

● Short Communication

CRYSTALLIZATION OF POLY(ETHYLENE OXIDE) CONFINED IN PORES OF ACTIVE CARBON

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The kinetics of isothermal crystallization of poly(ethylene oxide) confined in pores of active carbon was studied by nuclear magnetic resonance relaxation. At equal temperatures the induction period of crystallization in pores differs from that in the bulk polymer. A model was developed that allows estimation of the effect of porous media on the statistical sum of the macromolecule considering the change of the polymer chain conformation in the melt. This model describes the following observed effects: invariability of the induction period temperature dependence in pores, the weak temperature dependence of the ratio of induction period for e bulk, and pore material. The change in the induction period in cylindrical pores was predicted with satisfactory precision.
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INTRODUCTION

There is fundamental interest in the effect of the finite size constraints on physical properties of polymers confined in porous media, including crystallization. Basic principles of bulk polymer crystallization were described by Wunderlich.¹ Recently we studied the kinetics of the isothermal crystallization of poly(ethylene oxide) (PEO) in pores of active carbon.² It was found that isotherms of this process are similar in many ways to the majority of the polymer systems. For example, the S-type shape of the crystallization isotherms was observed, and the degree of the crystallinity attained as a result of the crystallization was less than 100%. At the same time for PEO confined in pores we found peculiarities that are not typical for PEO crystallization in the bulk. The degree of crystallinity attained decreased when the crystallization temperature (T_c) was increased. At the same time, the T_c induction period was longer, and the rate of the process was smaller for the polymer confined in pores. The isotherms of crystallization in Avrami plots was characterized by $n \sim 1$, compared to isotherms of the bulk crystallization described by $n \sim 2$. In this work we

analyze the nature of the induction period change for polymers confined in pores.

The studied samples were PEO with $M = 40000$, $M_w/M_n \sim 1.1$ (Fluka-Buchs), and active carbon (ASG-100) with cylindrical pores. The mean pore diameter was estimated as $\sim 480 \text{ \AA}$ from mercury porosimetry. Crystallization was studied directly in a nuclear magnetic resonance relaxometer probehead. The time of temperature equilibration in the sample was less than 1 min. The measured parameter was the dynamic degree of crystallinity, which was determined from the size of the transverse relaxation decay component with relaxation time $\sim 10 \text{ \mu s}$, typical for the crystal phase of PEO. The induction period was determined as the time from the beginning of the process up to the moment when the first evidence of the crystallinity appears.

THEORY

Let ΔG_i be the free energy of a critical size nucleus formation. $\Delta G_i = \Delta H_i - T_c \Delta S_i$, where ΔH_i is the enthalpy of fusion, and $T_c \Delta S_i$ is the entropic term. Let us assume that the induction period, τ_i , is:

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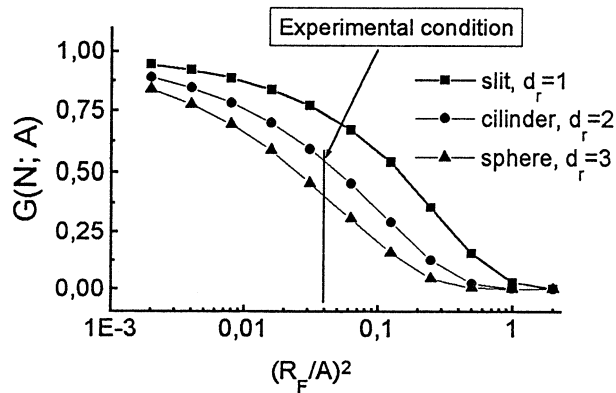


Fig. 1. The calculated dependencies $G(n; A) = \tau_{iv}/\tau_{ip}$ on $(R_F/A)^2$. In our system $d_r = 2$ (cylindrical pores), $R_F \sim 90 \text{ \AA}$, $A \sim 480 \text{ \AA}$, $(R_F/A)^2 \sim 0.035$, $G(n; A) \sim 0.55$.

$$\frac{1}{\tau_i} = C \times \exp \left\{ -\frac{\Delta G_i}{kT_c} \right\}. \quad (1)$$

The difference between the entropic terms in bulk and pores is equal to:

$$\Delta S_{iv} - \Delta S_{ip} = k \times \log \left\{ \frac{Z_v}{Z_p} \right\}, \quad (2)$$

and the ratio of the induction periods in bulk, τ_{iv} , and pores, τ_{ip} , is:

$$\frac{\tau_{iv}}{\tau_{ip}} = \left\{ \exp \left(-\frac{\Delta H_{ivp}}{kT_c} \right) \right\} \times \frac{Z_p}{Z_v}, \quad (3)$$

where Z_v and Z_p are the numbers of the energetically equivalent conformations of a macromolecule in bulk and in porous space, respectively. The difference between the enthalpies in bulk and porous medium, ΔH_{ivp} , is determined predominantly by the interaction of the macromolecule with the pore surface.

We define, $Z_p = Z_v G(n; A_1, A_2, A_3)$, where $G(n; A_1, A_2, A_3)$ is the probability to remain inside the pore after n steps of the length a starting from an arbitrary point inside the pore, a is the length of a Kuhn's segment, A_i are characteristic sizes of the pore in the directions of coordinates x, y, z . As a consequence of random three-dimensional motion, there are $N/3$ steps along each coordinate. Assuming that interaction of a molecule with a pore surface is slight, one can project this probability onto the orthogonal coordinates and investigate the probability of first reaching the boundary $[0, A_i]$ after T steps from a point with coordinate x . The solution of this problem for an infinitely flexible chain is:

$$G(n; A_1, A_2, A_3) = \prod_{i=1}^3 \left\{ \sum_{m=0}^{\infty} \frac{8}{\pi^2 (2m+1)^2} \times \exp \left[-\pi^2 (2m+1)^2 \frac{\alpha^2 N}{3A_i^2} \right] \right\}. \quad (4)$$

Eq. (4) can be simplified. At $m = 0$ we have:

$$G(n; A_1, A_2, A_3) \approx \left[\frac{8}{\pi^2} \times \exp \left(-\frac{\pi^2}{3} \times \frac{a^2 N}{A^2} \right) \right]^{d_r}.$$

After substitution in Eq. (3):

$$\frac{\tau_{cv}}{\tau_{cp}} \approx \left\{ \exp \left(-\frac{\Delta H_{ivp}}{kT} \right) \right\} \left[\frac{8}{\pi^2} \times \exp \left(-\frac{\pi^2}{3} \times \frac{a^2 N}{A^2} \right) \right]^{d_r}.$$

In particular cases of the different dimensions of the restrictions d_r we have $d_r = 0$ (bulk melt); $d_r = 1$ (melt in layer, slit);

$$A_1^2 \sim \frac{\pi^2}{3} \cdot R_F^2, A_2^2 \sim A_3^2 \gg \frac{\pi}{\sqrt{3}} \cdot R_F^2,$$

$d_r = 2$ – (melt in canal):

$$A_1^2 \sim A_2^2 \sim \frac{\pi^2}{3} \times R_F^2, A_3^2 \gg \frac{\pi}{\sqrt{3}} \times R_F^2,$$

$d_r = 3$ – (melt in closed spherical pore):

$$A_1^2 \sim A_2^2 \sim A_3^2 \sim \frac{\pi^2}{3} R_F^2.$$

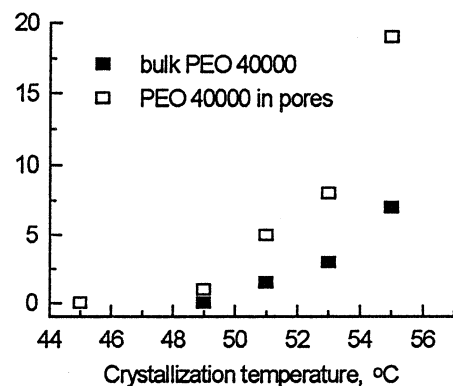


Fig. 2. The experimental dependencies of the induction period (min) on crystallization temperature for bulk PEO and for PEO in pores of the active carbon.

The results of the calculation according to Eq. (4) are presented in Fig. 1. $R_F = (d^2N)^{0.5}$ is the Flory radius of the macromolecule in the bulk melt.

RESULTS AND DISCUSSION

The dependencies of the induction period on crystallization temperature for bulk and confined melts are presented in Fig. 2. We see that for PEO confined in pores τ_i increases as T_c is increased, similarly as in the bulk PEO. When $\Delta H_{ivp} \sim 0$, the shape of the temperature dependence is similar to that for bulk PEO, as predicted by Eq. (3).

As is evident from Fig. 2, confinement in pores at

equal T_c values lead to an increase τ_i . The ratio τ_{iv}/τ_{ip} is independent of crystallization temperature and equal to ~ 0.45 . This is only a little less than the prediction of our model (~ 0.55 , in Fig. 1), so the agreement between the calculated and experimental data is rather good.

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