THERMAL ANALYSIS OF SECONDARY CRYSTALLIZATION IN POLYMERS

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With a particular experimental technique of differential scanning calorimetry, the melting of the secondary crystals in polymers is observed separately from the melting of the primary crystals, and methods for the detection and quantitative analysis of the secondary crystals have been developed. By this means, a number of particular features of secondary crystals could be found which are not mentioned in the literature. Two types of crystal formation are found for linear polymers, with no regard as to kinetics, growth and other characteristics of crystallization. Secondary crystallization is interpreted as the formation of crystals of "fringed micelle" type. The equation describing secondary crystallization is deduced. It is shown that some specific features of the DTA and DSC curves of polymers are caused by the behaviour of secondary crystals in the polythermal regime.

It is known that, after completion of the crystallization in polymers, slow and long changes in the characteristics are observed in the same direction as during crystallization. This phenomenon was detected by the method of dilatometry [1, 2] and interpreted as a continuation of the crystallization. Indeed, X-ray analysis and infrared spectroscopy substantiated an increase in crystalline characteristics during this process [3, 4]. The phenomenon was called "secondary crystallization" (SC) [5, 6]. As a process of additional crystallization, SC did not arouse any particular interest. Further, in all the methods in both X-ray analysis and infrared spectroscopy, it is very difficult to differentiate between the secondary crystals and the primary crystals, and their study therefore entails great difficulties. For these reasons SC has not been greatly studied. Our review of the literary data on the nature of SC has shown that the existing concepts of SC are not supported by experimental evidence, though they seem logical. X-ray analysis and infrared spectroscopy data only serve to show that the secondary crystals have some crystalline properties. The growth or perfection of the primary crystals during SC may not occur at all. There are several publications in which the X-ray method has

not detected any changes in the crystalline phase during SC [7, 8]. Until recently, insufficient attention was paid to the fact that NMR usually assigns the secondary crystals to the amorphous phase [9].

In contrast to other methods, we have found that the secondary crystals are displayed separately from the primary crystals in a particular experimental technique of dynamic calorimetry. This gave us the opportunity to analyse them quantitatively and to study their properties. The results of our investigations did not substantiate the existing concepts of the nature of SC, which consider this process as the perfection of the primary crystals and their additional crystallization due to amorphous sections crystallizing with difficulty. The secondary crystals differ significantly from the primary crystals as concerns their properties.

While examining the melting peaks after different stages of crystallization, we found the possibility to investigate SC apart from the primary crystallization. Thermal curves obtained for polyurethane by means of DSC-2 scanning calorimetry are given in Fig. 1. The curves are superimposed; the temperature and the baseline are matched. The distinct separation of the melting peaks of the primary (A) and the secondary (B) crystals is observed. It is also obvious that the SC process is not simultaneous with the primary crystallization, but starts after the crystallization is 20–30% over, i.e. when the first crystallites have already been formed in the system. The results of our experiments showed that the formation of the secondary crystals does not influence the melting of the primary crystals. The curves reveal no changes in either the value of the thermal effect of melting, the
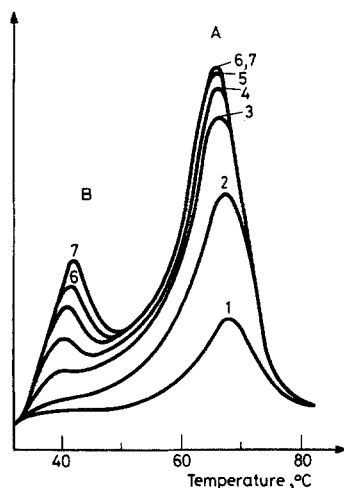

Fig. 1 Melting curves of different stages of crystallization for polyurethane synthesized from poly(ethyl sebacicatediol), poly(tetrahydrofuran urethane). Time of crystallization: 2 (1), 3 (2), 4.5 (3), 6 (4), 8 (5), 10 (6) and 14 (7) min. Temperature of crystallization: 20°. Melting peaks of primary crystals (A), and of secondary crystals (B)

temperature range of melting of the shape of the melting peak. This is illustrated in Fig. 2, where the DSC curves for the heating of poly(ethylene terephthalate) after crystallization at 160° during various periods of time are given. The thermal effect of melting of the primary crystals is not changed even during crystallization for 140 hours. If SC had been a continuation of the primary crystallization in any form additional crysallization or crystallite perfection, it would surely have influenced the melting of the crystals. In this case the most sensitive element is the shape of the melting peak, as shown earlier [10]. The experiment testifies to the fact that the secondary crystals are not included in the primary crystals.
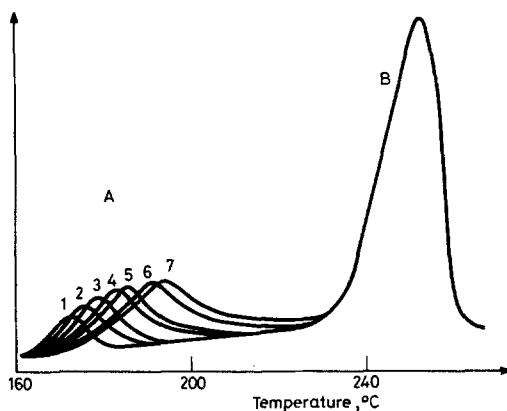

Fig. 2 Melting curves for PET from crystallization at 160° for various times: 0.08 (1), 0.18 (2), 4.5 (3), 18 (4), 24 (5), 69 (6) and 140 (7) hours. *A* and *B* are the melting peaks of the secondary and of the primary crystals, respectively

The correspondence of the peaks in the DSC curves to the melting of the secondary crystals was determined from the results of X-ray analysis. For this purpose, the experimental conditions under which the SC was recorded as the only process during X-ray analysis are completely reproduced in the DSC–2. As an example, in Fig. 4 the curves for the change in the quantity of the secondary crystals, obtained from the results of X-ray analysis [4], are compared with those determined from the DSC curves (Fig. 3). The difference between curves I and II (Fig. 4) depends in practice on the results of X-ray analysis having been calculated following the end of the primary crystallization, and the results of the calorimetry additionally show the quantity of secondary crystals formed during the primary crystallization.

The investigation of the secondary crystals showed that they have some crystalline properties. Their formation and decay are accompanied by a thermal effect, i.e. by an abrupt alteration of enthalpy (Figs 1–3, 6). We have obtained some data showing that the secondary crystals have the same perfection processes as
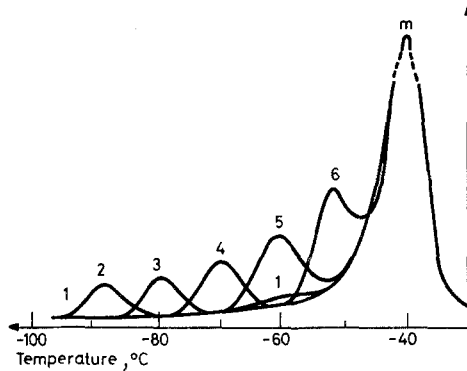
Fig. 3 DSC curves for poly(dimethylvinylsiloxane), illustrating the occurrence of endothermic effects in samples (2–6). (I)-heating curve of a sample in which practically only primary crystallization has occurred, m = melting peak. Time of crystallization: 1 min (1), 1 hour (2–6). Temperature of crystallization: -70 (1), -100 (2), -90 (3), -80 (4), -70 (5) and $-60°$ (6)
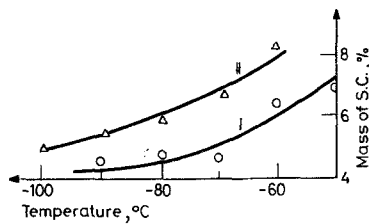

Fig. 4 Masses of secondary crystals obtained from X-ray analysis [4] (I) and from endothermic effects (2–6, Fig. 3) (II)

those of polymeric crystals, i.e. recrystallization (melting and new crystallization during heating) and reorganization (solid-phase perfection). Recrystallization is detected from an increase in the thermal effect of melting of the secondary crystals on increase of the heating rate. This is shown in Fig. 5 for a number of polymers. Such a dependence can only be explained by recrystallization. In this case the thermal effect of melting is superimposed on the thermal effect of crystallization. The latter process is slower, and therefore the value of the endothermic effect becomes larger on increase of the heating rate. Reorganization becomes apparent from the increase in the melting temperature (T_m) of the secondary crystals during annealing (Fig. 2). Nevertheless, the given crystalline properties of the secondary crystals differ from those of the primary crystals. Their melting temperature is not equal to T_m for the primary crystals. Our measurements showed that the crystallization of the secondary crystals is 2–3 orders slower and their reorganization is 3–4 orders faster than that of the primary crystals. The secondary crystals have a number of properties which differ greatly from those of the primary
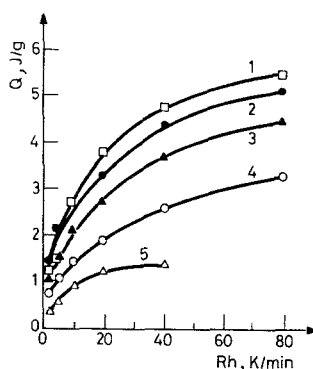
Fig. 5 Influence of heating rate on the thermal effects of melting of secondary crystals for various polymers: 4.6-polyurethane (1), stereospecific polybutadiene (2), poly(ethylene terephthalate (3), polyethylene (4), polypropylene (5). Time of annealing: 15 min (1, 3, 4, 5) or 30 min (2). Temperature of annealing: 97 (1), −55 (2), 187 (3), 47 (4) and 87° (5)

crystals. For example, their T_m increases with increasing melting rate, whereas in the primary crystals T_m decreases under similar conditions. Thus, in PET on increase of the heating rate from 2.5 to 80 deg/min^{-1}, T_m of the primary crystals is lower by about 20°, while the T_m of the secondary crystals is higher by about 3°. The secondary crystals prevent the primary crystals from recrystallizing [11], and this proves that they do not form part of the primary crystals. SC appears only in the presence of the formed crystallites (Fig. 1). SC is known not to comply with the kinetic equation of Kolmogorov–Avrami [12, 13]. We have obtained data which show that the rate constant of SC increases monotonously with increasing temperature, and it passes through a maximum during the primary crystallization. The primary crystallization includes a certain period of induction, and the maximum rate of SC is observed at the initial point. The decreases in the enthalpy and in the entropy of SC are on the average 20–30% less than those for primary crystallization (Table 1).

The experimental data testify to the fact that the secondary crystals have some properties similar to those of amorphous bodies: their structure is mobile and sensitive to different effects. For example, an increase in the temperature gradient of PET from 20 to 80 deg/min accelerates the reorganization of the secondary crystals by a factor of 3.5. Hence, they are subject to the influence of even the temperature gradient. Thus, the secondary crystals exhibit a certain dualism in their properties. However, this fact cannot be related to the defectness of the secondary crystals. Some defects are always present in crystals, but they do not change the quality of the properties of the crystals. The difference between defective and secondary crystals is revealed in the fact that the same effect upon them produces opposite results. For example, during annealing all the defects decrease, but the quantity of the

Table 1 Parameters of secondary crystallization; calculated and experimental masses of secondary crystals for experimental conditions given in Fig. 6 ($T_m = 230\ °C$, $\tau = 10$ min, $K_1 = 0.02895$ K^{-1}, $K_2 = 1.870$, $K_3 = 0.8696$, min, $m_c = 1 - m_a$, $m_1 = 0.118$ g)

ΔT, K	Q_s, J·g^{-1}	ΔH, J·g^{-1}	m_a, g	m_s, g		
				exp.	calc.	differ. %
80	4.45	64.9	0.46	0.087	0.086	1
70	5.11	67.0	0.46	0.096	0.093	3
60	5.43	70.7	0.47	0.099	0.096	3
50	5.79	72.0	0.48	0.102	0.107	5
40	6.53	78.2	0.49	0.109	0.112	3
30	7.67	82.7	0.52	0.120	0.127	6
20	9.80	89.2	0.55	0.142	0.143	1
10	12.9	95.6	0.56	0.172	0.163	5
0	17.1	101.4	0.60	0.204	0.203	1

secondary crystals increases. The dualism detected in the properties of the secondary crystals is to be referred to the particular features of their structure formation. Kargin and Slonymsky [14] pointed to dualism in the properties as a characteristic of polymers. In the secondary crystals this feature is quite evident.

The properties of the secondary crystals mentioned above give a reliable criterion for defining their presence under any conditions. Using this fact, we have found that the endothermic effects occurring during heating of the polymer at the annealing temperature are also caused by melting of the secondary crystals. Figure 6 shows the formation of the secondary crystals during the annealing of crystalline PET for equal periods of time at different temperatures. Each curve contains a melting peak of the primary crystals [10], and one melting peak of the secondary crystals [1–9]. In Fig. 6 it is shown that in polymers the secondary crystals can be formed in large quantities. It appears that small endothermic peaks sometimes displayed in the DSC curves during the initial heating, or when the conditions of heating are changed, also result from melting of the secondary crystals. Until recently, their origin remained obscure. They were usually regarded as an instrumental error or due to primary crystallization [15]. Figure 7 gives curves for PET with different occurrences of SC. These were obtained by secondary heating after the corresponding stoppage, a change in the cooling conditions, annealing, and so on.

The structure formation of the primary crystals in polymers with flexible chains is well studied [5, 6]. Electronic microscopy data and X-ray analysis data testify directly to the existence of lamellar crystallites consisting of folded macromolecules. It has been assumed till now that the perfection and the additional crystallization of these lamellar crystallites is the essence of the process of SC. However, the results presented in this paper show that the other crystal formation
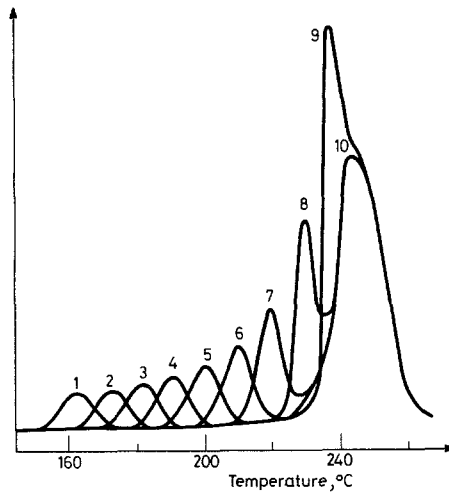
Fig. 6 Heating curves for crystalline PET from annealing for 10 min at temperatures: 150 (1), 160 (2), 170 (3), 180 (4), 190 (5), 200 (6), 210 (7), 220 (8) and 230° (9). Melting peaks of secondary crystals (1–9), and of primary crystals (10). Temperature of crystallization: 150°. Heating rate: 40 deg/min^{-1}
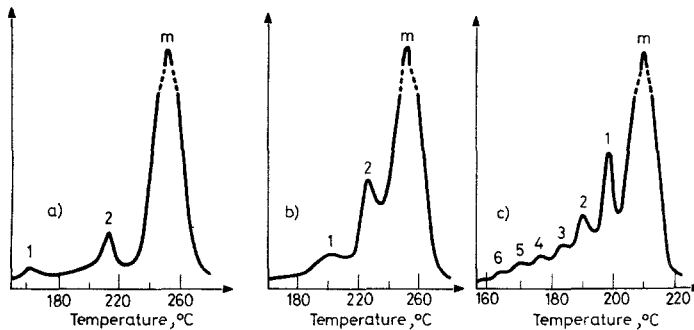

Fig. 7 Melting peaks of secondary crystals formed: at beginning of heating (A–1), at temperature of stopping of heating (A–2), during change in cooling (B–1), during crystallization (B–2), during annealing at: 220°, for 1 min (C–1); 200° for 6 min (C–2); 185° for 10 min (C–3); 170° for 10 min (C–4); 155° for 15 min (C–5); and 140° for 15 min (C–6)

occurs during the SC because the overall properties of the secondary crystals differ significantly from those of the primary crystals, i.e. from the lamellar formations including the folded molecules. Hence, two type of crystal formation exist in the crystalline polymer at the same time.

Compared with the formation of crystals occurring in the adjacent molecules, the growth of crystallites and nucleation especially, which is manifested as self-folded molecules, is thermodynamically advantageous [5]. However, this process is based

on a certain degree of freedom and mobility of the molecules. According to this requirement, the initial stage of the crystallization is most favourable for the formation of the folded molecules. After the formation of some quantity of crystallites of the folded chains, the amorphous parts communication chains, ends of loops, etc. remaining between them do not have the conditions for their folding. However, some of them preserve a potential ability for crystallization. The only way they can do this is through aggregation with the adjacent molecules. Such a model of crystallization, when small crystallites interchanging with the amorphous parts are formed, has been well studied theoretically [5] and is called the "fringed micelle" model. Thus, in our interpretation, the difference observed in the above experiments in the properties of the primary and the secondary crystals is explained by the formation of the fringed micelles occurring during the SC. The crystallization of the fringed micelles is inhibited due to the difficulties in nucleation. During the SC, such an obstacle is practically absent because the uneven surface of the lamellar crystallites comprises a nucleus itself and accelerates nucleation.

Using the criteria obtained from this work, we have found two types of formation of crystals in all the typical linear crystallizing polymers, no matter what degree of crystallinity and what kinetic factors of crystallization they have. The literature supposition [5] of the possibility of formation of fringed micelle crystallites during crystallization from the glass state at the temperature of the glass transition is not substantiated. It follows that, though the earlier notion of the fringed micelles was a single model of the crystallization of polymers, experimental data on the properties of such crystals had not been obtained. The data presented in this paper probably provide the first experimental information about them.

We should point out that detection of the coexistence of two formations of crystals necessitates certain changes in the-model of non-deformed crystalline polymers which has been adopted so far. Further, a simple explanation is given to some phenomena, the interpretation of which has been difficult (for example, to continuously increasing thickness of folds in the lamellar crystals at increasing temperature). Compared with the crystals of the folded chains, the fringed micelles can be formed at a lower degree of regularity of the structure. On this basis it is possible to suppose that they can be formed under conditions where folded crystals cannot form, e.g. at temperatures higher than the T_m of the folded crystals. Indeed, we have managed to crystallize a number of polymers (polybutadiene, polychloroprene, rubber) using crystalline powder of Al_2O_3 or SiO_2 at temperatures 20–30° higher than the T_m of the crystals of the folded chains. The properties of the crystals obtained have turned to be analogous with those of the secondary crystals described in this work.

From an analysis of this interpretation, it is possible to obtain the following equation describing SC in the temperature range between glass transition and melting:

$$m_s = \frac{m_1}{1 + K_1 \Delta T} \cdot \frac{K_2 \tau}{K_3 + \tau} \cdot \frac{\Delta H_m}{\Delta H} \cdot \frac{m_a}{m_{am}} \cdot \frac{m_c^{0.5}}{m_{em}^{0.5}} ;$$

where K_1, K_2, K_3 are constants depending upon the sample under investigation (they are determined experimentally); m_s, m_1 are the masses of the secondary crystals under given conditions and per unit of time at the temperature of the beginning of melting (T_m^b) respectively; τ is time; $\Delta T = T_m^b - T$; ΔH is the enthalpy of crystallization; m_a, m_c are the initial masses of the amorphous and of the crystalline phases respectively; index "m" points to the value of the parameter at T_m^b.

Table 1 present the values from the right-hand part of the formula and the masses of the secondary crystals calculated from these values for the conditions of the experiment, the DSC curves of which are shown in Fig. 6. The data obtained have been compared with the experimental values of m_s determined from the heating effect of melting Q_s), and from the enthalpies of formation of the secondary crystals (ΔH_s) according to the formula: $Q_s \cdot \Delta H_s^{-1} = m_s$ [16]. The difference between the experimental and the calculated results does not exceed the error in the measurements of the parameters given.

The properties of secondary crystals and the pecularities of their behaviour found in this work are of interest not only theoretically, but also practically, especially in the technology of polymers, in biology and in medicine.

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Zusammenfassung — Es wird gezeigt, daß durch DSC bei einer besonderen experimentellen Technik zwischen dem Schmelzen von primären und sekundären Kristallen in Polymeren unterschieden werden kann. Methoden zur Detektierung und quantitativen Analyse sekundärer Kristalle wurden entwickelt. Mit diesen Methoden wurde eine Anzahl von in der Literatur noch nicht beschriebenen Besonderheiten der sekundären Kristalle festgestellt. In linearen Polymeren wurden zwei Typen der Kristallbildung festgestellt, die sich nicht auf die Kinetik, das Wachstum und andere Charakteristika der Kristallisation beziehen. Die sekundäre Kristallisation wird als die Bildung von Kristallen des „fransigen Mizell-typs" interpretiert. Die die sekundäre Kristallisation beschreibende Gleichung wird abgeleitet. Es wird gezeigt, daß einige spezifische Züge der DTA- und DSC-Kurven von Polymeren durch das Verhalten von sekundären Kristallen verursacht werden.

Резюме — Показано, что в методе сканирующей калориметрии при определенной методике эксперимента плавление вторичных кристаллов проявляется отдельно от плавления первичных кристаллов. На этой основе разработали способы обнаружения и количественного анализа вторичных кристаллов. Применение их позволило выявить ряд особенностей вторичных кристаллов, не отмеченных в литературе. Два типа кристаллических образований обнаруживаются в линейных полимерах независимо от кинетических, валовых и других характеристик кристаллизации. Вторичная кристаллизация интерпретирована как образование кристаллов типа бахромчатых мицелл. Выведено уравнение, описывающее вторичную кристаллизацию. Показано, что ряд особенностей термограмм ДТА и ДСК полимеров обусловлены поведением вторичных кристаллов в политермическом режиме.