Glass Transition Temperature Determination of Poly(ethylene terephthalate) Thin Films Using Reflection−Absorption FTIR

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ABSTRACT: By using the in-situ reflection−absorption infrared technique, the glass transition temperatures of poly(ethylene terephthalate) thin films were determined by detecting the abrupt change in the absorbance ratio of two comparable bands at 1340 cm^{-1} (trans conformation) and 1370 cm^{-1} (gauche conformation) during heating. It was found that the T_g of thin PET films reduces with respect to that of bulk sample and has a great dependence on the film thickness. The conformational energy difference (ΔE) between trans and gauche states of each film was also calculated. The results indicate that the thickness dependence of calculated ΔE is nearly consistent with that of T_g measured. Furthermore, the relaxation behavior of the PET chains in thin films prepared by spin-coating and the influence of annealing on the T_g measured were also investigated.

Introduction

Nowadays much focus is given to the anomalous physical property of polymers in confined geometry such as thin films due to its importance in science and technology.[1,2] The confinement effect on the glass transition dynamics has been observed in a large number of polymer thin film systems.[3−17] Conventional methods used to measure the glass transition temperature (T_g) of bulk polymers including differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) are not well suited to the T_g characterization of polymer thin films. Therefore, lots of methods such as ellipsometry,[3−9] X-ray reflectivity,[10,11] local thermal analysis,[11,12] positron lifetime spectroscopy,[13] and Brillouin light scattering[14,15] have been developed to investigate the T_g of polymer thin films.

Fourier transform infrared (FTIR) spectroscopy is an important technique for characterizing the glass transition of polymers. The utility of FTIR stems from the specificity of the IR probe to different submolecular and segmental constituents of polymeric systems, which gives this method a unique capacity to elucidate the molecular origin of transition phenomena.[16] However, because of the limitation of sensitivity and signal-to-noise ratio, its application in characterizing the T_g of polymer thin films was relatively rare, and the studies usually concentrated on some specific polymers such as poly(methyl methacrylate) (PMMA).[16,17] Among these studies, Shin et al.[16] measured temperature-dependent FTIR spectra of PMMA thin films. From these spectra, two-dimensional (2D) maps of the first derivative of the absorbance with respect to temperature over the space of wavenumber and temperature were constructed. These maps were used to determine the T_g and to investigate the subtle temperature dependence of the population of trans and gauche conformers in three PMMA thin films with different stereoregularities. Grohens et al.[17] deduced the T_g of PMMA thin films with different stereoregularities from the infrared spectra subtraction. Both of these works using FTIR put emphasis on studying the effect of stereoregularity on T_g of PMMA; the investigation of thickness dependence of T_g for thin films, however, has not been involved.

Poly(ethylene terephthalate) (PET) is a semicrystalline polymer of considerable commercial importance. It has been used to make a variety of products such as films, fibers, and bottles. Even though the property of PET has been extensively studied, the glass transition of its thin films has not been reported so far. In this study, the T_g of PET films was determined by temperature-dependent reflection−absorption infrared (RAIR) spectra. Different from the earlier works, a method was suggested in our present study by choosing two bands that are sensitive to the conformational changes in the RAIR spectra. The T_g of polymer thin films was determined from the abrupt change of the plot for the absorbance ratio of the two bands vs the temperature. The conformational energies of the thin films were also calculated to verify the results. Moreover, the relaxation behavior of the PET chains in thin films prepared by spin-coating and the influence of annealing on the T_g measured were also investigated.

Experimental Section

Sample Preparation. PET pellets ($M_w \sim$ 36 000−41 000 g/mol, $M_w/M_n \sim$ 1.8−2.05) were produced by Changzheng Chemical Industries, Beijing. The PET pellets were dissolved in chloroform−trifluoroacetic acid (volume ratio 9:1). Thin films of different thickness were prepared by spin-coating PET solutions of various concentrations at a speed of 2000 rpm about 60 s onto the gold-coated glass wafers. All glass wafers were cleaned in fresh piranha solution (30% H_2O_2 mixed in 1:5 ratio with concentrated H_2SO_4) prior to spin-coating. Then the thin films were kept under vacuum at ambient temperature for 2 days to remove the residual solvent. Before measurement, all samples were annealed at about 85 °C for 4 h and then slowly cooled to room temperature. The films after annealing at 85 °C for 4 h were amorphous as the fraction of

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trans conformer is nearly 10%[18−22] (see the section "Relaxation Behavior of Spin-Cast Thin PET Films during Annealing").

Thickness Determination. Thickness measurement of thin films was performed with a NanoScope A MultiMode atomic force microscope (AFM) (Digital Instrument) in tapping mode. The film thickness was determined by AFM height profile after partially removing the thin film from the glass wafers. The thicknesses of gold film and PET−gold film were measured. They were defined as the distance between the glass surface and the average of all height values taken in a line scan across the sample surface.[23] To minimize the experimental errors, several height profiles taken from different locations of one sample were averaged. Then the thickness of PET thin film was acquired by subtracting the gold film thickness from that of PET−gold film. Considering the absorbance of RAIR spectra increase almost linearly with thickness for thin films having thickness less than about 400 nm,[24] most of the film thicknesses were deduced by comparing their intensities of the 1410 cm^{-1} band in IR spectra, which is related to thickness variations,[25] with that of several AFM-measured thicknesses of the films.

Reflection−Absorption FTIR Measurement. Reflection−absorption FTIR 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 an average of 32 scans and a resolution of 4 cm^{-1}. The incidence angle is fixed at 83° for getting the best signal recording. The polarization of the incoming beam was parallel to the plane of incidence (p-polarized). A homemade heating stage was used to assist obtaining the in-situ FTIR spectra in the temperature range from ambient temperature to100 °C. Accuracy of temperature was controlled to be ±0.3 °C.

Results and Discussion

The polymer transition in different temperature reflects a certain type of segmental motion. This motion can result in the changes of partial molecular conformation and relevant intramolecular and intermolecular interactions (e.g., dipole−dipole effect, hydrogen bond effect). FTIR has a great advantage on characterizing the conformation in polymer and molecular interactions. This method offers an opportunity for understanding the structure basis of the transitions in polymers since, in general, the structural origins of bands in the infrared spectra of most polymers are known or can be determined. As it reaches the transition temperature of a polymer, anomalous changes of the absorbance or location in some infrared bands representing a certain kind of conformation and interaction may occur.[26−29] Since the T_g represents actually a type of structural relaxation, the aforementioned changes usually occur in the vicinity of the T_g of a polymer. The T_g is a temperature at which there is an onset of motion of chain segments in the amorphous region of a polymer, and the polymer goes from a hard, glassy state to a soft, rubbery one. In molecular chain structure of PET, the $-O-CH_2-CH_2-O-$ moiety shows gauche and trans conformers through the internal rotation of the C−C bond. In crystalline regions the $-O-CH_2-CH_2-O-$ moiety adopts a trans conformation, while in amorphous regions it is mainly in the gauche conformation with some small contribution of trans conformation. A number of studies have appeared for the infrared spectroscopic characterization of contributing conformers of the PET chains.[22,30−33] 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.[31] The intensities of these two bands are comparable in the spectrum of amorphous PET. When the PET is heated through the temperature region of glass transition, the conformer transition from gauche (1370 cm^{-1}) to trans (1340 cm^{-1}) will take place. Abrupt changes that marks T_g in the absorbance ratio of 1340 and 1370 cm^{-1} bands have been found during glass transition for bulk PET.[18,34] Considering that FTIR provides us the information about different submolecular and segmental constituents of polymeric systems, it is reasonable for applying A_{1340}/A_{1370} to determine the T_g of thin PET films. In this work, we make an effort to determine the glass transition temperature of PET thin films using the abovementioned method. Before the T_g measurements, an investigation on the relaxation process of the spin-cast films by RAIR was carried out, in which the bands 1340 and 1370 cm^{-1} were also used. This will be discussed in the following section.

Relaxation Behavior of Spin-Cast Thin PET Films during Annealing. For glassy thin polymer films, a possible cause for the anomalous behavior may originate from sample preparation. The widely used process of spin-coating can potentially produce samples that are far from equilibrium. Although in most studies the used thin films have been annealed above the bulk glass transition to remove residual solvent and relax internal stresses, it is not clear whether this represents sufficient annealing. Therefore, in this work, in-situ RAIR measurement during annealing of thin PET films with different thickness prepared by spin-coating was carried out, from which a thorough understanding on the relaxation behavior of the thin films during annealing and its dependence on film thickness may be obtained. Since the glass transition temperature of PET is 74.5 °C (DSC, 20 K/min)[35] and PET tends to crystallize at temperature above 100 °C, we chose 85 °C as the annealing temperature.

Figure 1a shows the FTIR spectra of 1340 and 1370 cm^{-1} bands for a PET film of about 71 nm in thickness at different times during annealing at 85 °C. It can be clearly seen that as the annealing time increases, the absorbance of 1340 cm^{-1} band grows apparently, while the absorbance change of 1370 cm^{-1} band can hardly be observed. The absorbance change of the 1340 cm^{-1} band can be clearly identified even if the sample was cooled to ambient temperature after annealing, as shown in Figure 1b. The intensity of 1340 cm^{-1} band is evidently higher than that of the unannealed sample. The absorbance changes of the two bands in Figure 1 indicate the occurrence of deorientation (or in other words, relaxation) of the PET chains during annealing. It is believed that the spin-coating method can cause orientation of the PET films. As a result, the molecular chains of PET are prone to be stretched and parallel to the surface of the film plane. Since the 1340 cm^{-1} band is parallel polarization,[32] its transition moment will take a direction parallel to the main chain and thus parallel to the film plane after spin-coating. For the p-RAIR, it selects only the polarization of the incident electric field perpendicular to the metal surface. If molecules are adsorbed onto the substrate with a preferred orientation, vibration modes having transition moments perpendicular to the surface will appear greater in intensity than modes having transition moments parallel to the surface.[36] For this reason, the absorbance of 1340 cm^{-1} band is low in RAIR spectra before annealing. When the films were annealed at temperature above T_g, the relaxation of molecular chain occurred and more transition moments of the 1340 cm^{-1} band tended to deviate

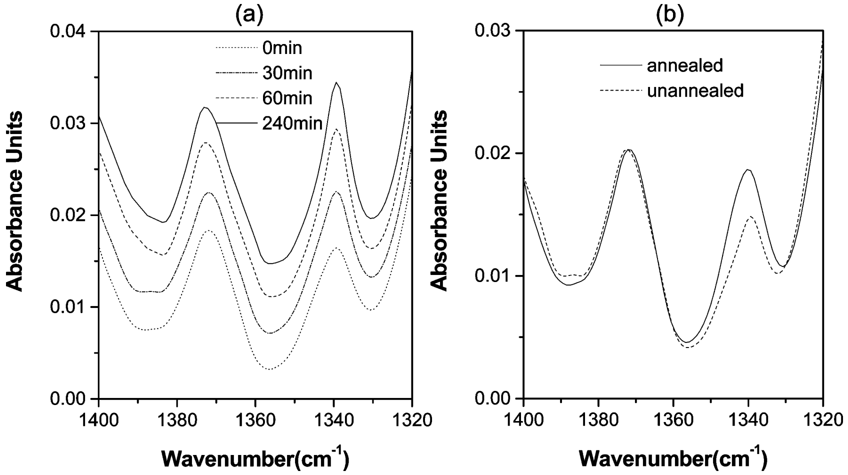

Figure 1. Reflection−absorption FTIR spectra of a 71 nm PET film with different thermal histories. (a) Films at different times during annealing at 85 °C. (b) Annealed (at 85 °C for 240 min) and unannealed films at ambient temperature.

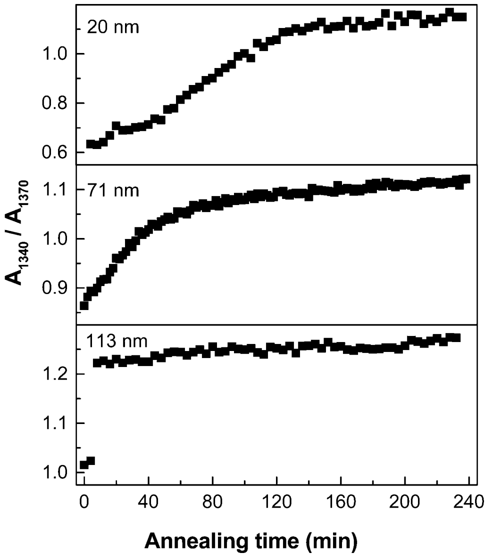

Figure 2. Changes of A_{1340}/A_{1370} as a function of annealing time.

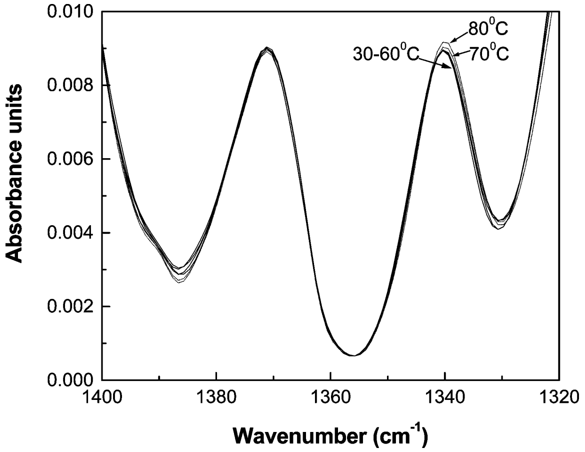

Figure 3. FTIR spectra of a 43 nm film for every 10 °C from 30 to 80 °C.

off the film plane. Thus, the absorbance of this band increased. For the band of 1370 cm^{-1}, its orientation is much weaker than that of the 1340 cm^{-1} band or even no orientation,[32,37] which contributed to the unapparent absorbance changes.

Plotting the absorbance ratio of the 1340 and 1370 cm^{-1} bands vs times assesses the relaxation processes of thin PET films with different thickness during annealing more quantitatively. This is shown in Figure 2. We choose the absorbance ratio of 1340 and 1370 cm^{-1} bands for the aim to eliminate the effect of film thickness changes during annealing. From Figure 2, it can be seen that the relaxation behavior depends strongly on the film thickness. As film thickness increases, it becomes easier to relax. This is probably because that for thinner films higher orientation is generated during film preparation, which can be deduced from the initial value of A_{1340}/A_{1370} for each film in Figure 2. As a result, it will take longer time to relax than the thicker ones. In addition, we found that all of the samples reach relaxation equilibrium state in the time scale measured. So we selected 4 h as the annealing time to relax the samples. To make sure whether the films annealed are amorphous, the fraction of trans conformer (T) of the films annealed is calculated by the following equation:[18,19]

$$T = \frac{A_{1340}}{A_{1340} + 6.6A_{1370}} \tag{1}$$

where A_{1340} and A_{1370} are integral absorbance of 1340 and 1370 cm^{-1}, respectively. The calculated T for all of the samples annealed for 4 h goes near to 10%, so it can be concluded that these films are nearly amorphous.[18−22]

T_g Determination of Thin PET Films. In-situ measurement of RAIR spectra were performed during heating the annealed PET samples at a rate of 1 °C/min from ambient temperature to 85 °C for determining the T_gs of thin PET films. The FTIR spectra of a 43 nm film for every 10 °C from 30 to 80 °C are displayed in Figure 3. It can be found that the absorbance of 1340 cm^{-1} nearly keep stable in the temperature region of 30−60 °C, while abrupt increase can be found in the spectra for 70 and 80 °C. The absorbance decrease of 1370 cm^{-1} in 70 and 80 °C is relatively unapparent compared with that of 1340 cm^{-1}. This attributes to the less absorption coefficient in the 1370 cm^{-1} band.[18,19] To get more quantitative description about this conformational transition process, plots that give the temper-

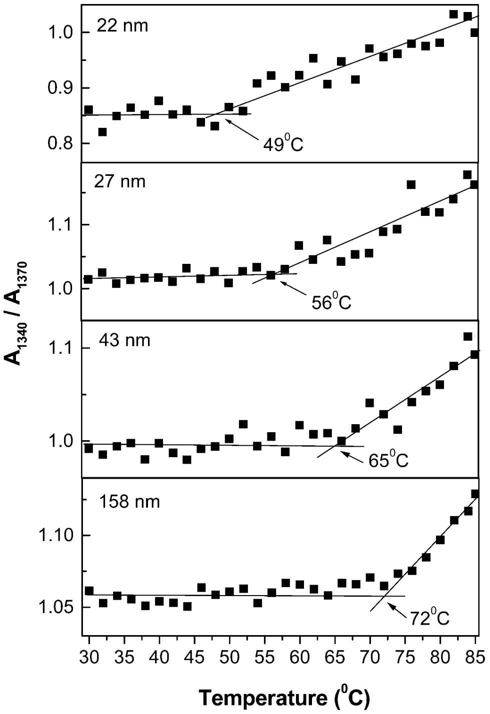

Figure 4. Changes of A_{1340}/A_{1370} as a function of temperature for different film thickness.

ature dependence of A_{1340}/A_{1370} for every 2 °C increase of thin PET films with different thickness are made and shown in Figure 4. In Figure 4, the point at which two straight-line segments intersect can be detected for each of the PET films. As mentioned above, this may represent the abrupt change point of the conformational transition from gauche to trans with increasing temperature and thus can be taken as T_g of each films. As indicated in Figure 4, the determined T_g depends remarkably on film thickness. The film thickness dependence in our present study is found to be similar to that of other works.[3−9] This will be discussed in a later section. We also found that it is more difficult to measure T_g in thinner films since the abrupt change in A_{1340}/A_{1370} at T_g is less obvious because of the high noise level in RAIR spectra. Such difficulties lead to an effective lower limit of sensitivity for RAIR technique to T_g measurement in extremely thin films.

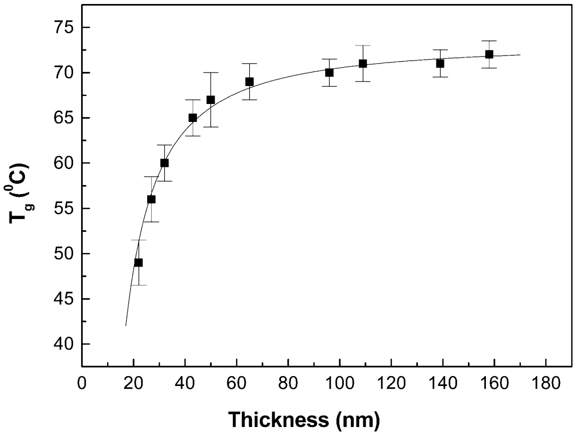

Figure 5. Measured glass transition temperature (T_g) vs film thickness for thin PET films. The solid line represents the best fit of eq 2 using $T_g^{\infty} = 73.3$ °C.

Figure 5 displays the plot of measured T_g vs film thickness for PET films. The data exhibit a monotonic reduction in T_g with decreasing film thickness. When the films are thinner than about 65 nm, substantial reduction in T_g can be identified. The lowest T_g is about 25 °C lower than the value of 74.5 °C for bulk samples measured by DSC. A number of models have been proposed to explain this kind of behavior. Among them, Keddie et al.[3] proposed the existence of a high-mobility region. It suggests that a high-mobility region exists below the bulk T_g, which expands as temperature, T, increases. The T_g is reached when the high-mobility region covers the entire film. By assuming that the thickness of the high-mobility region, ξ_T, expands according to $\xi_0(1 - T/T_g^{\infty})^{-1/\nu}$, a model for the thickness dependence of T_g was thus obtained:

$$T_g(t) = T_g^{\infty}[1 - (\xi_0/t)^{\nu}] \qquad (2)$$

where T_g^{∞} is the bulk T_g and ν is a constant. It was reported that a number of different factors may render the free surface region of a polymer with added mobility[38−45] such as segregation of chain ends,[38−41] density gradient in polymer surface,[42] reduction in polymer entanglement,[43] and so on. Of course, there are also studies that argue against this high-mobility model.[15,46−48] In the present case, we applied our data to eq 2, and the results showed a good fit (smooth line in Figure 5). The best fit has been achieved by choosing $T_g^{\infty} = 73.3$ °C, $\xi_0 = 2.9$ nm, and the exponent $\nu = 1.4$, among which the T_g^{∞} is in good agreement with the bulk T_g measured by DSC. For the parameters ν and ξ_0, Keddie supposed that ν is a constant for amorphous materials but ξ_0 is material dependent.[3] This is supported by comparing our data with the results of PMMA for $\nu = 1.9 \pm 0.6$ and $\xi_0 = 7.2 \pm 3.6$ nm if experimental errors are considered.[3]

As mentioned above, the relaxation behavior of thin PET films depends strongly on the film thickness. Films with different thickness take different times to relax. Now a question may be raised about whether there is influence of the annealing time on the measured T_g. To make this question clear, the T_gs of PET films annealed for different times, e.g. 30 min and 10 h, were measured. Also, four different thicknesses, i.e., 23, 45, 60, and 118 nm, were adopted. The corresponding result is shown in Figure 6. We found that all the measured T_gs of those annealed for 10 h are nearly unchanged compared with those annealed for 4 h. However, if the films were annealed only for 30 min, it becomes more difficult to detect the abrupt changes in the plot with decreasing film thickness though the thicker films (60, 118 nm) remain the same T_g as 4 h annealed films. From Figure 2, it can be concluded that 30 min annealing is not enough for the used films to relax entirely. Moreover, the thinner films should have the higher degree of residual orientation than the thicker ones after annealing. During the heating process for the T_g measurement, the relaxation will continue simultaneously with the conformation transition induced by increasing temperature, and both of them will contribute to the increase of A_{1340}/A_{1370}. For this reason, the abrupt change in glass transition for thinner films may be masked. For the case of 10 h annealing, the T_g of the films remains the same as that of 4 h, and a nearly amorphous state is confirmed by eq 1. However, the possibility of crystallization is nonnegligible for further annealing.

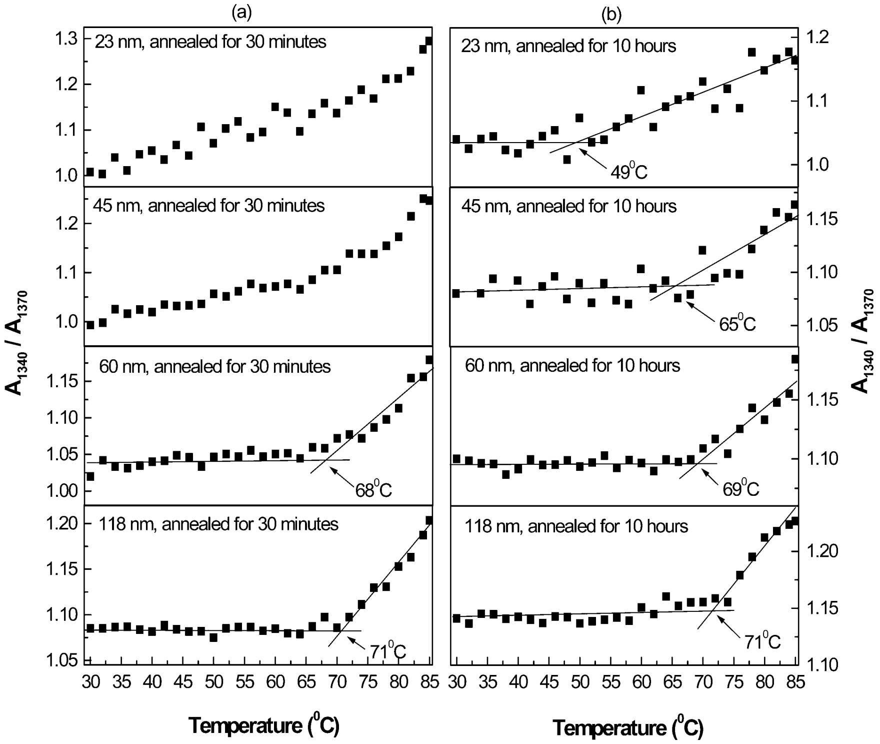

Figure 6. Changes of A_{1340}/A_{1370} as a function of temperature for different annealing time and film thickness.

Conformational Energies Calculation of Thin PET Films. Conformational energy, which is directly affected by the chain rearrangement, has an intimate relation with T_g of polymers. Through studying the stereoregular PMMA,[49] Gibbs and DiMarzio proposed that conformational energy is a primary factor in determining the glass transition temperature of a polymer. O'Reilly et al.[50,51] reported that the T_g of a bulk polymer could be determined from the conformational energy calculated using FTIR spectroscopy. The conformational energy obtained from FTIR spectroscopy was claimed to be consistent with that predicted by the rotational isomeric state calculation. The conformational energy calculation has also been applied to study polymer thin films. Grohens et al.[17] studied the interfacial conformational energy of stereoregular PMMA on aluminum substrate using RAIR spectroscopy. Their results showed a large increase in conformational energy of thin film samples as compared to that of the bulks. Furthermore, the glass transition temperature deduced from the spectral subtraction also exhibits a large increase for i-PMMA. They interpreted these results in terms of interfacial gauche to trans conformational changes and restrictions in molecular motions due to strong specific interactions between PMMA and aluminum.

The calculation of conformational energy was employed in this study to verify our results of the measured T_g. At temperature below T_g, as the long-range molecular motions of PET chains are restricted, the conformational energy calculated at those temperatures may only refer to side-chain conformational changes. So a temperature range from T_g to 85 °C was chosen for the measurement of energy difference between trans and gauche conformational states. In this temperature region, the Van't Hoff equation can be used to calculate the conformational energy difference ΔE between trans and gauche conformational states. The Van't Hoff equation is as follows:

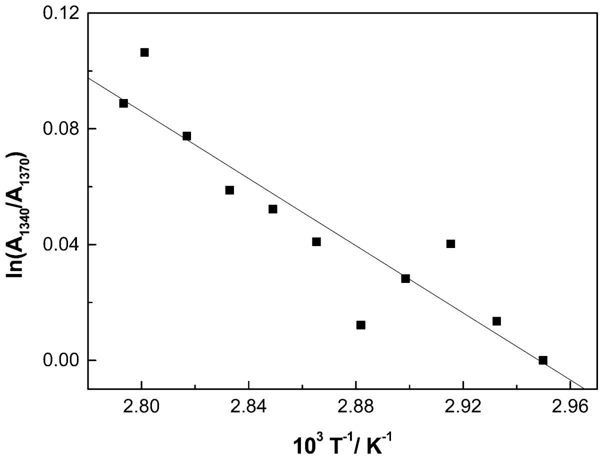

Figure 7. Van't Hoff plot of ln (A_{1340}/A_{1370}) vs reciprocal temperature for PET film of 43 nm in thickness (in temperature range 66−85 °C).

$$\ln \frac{A_{1340}}{A_{1370}} = \ln K - \frac{\Delta E}{RT} \tag{3}$$

where K is constant and R refers to the gas constant. By plotting $\ln(A_{1340}/A_{1370})$ vs reciprocal temperature, the ΔE of thin PET films can be acquired from the slope of the resulting line, as shown in Figure 7.

Table 1 lists the calculated ΔE and the corresponding T_g value in the temperature range of T_g − 85 °C for the PET films of varying thickness. The result indicates that the calculated ΔE exhibits similar thickness dependence as the measured T_g. The ΔE decreases with the film thickness and T_g. The ΔE change is more clearly with films thinner than 65 nm, while it is not obvious with

Table 1. Conformational Energies Difference (ΔE) of Bulk PET and Its Spin-Coated Films on Gold Surface in the Temperature Range of $T_g - 85$ °C

thickness (nm)	ΔE (J/g)	T_g (°C)	thickness (nm)	ΔE (J/g)	T_g (°C)
22	22.9 ± 2.1	49	96	27.5 ± 2.1	70
27	22.7 ± 2.8	56	109	28.3 ± 0.9	71
32	24.4 ± 2.9	60	139	29.4 ± 2.7	71
43	25.1 ± 3.6	65	158	28.4 ± 1.6	72
50	26.4 ± 3.3	67	bulk	28.6	74.5
65	27.9 ± 2.6	69			

films thicker than 65 nm. This may be associated with the fact that the T_g of thicker films almost approaches that of the bulk materials. Therefore, in a narrow temperature range of $T_g - 85$ °C, the ΔE distinction among them and bulk sample is difficult to be determined accurately. The result of calculated ΔE can be taken as quantitative evidence for the easier occurrence of conformational rearrangement in thinner film than in thicker one. Moreover, in accordance with the lower T_g of thin PET films compared with that of bulk samples, it can be found that nearly all the ΔE's s of thin PET films are always lower than that of bulk PET of 28.6 J/g.[18] Our result of thickness dependence for ΔE is opposite to that of Grohens concerning the PMMA on aluminum substrate.[17] This may be associated with the different interfacial interactions exist between polymer and substrate.

Conclusions

In-situ RAIR spectroscopy was used to investigate the relaxation behavior of thin PET films prepared by spin-coating and measure the glass transition temperature of the films. The measured T_gs of the PET thin films were found to have great thickness dependence. To verify the experimental results, the conformational energy differences (ΔE) of PET films were also calculated. The thickness dependence of calculated result of ΔE was found nearly consistent with that of the measured T_g.

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