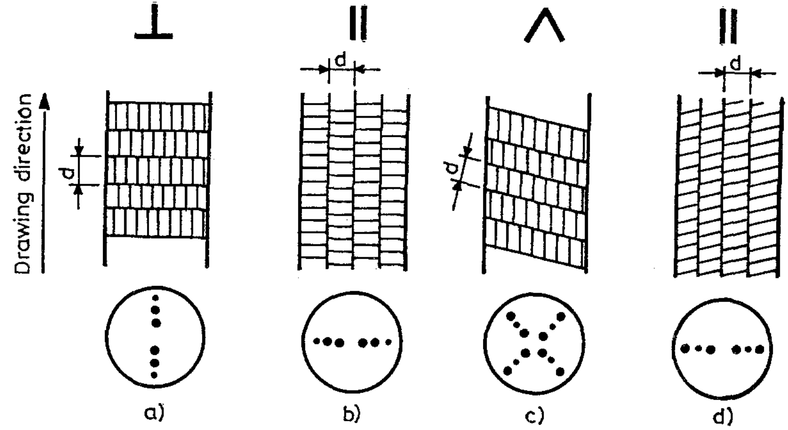

**Fig 2** Layer orientation of HE, CA(a, b) and carbonic acids (c, d) in pores of the polymeric matrix and the location of corresponding reflections on X-ray patterns

Nylon-6 and PP, and also in PET which crystallizes in the course of stretching in AAM.

In a consideration of the LMC orientation type, one should take into account the elastic stresses arising in polymers and thereby affecting the LMC orientation [5]. It has been found that this factor comes into play for the narrow pores containing *n*-carbonic acids. The crystallites are easily deformed via crystallite blocks shifting along planes (001) without any change in the interplanar spacings. Therefore, different types of LMC orientation will be realized in narrow and wide pores, as has already been observed for PET and PP/*n*-carbonic acid systems.

### *LMC phase composition*

The LMC phase composition in polymeric matrices was determined by means of DSC and X-ray analysis. DSC curves of HE in the free state and in polymer matrix crazes are presented in Fig. 3. The two peaks in the DSC curve (curve 1) are associated with the HE polymorphic transition from the R to the A-modification. In curves 2–4, one can observe only one broad low-temperature peak relating to the HE melting in the polymer. Hence, it can be concluded that in different polymeric matrices HE can exist only in the high-temperature R-modification. Similar results confirming the existence of the high-temperature LMC modification in crazes were obtained for TDA (Fig. 4) and CA [6, 7]. The narrow high-temperature symmetrical peak (curves 1' and 2', Fig. 4) corresponding to TDA melting (crystallization) in the free state can be assigned to the melting of free surface LMC.

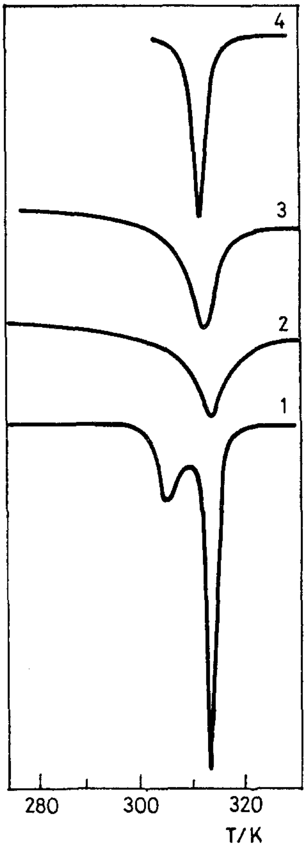

**Fig 3** DSC melting curves of HE in the free state (1) and in the polymeric matrices: HDPE(2), Nylon-6(3), PET(4)

It has been shown that TDA molecules crystallize in the C'-form in the micropores of polymeric matrices; at low concentrations, CA molecules assume the α–modification. With increase of the CA content in the polymer, its low-temperature β–modification is realised. It is know that in the free state this modification is unstable and gradually transforms into the γ–form.

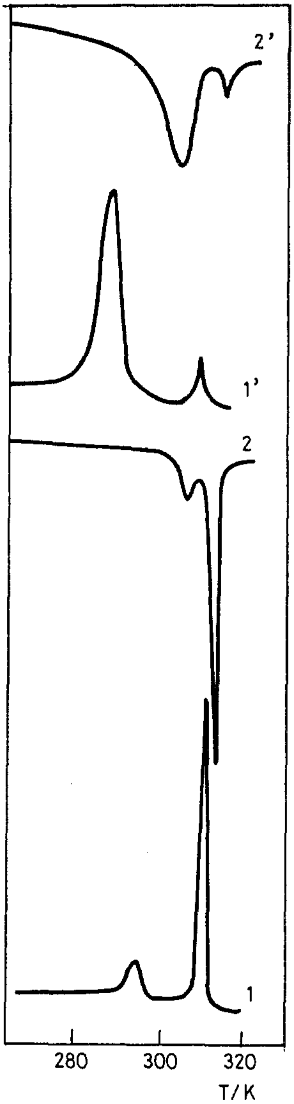

**Fig 4** DSC melting (2,2') and crystallization (1,1') curves of TDA in the free state (1,2) and in the micropores of oriented PET (1',2')

The LMC phase composition in various polymers was also analysed by means of the X-ray scattering technique. A comparison of the interlayer spacings og LMCs crystallized in the micropores with those for bulk LMC reported in the literature is presented in Table 1. It has been shown that whatever the polymeric matrix type, the interlayer spacing does not change. This means that a similar LMC phase state is observed in different polymers. Analysis of the data presented in Table 1 shows that in all the matrices studied the C'-form of TDA molecules and the β-form of CA (at high CA content) are realised. It is worth mentioning that in the free state these modifications are known to be unstable at room temperature.

The high stability of LMC modifications unstable in the free state could be explained by the high dispersity of the microporous structure. In the micropores, all the polymorphic transitions may proceed in the temperature region where the radius of the critical nucleus of the low-temperature phase is less than or equal to the pore radius. If the temperature at which the above condition holds does not fall in the region where the rate of new phase formation is high enough, no phase transition occurs and only the high-temperature polymorphic LMC modification is realized.

### *LMC phase transitions*

LMCs crystallized in the micropores of the crazed oriented matrices are found to be in a highly dispersed state. Therefore, analysis of LMC phase transitions in the systems studied should be carried out with consideration to the surface component of thermodynamic potentials (free energy, enthalpy, entropy). Let us express the LMC thermodynamic potentials as the sum of the volume and surface components. Then, taking into account the invariability of the system specific surface upon the LMC phase transitions in the polymer micropores, it is easy to derive the following equations describing both the change in the specific surface components of the thermodynamic potentials at the polymer-LMC interface and the dependence of the thermodynamic parameters of the LMC melting process in the pores on the pore size $r$:

$$\Delta T_m = T_v - T_A = \frac{2\Delta\sigma}{r}\frac{T_v V_m}{\Delta H_v} \qquad (1)$$

$$\Delta H = \Delta H_v - \frac{2\Delta h V_m}{r} \qquad (2)$$

$$\Delta S = \Delta S_v - \frac{2\Delta s V_m}{r} \qquad (3)$$

where $T_v$, $\Delta H_v$ and $\Delta S_v$ are the melting temperature, enthalpy and entropy of melting of LMC in the free state, respectively; $T_A$, $\Delta H$ and $\Delta S$ are the melting temperature, enthalpy and entropy of melting of LMC in the pores of the polymeric matrices, respectively; $\Delta\sigma$, $\Delta h$ and $\Delta s$ are the changes in the specific surface components of free energy, enthalpy and entropy at the LMC/polymer interface upon LMC melting; $V_m$ is the molar volume of LMC; and $\Delta\sigma=\sigma_1-\sigma_2$, $\Delta h=h_1-h_2$ and $\Delta s=s_1-s_2$, where subscripts 1 and 2 denote the specific surface components of the thermodynamic potentials at the interfaces between the LMC crystal and the polymer, and between the LMC melt and the polymer, respectively. Equation (1) is the Thompson–Gibbs equation modified for the systems under study. Since the values of $\Delta h$ and $\Delta s$ are positivve, the values of the enthalpy and entropy of the LMC melting in the pores should always be lower than those of the LMC in the free state.

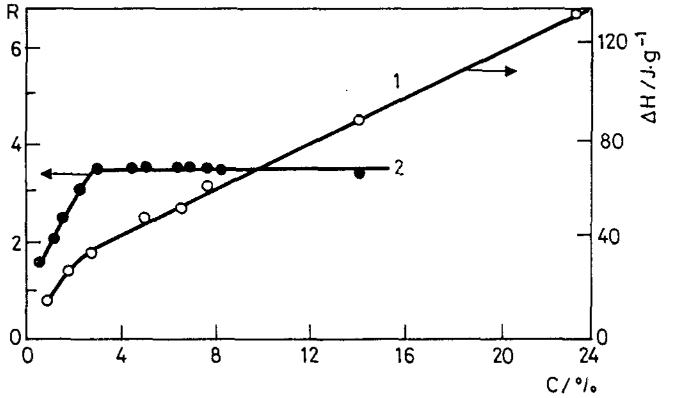

**Fig 5** Melting heat (1) and the dichroism of the absorption band 2925 cml (2) of TDA immobilized in PTFE

In Fig. 5, the melting heat $\Delta H$ of TDA is plotted against its content in a PTFE matrix [8]. It is seen that the value of $\Delta H$ corresponding to TDA in PTFE crazes is lower than that in the free state (142 J/g). Moreover, this value decreases with decrease of the TDA content. Such a decrease of $\Delta H$ upon TDA content lowering (down to ~3%) could be explained by a decrease in TDA crystallite sizes according to Eq. 2. In this case, the crystallinity will not change appreciably since the TDA molecule orientation in a polymeric matrix estimated by IR-dichroism ($R$) is constant at TDA contents >3 wt.%. When the TDA content is <3%, there is a sharp break in the plots of $\Delta H$ and $R$ *vs.* the TDA concentration in the PTFE matrix, which is ascribed to TDA particle amorphization.

It is worth mentioning that not only the LMC melting process, but also the crystallization of the LMC incorporated in the porous polymer structure, is dependent on the pore sizes of the polymeric matrix. This is convincingly proved by a DSC study of the TDA melting and crystallization in PTFE crazes (Fig. 4). LMC crystallization within polymeric micropores proceeds at temperatures at which the critical nucleus radius becomes equal to the pore radius. Therefore, the equation describing the lowering of the crystallization temperature ($\Delta T_{\mathrm{cr.}}$) of LMC in polymer micropores, derived within the framework of heterogeneous nucleation theory:

$$\Delta T_{\mathrm{cr.}} = \frac{\sigma_{\mathrm{cr/m}} + \Delta\sigma}{r}\,\frac{T_{\mathrm{v}}V_{\mathrm{m}}}{\Delta H_{\mathrm{v}}} \tag{4}$$

where $\sigma_{\mathrm{cr/m}}$ is the specific LMC free energy at the crystal-melt interface, can be used to obtain the following equation (for $r$ and $\Delta\sigma$ determination will consideration of Eq. 1):

$$r = \frac{\sigma_{\mathrm{cr/m}}}{2\Delta T_{\mathrm{cr}} - \Delta T_{\mathrm{m}}}\,\frac{2T_{\mathrm{v}}V_{\mathrm{m}}}{\Delta H_{\mathrm{v}}} \tag{5}$$

$$\Delta T\sigma = \frac{\sigma_{\mathrm{cr/m}}\,\Delta T_{\mathrm{m}}}{2\Delta T_{\mathrm{cr}} - \Delta T_{\mathrm{m}}} \tag{6}$$

On calculating $\sigma_{\mathrm{cr/m}}$ from Eqs 1–6, one can determine the mean pore radius $r$ and $\Delta\sigma$, $\Delta h$ and $\Delta s$ for the LMC melting process in polymeric matrix micropores. On the other hand, having determined the pore (crystallite) sizes by any independent method, one can calculate the values of $\Delta\sigma$, $\Delta h$, $\Delta s$ and $\Delta\sigma_{\mathrm{cr/m}}$. It has been shown that $\Delta\sigma$ lies in the range ~ –1–5 mJ/m$^2$; $\Delta h$ in the range ~20–100 mJ/m$^2$; and $\Delta s$ in the range ~ 0.05–0.3 mJ/m$^2$·deg [9, 10]. The negative value of $\Delta\sigma$ corresponds to the increase in the LMC melting temperature in the polymeric matrix relative to the free state (systems of HE, CA and HDPE). $\sigma_1$ becomes less than $\sigma_2$. This could be explained by a strong epitaxial interaction between the polymer and LMC crystallites.

**Table 2** Parameters of porous structure of oriented polymers

| System | Diameter of fibrilis / nm | Pore diameter / nm | |
|---|---|---|---|
| | | SAXS data | DSC data |
| PET–HE | 8.0 | 6.0 | 6.5 |
| PET–TDA | 10.5 | 7.0 | 5.0 |
| PC–TDA | 29.0 | 7.0 | 5.0 |
| Nylon–6–CA | 8.3 | 4.6 | 7.0 |

In order to verify the above thermodynamic approach for an analysis of the LMC phase transitions in the porous structure of polymeric matrices by means of SAXS (Porod's technique), the craze structure parameters (mean pore and fibril sizes) were determined. The results of this study are compared with the DSC data

[11] in Table 2. The good agreement between the values obtained with the different methods is observed. This provides undeniable evidence that the thermodynamic analysis of the LMC phase transitions in the crazes of polymeric matrices is valid.

## Conclusion

State of the LMC in a polymeric matrix has a number of peculiarities. The LMC crystallites are oriented in the polymer micropores. Their phase composition is found to be different from that in the free state.

The melting temperatures of LMCs in polymeric matrices are shifted (in most of the cases studied to lower temperature ). The enthalpy and entropy of the melting process are decreased. It has been demonstrated that such behaviour is due to the high dispersity of the systems studied, and also to the tremendous contribution of the surface component of the principal thermodynamic potentials (free energy, enthalpy and entropy) to the total thermodynamic potential of the system.

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**Zusammenfassung** — Mittels DSC- uns SAXS-Techniken wurden die Orientierung, Phasenzusammensetzung und Phasenumwandlungen einer Reihe von langkettigen niedermolekularen Verbindungen (LMC) wie z.B. Heneikosan, Zetylalkohol und normalen Fettsäuren untersucht, die in porösen Strukturen (Haarrissen) von in flüssigem Medium ausgerichteten polymeren Matrizen eingebracht wurden. Es konnten verschiedene LMC-Kristallit-Typen in Haarrissen von polymeren Matrizen beobachtet werden. Es wurde gezeigt, daß der LMC-Phasenzustand in Haarrissen durch eine höhere Stabilität der Hochtemperatur-Polymermodifikationen charakterisiert ist. Die LMC Schmelztemperatur in Haarrissen nimmt im allgemeinen ab, genauso wie die Schmelzenthalpie (Wärme) und die Entropie. Der Grund für die beobachteten Veränderungen der LMC-Eigenschaften liegt in der großen Dispersität (40-100 nm) der LMC-Partikel in den Haarrissen, woraus sich ein sichtbarer Anstieg der Polymer/LMC Grenzflächeneinwirkung auf die grundlegenden thermodynamischen Parameter des untersuchten Systemes ergibt.