Crystallization Kinetics of Poly(ethylene oxide) in Mixtures with Tetrahydronaphthalene and Oligo(dimethyl siloxane-*b*-ethylene oxide) Copolymer

Samy A. Madbouly

Cairo University, Faculty of Science, Department of Chemistry, Orman-Giza 12613, Egypt

Summary: The crystallization behavior of poly(ethylene oxide) (PEO) in mixtures with oligo(dimethyl siloxane-*b*-ethylene oxide) (COP) and tetrahydronaphthalene (THN) has been investigated. The crystallization kinetics studied isothermally and non-isothermally using an automated device that monitors the light passing through the systems as functions of time and/or temperature. The crystallization kinetics was found to be strongly influenced by the COP concentration in the mixtures. A substantial decrease in the induction time, t_0 (the time needs for the onset of crystallization) and a considerable shift in the crystallization temperature ($T_{l/s}$) to higher temperatures have been observed with increasing the concentration of COP in the mixtures during the isothermal and non-isothermal crystallization processes, respectively. This behavior may be attributed to the difference in the interaction parameters of PEO with THN and COP. The isothermal crystallization kinetics for this system was analyzed on the bases of Avrami approach.

Keywords: Avrami equation; crystallization; isothermal; kinetics; non-isothermal

Introduction

Knowledge of crystallization kinetics of semi-crystalline polymers and blends is essential for controlling the processing condition and consequently the utility of materials for a given application. It is well established that the crystallization and melting behavior of crystalline polymers depends on the rate of temperature changes[1] and is influenced by the presence of another component. Furthermore the structure parameters, such as lamellar thickness, crystal interphase and spherulitic growth rates are substantially modified by second component.[2-4] The isothermal crystallization kinetics can be adequately described by Avrami equation. The non-isothermal crystallization is a rather complicated and can be described by a modified

 DOI: 10.1002/masy.200351311

Avrami equation which considered the isothermal process as a sequence of infinitesimal small isothermal stages. Our goal here is to investigate the isothermal and non-isothermal crystallization kinetics of PEO in mixtures with two components of different interactions. The crystallization kinetics of PEO (15 wt% in all mixtures) might be changed by replacing the favorably interacted component (THN) by the poorly interacted one (COP). The crystallization kinetics will be analyzed on the bases of Avrami and modified Avrami approaches for isothermal and non-isothermal crystallization, respectively.

Experimental Part

Poly(ethylene oxide), PEO, and poly(dimethyl siloxane-*b*-ethylene oxide), COP, were obtained from Fluka Chemical Co., Germany. The M_w and M_w/M_n of PEO were 27 kg/mol and 1,3, respectively. The COP contains 75 wt% EO and is relatively low molecular weight (M_w = 0.6 kg/mol), its M_w/M_n = 1,3. The solvent 1,2,3,4-tetrahydronaphtalene, THN, was also obtained from Fluka Chemical Co., Germany with 99.8 wt% purity and 205 °C boiling point and was used as supplied. The three components are mixed together and stirred at a temperature higher than the melting point of PEO (70 °C) to prepare blends of different compositions. The non-isothermal crystallization kinetics was investigated by measuring the light transmittance as a function of temperature at constant cooling rate from the melt. In the case of isothermal crystallization, the melt sample is quickly quenched to the desired crystallization temperature and the light transmitted passing through the sample monitoring with time. The data are stored in terms of I/I_0 as functions of time and temperature. The detail of the apparatus is described elsewhere.[5]

Results and Discussion

We have found previously that THN/COP/PEO mixture exhibits liquid-liquid (LL) phase separation upon cooling followed by liquid-solid (LS) transition or crystallization.[5] Figure 1 shows the equilibrium phase diagram of the ternary system with keeping the wt% of PEO constant (15 wt%) as shown in the inset of Figure 1. T_{cp} (cloud point) and T_m (melting point) as a function of composition are represented in terms of w^*_{COP}, the weight fraction of COP in the binary subsystem THN/COP ($w^*_{COP} = m_{COP} /(m_{COP} + m_{THN})$). We will investigate the

combined effects of COP and THN on the crystallization of PEO for the mixtures exhibit only LS transition (left hand side of Figure 1). The effect of LL transition on the crystallization kinetics is beyond the scope of the present work and will be considered elsewhere.

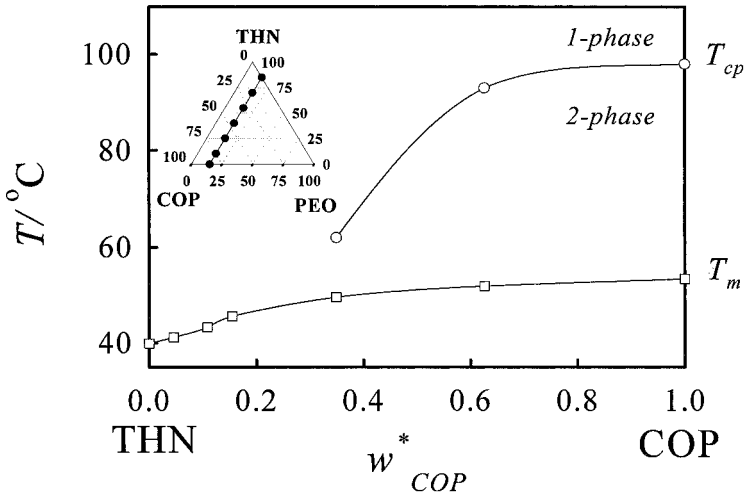

Fig. 1. Phase diagram of the ternary system THN/COP/PEO (PEO = 15wt%). The inset illustrates where this section through the Gibbs phase triangle is performed.

Figure 2 demonstrates the crystallization time dependence of the transmitted light of different blends at 39 °C. The crystallization occurs isothermally at the onset of decreasing the transmitted light of a completely transparent sample (melt sample). The induction time of crystallization, t_0, is defined as the time at which the transmitted light starts to decrease due to the beginning of crystallization. It is apparent that although the concentration of PEO is constant for all mixtures, the crystallization process accelerated to a great extent with increasing the concentration of COP in the mixtures. The induction time, t_0, for THN/COP/PEO = 85/0/15 is about twenty times greater than the corresponding value for THN/COP/PEO = 55/30/15 as shown in the inset of Figure 2. This behavior is unexpected and may be attributed to the different interaction parameters of THN and COP with PEO. The interaction parameter between THN and PEO has been determined from the depression of equilibrium melting point in a previous work[5] and its average value was a bout –0.35. This

value of the interaction parameter should be very small compare with the interaction parameter between COP and PEO (immiscible mixture). Therefore the replacement of THN (favorably interacted) by COP (poorly interacted) should give some effect on the crystallization kinetics even for constant concentration of PEO in the mixtures.

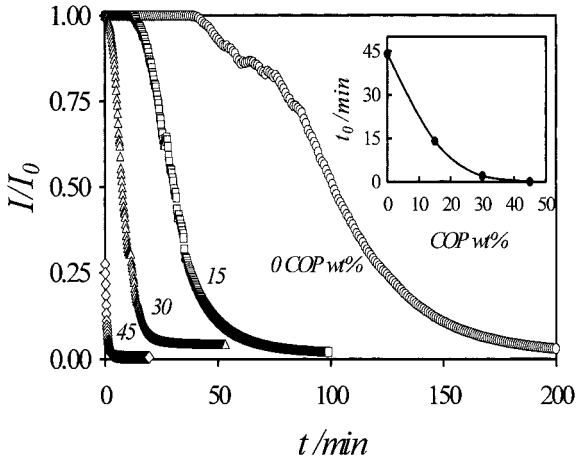

Fig. 2. Crystallization time dependence of the transmitted light for THN/COP/PEO mixtures at 39 °C for different compositions. The inset shows the COP dependence of the induction time, t_0.

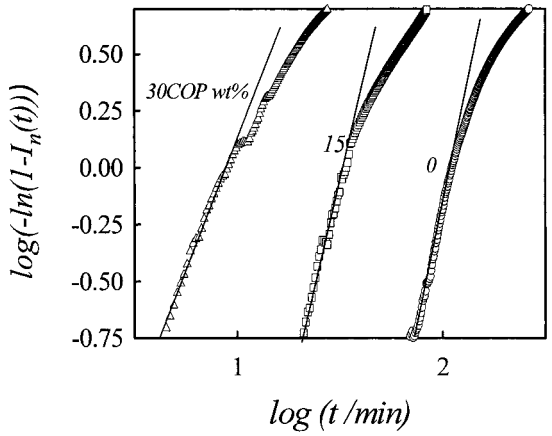

Fig. 3. Avarmi-type plot for the normalized light transmittance for different compositions.

The overall crystallization kinetics of PEO in the mixtures (Figure 2) can be described by Avrami equation[6]

$$X_t = 1 - \exp(-kt^n) \quad (1)$$

where X_t is the weight fraction crystallized at a time t, k is the rate constant which is a function of crystallization temperature, and n is the Avrami exponent. The rate constant, k, includes the combined effects of nucleation and growth; however, the Avrami exponent provides qualitative information about the nature of the nucleation and growth process. The X_t is equivalent to the normalized light transmittance, $I_n(t) = (I(t) - I(0))/(I(\infty) - I(0))$ where *I(t)* is the light trnsmittance at time *t*, *I(0)* is the melt value, and $I(\infty)$ is the value at the end of crystallization process. The plot of $\log(-\ln(1 - I_n(t)))$ *vs.* $\log t$, yields straight line with a slope equal to n and an intercept equal to $\log k$. Clear deviations from the initial liner parts of the plots have been observed due to the secondary crystallization which is not considered in Avrami approach (see Figure 3). The Avrami exponent was ranged from 2.4-3.6 for these mixtures. The crystallization rate constant, log*k*, increases from –5.7 to 0.2 with increasing the wt% of COP in the mixtures i.e. the crystallization rate increases with increasing the wt% of COP in the mixture.

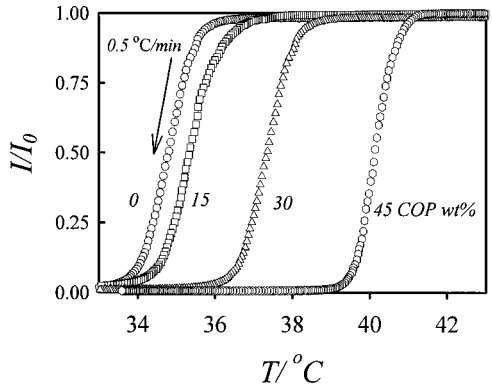

Fig. 4. Non-isothermal crystallization for THN/COP/PEO mixtures of different COP wt% at 5 °C/min cooling rate.

The temperature dependence of the transmitted light during the non-isothermal crystallization process at 0.5 °C/min cooling rate from the melt for different wt% COP is shown in Figure 4. Obviously, the onset crystallization temperature shifts to higher temperature with increasing the concentration of COP in the mixtures i.e. the process accelerated strongly with replacing the THN by COP. The Avrami approach of isothermal crystallization kinetics described above has been modified[7-9] to be used for non-isothermal crystallization by convert the crystallization temperature to crystallization time by the relationship $t = (T_0 - T)/\dot{q}$ where T_0 is the onset temperature of crystallization and $\dot{q}$ is the cooling rate (0.5 °C/min). Avrami-type plot for the non-isothermal crystallization (data of Figure 4) is shown in Figure 5. The kinetic parameters of the Avrami analysis can be also obtain from the slope and intercept. The values of Avrami exponent, *n*, are in the same order of magnitude as in the isothermal crystallization kinetics (about 3). In order to describe the combined effect of COP and THN on the crystallization kinetics of PEO in the mixtures we will use the $t_{0.5}$ (the time required for $I_n(t)$ = 0.5) to describe the kinetics rates of isothermal (Figure 2) and non-isothermal (Figure 4) crystallization processes as shown in Figure 6. One can see that in both cases the $t_{0.5}$ decreases or the crystallization rate increases with increasing the concentration of COP in the mixtures.

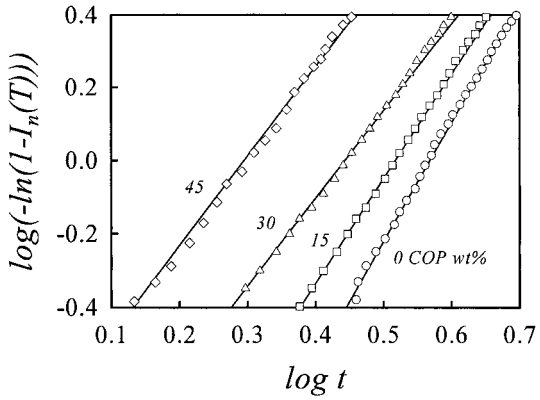

Fig. 5. Avarmi-type plots for non-isothermal crystallization as a function of COP wt%.

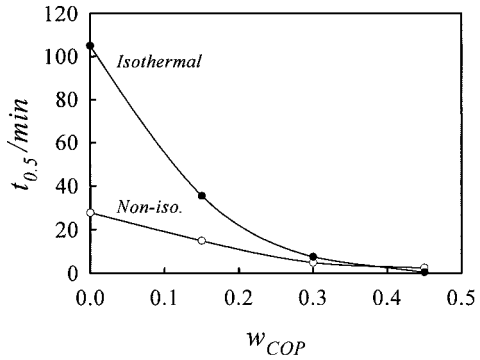

Fig. 6. $T_{0.5}$ for isothermal and non-isothermal crystallization as a function of COP.

The isothermal crystallization rate at 39 °C is very slow compare to the non-isothermal crystallization rate at $\dot{q} = 0.5$ °C/min for mixtures of low concentration of COP. This is clearly attributed to the fact that the non-isothermal process at $\dot{q} = 0.5$ °C/min is quite far from the isothermal condition, the two kinetics processes might be identical if the non-isothermal process carried out at infinitesimal small cooling rate. The two crystallization rates approach each other at higher content of COP as clearly seen in the Figure.

Conclusion

The combined effect of oligo(dimethyl siloxane-*b*-ethylene oxide) (COP) and tetrahydronaphthalene (THN) on the crystallization kinetics of PEO has been investigated. The crystallization kinetics of PEO in the mixtures was accelerated to a great extent by replacing the THN by an equivalent amount of COP. This behavior attributed to the different interaction of PEO with THN (favorably interacted component) and COP (poorly interacted component).

Acknowledgment

The author is grateful to the Alexander von Humboldt-Stiftung for support of his stay in Germany. He also devotes his sincere appreciation to Professor Bernhard A. Wolf, University of Mainz for valuable discussion.

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