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KINETICS OF NON-ISOTHERMAL CRYSTALLIZATION OF OLIGOETHYLENETEREPHTHALATE-OLIGOOXYETHYLENE BLOCK COPOLYMERS

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ABSTRACT

Differential Scanning Calorimetry (DSC) data on non-isothermal crystallization of oligoethyleneterephthalate(OETPH) and the oligooxyethylene (OOE) phase in OETPH-OOE block copolymer from a melt at different cooling rates were treated in terms of the Ozawa equation.

It was established that the crystallization of OETPH and OOE blocks follows the Ozawa equation.

The crystallization of OETPH and OOE blocks is more difficult than the crystallization of polyethyleneterephthalate(PETPH) and polyoxyethylene (POE) homopolymers. This is especially the case for the OOE blocks which crystallize on cooling in the presence of a solid crystalline-amorphous phase.

INTRODUCTION

OETPH-OOE block copolymer consist of two types incompatible crystallizable blocks which differ considerably in their melting temperatures, crystallization temperatures and glass transition temperatures, respectively. It is normal to expect that the presence of the one block influences the crystallization kinetics of the other, which is the subject investigated in the present publication.

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EXPERIMENTAL

OETPH-OOE block copolymer investigated is produced from dimethylterephthalate and a mixture of ethylene glycol and oligoethylene oxide as initial compounds in the ratio of 1:2. Oligoethylene oxide with a mean molecular weight M_n= 4000 was added in the initial stage of preesterification of dimethylterephthalate. Polycondensation had been carried out at a temperature from 250 up to 275°C. The content of OOE blocks in the OETPH-OOE block copolymer was 50 weight %. Fibres with a diameter of about 1,5 mm were extruded from it at a temperature of 285°C, then they were cooled down to an ambient temperature by air, having a temperature of 25°C.

The kinetics of non-isothermal crystallization of OETPH and OOE phases in the block copolymer have been investigated by a differential scanning calorimeter (DSC-111), supplied by Setaram, France, using the Ozawa methods /1/.

The samples of the OETPH-OOE block copolymer were heated at a rate of 10°/min up to 310°C under argon and annealed in a molten state for 3 min. After that they were cooled down to a temperature of -50°C at varying constant rates in the range from 1,5°C/min to 10°C/min.

The degree of conversion and the crystallinity (α_c(T)), respectively of OETPH and OOE blocks for each temperature in the range of crystallization are determined from the crystallization calorimetric curves by graphical integration.

The experimental data of the temperature dependence of crystallinity of OOE and OETPH phases have been processed by the logarithmic Ozawa equation with its graphical solution:

$$\log /-\ln (1-\alpha_c(T)) / = \log X_c(T)-n.\log V$$

where X_c is the crystallization function on cooling, dependent on the temperature and independent on the rate of cooling V, T is the temperature, and n is the exponential Ozawa coefficient, which varies from 1 to 4, depending on the nucleation mechanism and the number of directions in which the nuclei grow.

The linear mode of the graphical dependences in the Ozawa coordinates $\log (-\ln (1-\alpha_c))/\log V$ at constant temperature proves the adequacy of the Ozawa equation for the kinetics of non-isothermal crystallization.

The kinetics of non-isothermal crystallization of PETPH and POE-4000 homopolymers have been investigated for comparison.

RESULTS AND DISCUSSION

The dependence of crystallinity (α_c) of OETPH and OOE phases in the block copolymer on the cooling rate at constant temperatures in the Ozawa coordinates are shown in Figs. 1 a and b. It can be seen that these correlations are straight lines, from which it is clear that the Ozawa kinetic equation can be applied for non-isothermal crystallization of OETPH and OOE blocks on cooling with a constant rate.

It has been established that the equation is also applicable for the non-isothermal crystallization of PETPH and POE homopolymers (Figs. 1 c and d).

The Ozawa coefficients n and the cooling functions X_c can be found from the slope and the intercept of the ordinate. They are given in Tables 1-4. Generally, the values of n and X_c decrease with the increase of the crystallization temperature.

The Ozawa coefficients n of OETPH and OOE blocks have lower values compared with the coefficients n of POE and PETPH homopolymers. At high(initial) crystallization temperatures the values of n for the homopolymers are about 2 and 3, respectively, which corresponds to two- and three-dimensional growth of the nuclei of POE and PETPH during the heterogeneous nucleation.

In the block copolymer the mean Ozawa coefficient n of OETPH blocks is 1,2 and it is n=0,45 for the OOE blocks. The conclusion is that during heterogeneous nucleation the crystal nuclei of the OETPH phase in the block copolymer grow uniaxially on cooling. The increase of the crystal nuclei of OOE blocks, determined from the values of the coefficient n, is considerably influenced by the OETPH blocks, when they are in a solid, crystalline-amorphous state at the crystallization temperature of the OOE blocks.

The values of the crystallization cooling function X_c of OETPH and OOE blocks are generally lower compared to X_c of the respective homopolymers, i.e. the crystallization of OETPH and OOE blocks in the copolymer take place at a slower rate in comparison with the crystallization of the homopolymers.

An exception is observed at the initial crystallization temperatures (18 and 17°C) of OOE blocks, where X_c is greater compared to X_c of POE homopolymers. This can be explained by the influence of the crystalline OETPH phase, which acts as an active nucleator for the crystallization of OOE blocks at these temperatures.

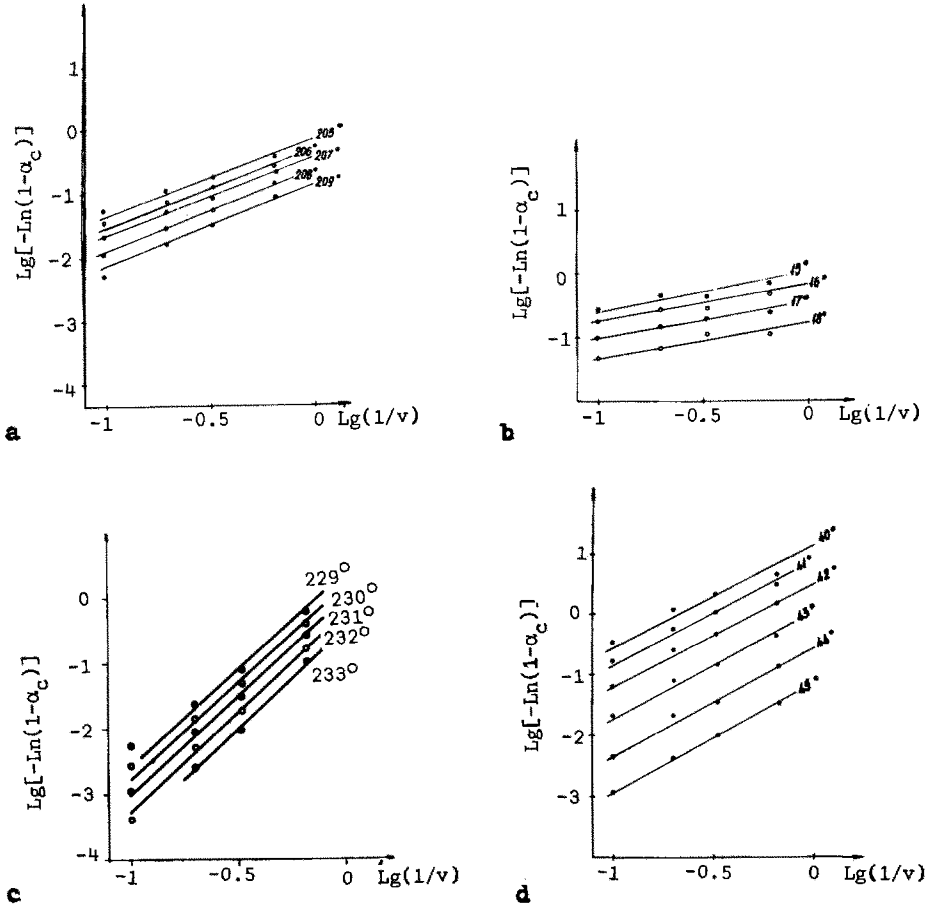

Fig. 1. Test of the Osawa equation for OETPH (a), OOE (b) blocks in OETPH-OOE block copolymer, PETPH (c) and POE-4000 (d) homopolymers.

TABLES 1-4

Ozawa coefficients n and crystallization cooling functions X_c of OETPH (Table 1) and OOE (Table 2) blocks in OETPH-OOE copolymer, PETPH (Table 3) and POE (Table 4) homopolymers as a function of temperature.

TABLE 1

T°C	n	lg X_c
209	1,6	-0,71
208	1,4	-0,59
207	1,2	-0,48
206	1,04	-0,39
205	0,95	-0,3

TABLE 2

T°C	n	lg X_c
18	0,43	-0,87
17	0,43	-0,51
16	0,48	-0,27
15	0,47	-0,07

TABLE 3

T°C	n	lg X_c
233	3,11	-0,47
232	3,11	-0,22
231	2,82	-0,11
230	2,57	-0,003
229	2,45	0,13
228	2,33	0,24

TABLE 4

T°C	n	lg X_c
45	1,8	-1,13
44	1,7	-0,58
43	1,6	-0,06
42	1,63	0,47
41	1,51	0,76
40	1,35	0,93

TABLE 5

Crystallinity (α_c) of OETPH and OOE phases in the block copolymer and of PETPH and POE homopolymers in accordance with the cooling rate.

Cooling rate, °C/min	α_c,%			
	Block copolymer		Homopolymers	
	OETPH blocks	OOE blocks	PETPH	POE-4000
1,5	19	25	44	73
3	24	25	40	73
5	26	24	41	82
10	20	25	39	73

It has been also established, that crystallinities α_c of the OETPH and OOE phases in the block copolymer, which are calorimetrically determined, are lower than α_c of the respective homopolymers and do not depend measurably on the cooling rate in the range investigated from 1,5 to 10°C/min.(Table 5)

CONCLUSIONS

It has been found from the results obtained by calorimetric investigations that the crystallization of OETPH and OOE blocks is more difficult than the crystallization of PETPH and POE homopolymers at the same cooling rate. This is especially the case for OOE blocks, which crystallize at a lower temperature in the presence of solid, crystalline-amorphous OETPH phases.

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REFERENCES

1 T. Ozawa, Polymer, 12 (1971) 150.