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Role of the Confined Geometry on the Crystallization of Poly(ethylene terephthlate) Ultrathin Films

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Abstract: The reflection-absorption infrared (RAIR) was employed to study the crystallization kinetic of poly (ethylene terephthalate) (PET) ultrathin films. During isothermal crystallization the thinner PET film shows a slower kinetic compared with the thicker film. Moreover, the final crystallinity of films with various thickness was found decrease with thickness. The result of fitting our data to Avrami equation showed that the Avrami exponents decrease with film thickness.

Keywords: RAIR, ultrathin films, crystallization.

Recently, there has been increasing interest in the effect of the restricted geometry on the properties of polymeric systems such as ultrathin polymer films as they are widely used in many technological applications[1-2]. Study of the transition or crystallization behavior in polymer ultrathin films with FTIR method is still rare even though this technique has a great advantage on characterizing the conformation and molecular interaction in polymer. RAIR is a well technique for the characterization of the ultrathin films with thickness of nanometer level. In this work the isothermal crystallization kinetic of ultrathin PET films was investigated by RAIR technique *in-situ*.

Ultrathin films of different thickness were prepared by spin-coating PET solutions of various concentrations at a speed of 2000 rpm about 60s onto the gold-coated glass wafers. All the samples were annealed at about 85°C (above T_g of PET) for 4 hours to relax and then slowly cooled to room temperature. Thickness measurement of ultrathin films was performed with NanoScope ⅢA MultiMode atomic force microscope (AFM) (Digital Instrument) in tapping mode. RAIR spectra in the region of 400-4000 cm^{-1} were collected with a Bruker EQUINOX 55 FT-IR spectrometer equipped with a MCT detector. The measurements were obtained by average 32 scans and resolution of 4 cm^{-1}. A homemade heating stage was used to assist obtaining the RAIR spectra *in-situ*.

In the infrared spectrum of PET, the 1340 and 1370 cm^{-1} bands have been assigned to the CH_2 wagging mode in *trans* and *gauche* conformers, respectively[3]. These two bands were chosen as key bands for determining the relative conformational population. The fractions of *trans* (T) conformers can be obtained by the equation[4]:

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$$T = A_{1340} / (A_{1340}+6.6\times A_{1370})$$

where A_{1340} and A_{1370} are the integral absorbance of the 1340 and the 1370 cm^{-1} bands, respectively. Approximate crystallinity can be estimated from the fraction of *trans* conformers of PET[5-6].

The RAIR spectra *in-situ* (in the region 1320-1390 cm^{-1}) for the PET film of about 41 nm in thickness during isothermal crystallization at 105℃ are shown in **Figure 1**. It can be clearly seen that as the crystallization time increases, the absorbance of 1340 cm^{-1} band grows apparently, while the decrease of the absorbance at 1370 cm^{-1} is relatively small. **Figure 2** shows the fractions of *trans* conformers of the films with different thickness during isothermal crystallization at 105℃. The differences in kinetic among the films with various thicknesses are evident. The crystallization rate is slower in thinner films compared to the thicker one. The fractions of *trans* conformers in each film reach a steady state after a period of times, but the final values (T_{max}) are not same.

Figure 1 RAIR spectra in 1320-1390 cm^{-1} region of a 41 nm PET film with different crystallization times during isothermal crystallization at 105℃.

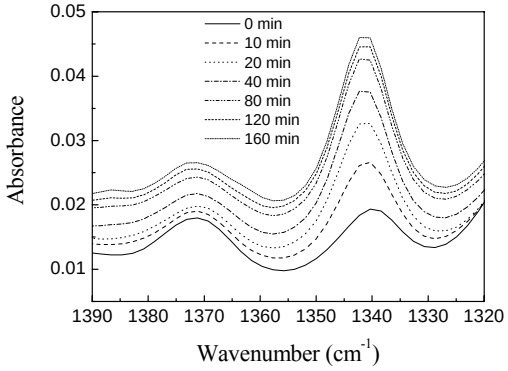


Figure 2 Changes of the fraction of *trans* conformers of PET films with different thickness during isothermal crystallization at 105℃.

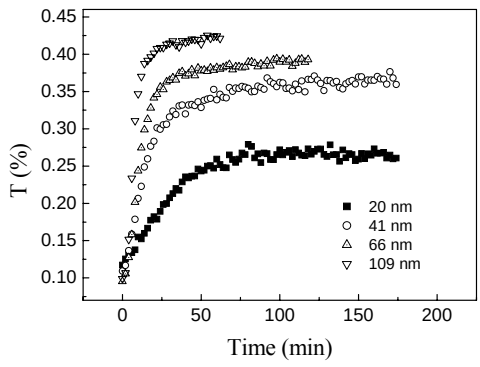
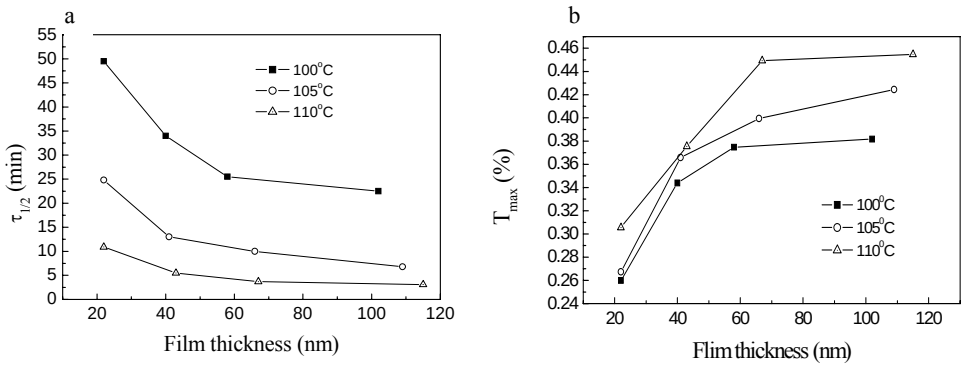


Figure 3 Plots of (a) half-crystallization time and (b) final crystallinity of PET films with different thickness isothermal crystallization at 100,105 and 110℃.



With decrease of the thickness, T_{max} becomes lower. **Figure 3** showed the functions of the film thickness to the half-crystallization time $\tau_{1/2}$ (a) and T_{max} (b) at 100, 105 and 110℃ isothermal crystallization. The $\tau_{1/2}$ can be determined from the normalized *trans* conformer fractions of each films and may serve as a crude measure for the crystallization rate. For all the crystallization temperatures studied, the $\tau_{1/2}$ grow with decreasing film thickness. Also it can be found that the T_{max} vary significantly with the film thickness at the three kinds of crystallization temperatures. The final crystallinity in thicker film prefers to reach a higher value.

Our results fitted to the Avrami equation. The rate of isothermal crystallization at any temperature can be shown by the Avrami equation[7-8]:

$$1-X_t / X_\infty = \exp(-k t^n)$$

where X_t is the crystallinity of the sample at the time t, X_∞ refers to the final crystallinity, K is a rate constant and n is Avrami exponent having a value between 1 and 4. We have selected only the initial stages of crystallization for the analysis. The n (dimensionalities of growth) and the K for the crystallization of ultrathin films are displayed in **Table 1**. The resultant k is complex with the variation of thickness and temperature. This is in accordance with the proposal[9] that the effect of temperature and thickness on k is very complicated since this parameter depends on a number of parameters such as the shape of the crystallite, the growth rate, the number of potential nuclei, and their probability of nucleation. The dimensionality of growth, however, changes regularly with the thickness for each crystallization temperature. Stein *et al.*[10] adopted the Avrami theory to thin polymer films by introducing a correction factor to account for the truncation in the spherical surface area due to the presence of a restraining upper boundary and concluded that the observed value of the Avrami exponent would be relatively small compared to the value for unrestricted growth. Our result for the thickness dependence of n is consistent with the above conclusion.

In conclusion, the *in-situ* RAIR technique was used to investigate isothermal crystallization kinetic of PET ultrathin films. The experimental results indicated that PET films with various thicknesses show different crystallization rate and final

crystallinity. Also it was found that the calculated Avrami exponents decrease with thickness. It is believed that the confined geometry in PET ultrathin films contributed to the above experimental results.

Table 1 Avrami exponent n and rate constant K of PET films with different thickness isothermal crystallization at 100,105 and 110℃.

Crystallization temperature (℃)	Film thickness (nm)	Avrami exponent n	Rate constant K
100	22	1.1	1.1×10^{-2}
	40	1.3	6.9×10^{-3}
	58	1.8	2.0×10^{-3}
	102	2.0	1.3×10^{-3}
105	22	1.2	1.2×10^{-2}
	41	1.5	1.6×10^{-2}
	66	1.9	0.9×10^{-2}
	109	2.3	0.7×10^{-2}
110	22	1.3	3.5×10^{-2}
	43	1.6	4.1×10^{-2}
	67	1.8	6.0×10^{-2}
	115	2.2	5.0×10^{-2}

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