

PRIMARY AND SECONDARY CRYSTALLIZATION OF POLY(ETHYLENE ADIPATE)

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Abstract

Secondary crystallization of PEA, occurring during DSC scan and performed after isothermal primary crystallization has been investigated. The high temperature exotherm peak has been attributed to the crystallization of amorphous fraction included between crystallites formed at the primary crystallization. The temperature position of the highest rate of the secondary crystallization depended on the temperature of the isothermal primary crystallization.

Keywords: crystallization, DSC, poly(ethylene adipate)

Introduction

Temperature scanning in a DSC experiment allows to observe these crystallization processes, which at this conditions occurs fast enough. It is known, that nucleation and growth of crystallites during primary and secondary crystallization processes and also during polymorph transitions take place in the whole temperature region between the glass temperature T_g and the melting temperature T_i [1-4].

In a DSC trace of heated from the amorphous state poly(ethylene adipate) (PEA) two exothermic peaks are present. In the literature the high temperature exothermic peak is explained in different ways.

This work has been focused on finding factors influencing the high temperature crystallization peak and on reinterpreting its occurrence.

Experimental

Material

Poly(ethylene adipate) of M_n 2000 was supplied by Chemical Works 'Zachem', Bydgoszcz.

Measurements

In order to eliminate the influence of the mass of the sample, almost all experiments were performed for the same sample (7.400 mg). The polyester was preliminary dried in vacuum at 105°C for ca. 4 h. Before every crystallization the sample was held at 100°C for 5 min to ensure complete melting and afterwards cooled at the maximal cooling rate (200 deg·min⁻¹) to 8°C. At this temperature the sample was allowed to crystallize for 1, 2, 3, 4, 5, 10, 20 and 45 minutes and also for 2, 3 or 17 h. After the crystallization the sample was cooled at the maximal cooling rate to -70°C and then the DSC curves were registered at the heating rate 10 deg·min⁻¹. One of measurements was made for a quenched amorphous sample, which was not crystallized at 8°C.

For the samples previously crystallized at 8°C the low temperature peak decreases with longer crystallization time and its temperature slightly increases. Similarly decreases the second exothermic peak, which also slightly shifts to higher temperatures. In the same time appears a next high temperature exotherm peak, which increases with the crystallization time at 8°C and like the other peaks slightly shifts to higher temperatures.

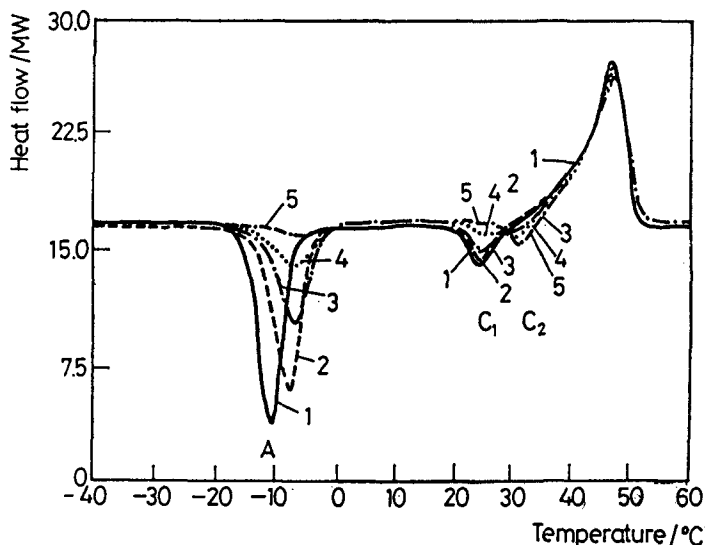


Fig. 1 Crystallization and melting behavior of PEA previously crystallized for different time

Results

For the sample heated from the glassy state two exotherm transition at -11°C and at 26°C and one endotherm transition at 47°C were found.

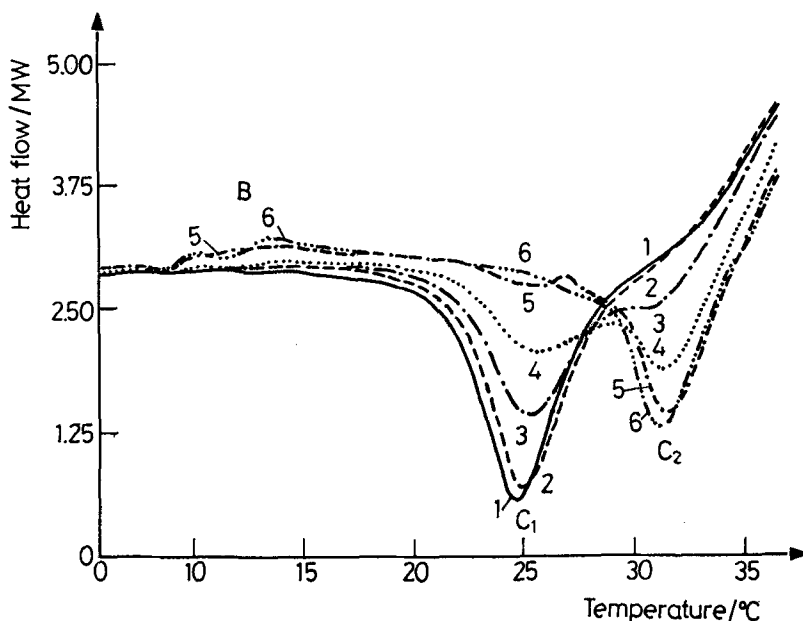


Fig. 2 Secondary crystallization of PEA previously crystallized for different time

After 5 min of crystallization at 8°C the first and the second exotherm peaks disappear and only the third exotherm peak remains (Figs 1 and 2). The endotherm peak at 47°C almost does not change. After longer crystallization at 8°C an additional endotherm peak appears, which with increasing crystallization time also increases and shifts to higher temperatures (from 10 to 14°C). The greatest changes of this peak occur for the crystallization times at 8°C from 5 to 45 min. For longer crystallization times (the longest crystallization time was 17 h) the changes are no more visible.

Discussion

The low temperature peak (A, Fig. 1), so called cold crystallization peak, is interpreted as connected with the primary crystallization. The second exotherm peak corresponds to the secondary crystallization (C_1 , Fig. 1). This transition might be a result of recrystallization of the material which already crystallized during primary crystallization [1].

The two high temperature exotherm peaks (Figs 1 and 2, C_1 and C_2) are connected with the presence in the crystallized sample of two crystalline fractions, one formed during the isothermal primary crystallization at 8°C and the other during the programmed heating after that (cold crystallization peak present in

these samples gives evidence for this explanation). If it is assumed that the high temperature peaks are an indication for recrystallization, than basing on the observed peaks, it may be presumed, that changes of the temperature of the primary crystallization causes changes in the polymorph transition of these crystallites. This assumption seems to be less probable, also because the temperature of the polymorph transition of the investigated polyester is higher than 36°C.

The high temperature exotherm peak may be also attributed to the secondary crystallization of the amorph fraction of the polymer, which was included in spaces between crystallites, formed at the primary crystallization [2]. The author of the cited work [2] claimed, that temperature increase is necessary for the secondary crystallization. It is known, that the secondary crystallization occurs also at the temperature of the primary crystallization, but considerably slower [5]. An evidence for this type of crystallization may be the exothermic peak (Fig. 2 B), which is visible for the investigated sample after 4 min of crystallization at 8°C, when the primary crystallization is almost completed.

This peak increases and shifts to higher temperatures at longer crystallization times at 8°C (from 10 to 14°C, Fig. 2, curves 5 and 6). After 45 min of crystallization no more changes are visible.

The secondary crystallization at temperatures from -11 to -6°C and at 8°C occurs slowly, to be indicated during a DSC scan. The rate of this crystallization increases with the temperature increase and at the region of the second exotherm peak (C_1 at ca 25°C, C_2 at ca 30°C) may be registered.

Conclusion

In the DSC thermogram of a quenched amorphous PEA sample 3 peaks are present:

1. An exotherm peak of the primary crystallization (-11°C).
2. An exotherm peak of the secondary crystallization (23°C).
3. An endotherm melting peak (47°C).

The high temperature exotherm peak of the secondary crystallization has been attributed to the crystallization of the amorphous fraction, included in spaces between crystallites formed at the primary crystallization.

The temperature position of the highest rate of the secondary crystallization depends on the temperature of the primary crystallization, e.g. secondary crystallization at 25 or 30°C follows primary crystallization -11 or 8°C, respectively.

References

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Zusammenfassung — Es wurde die Sekundärkristallisation von PEA während eines DSC-Scans und nach einer isothermen Primärkristallisation untersucht. Der exotherme Hochtemperaturpeak wurde der Kristallisation der amorphen Fraktion zugeschrieben, die zwischen den bei der Primärkristallisation gebildeten Kristalliten eingeschlossen wird. Die Temperaturlage der höchsten Geschwindigkeit der Sekundärkristallisation hing von der Temperatur der isothermen Primärkristallisation ab.