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Thermal Behavior of Rigid Amorphous Phase in Poly(ethylene naphthalene-2, 6-dicarboxylate) Film

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Abstract :The thermal behavior of the rigid amorphous phase (RAF) of poly(ethylene naphthalene-2, 6-dicarboxylate) (PEN) has been characterized well by differential scanning calorimetry (DSC). The RAF is supposed originating from an anisotropic interphase without lateral order between isotropic amorphous and crystalline phase. However, there were no direct proofs to confirm such suggestion. The kinetic mechanism of formation of the RAF has not been studied. In the present work, the identity of the RAF in molecular conformation was assured by Fourier transform infrared spectroscopy (FTIR). The kinetics of the formation of RAF was firstly traced by time resolved FTIR measurement. It was found that the RAF grew simultaneously with the growth of crystal, but had some delay in relatively low isothermal crystallization temperature. The study of Avrami's equation by FTIR spectroscopy was also carried out.

1. Introduction

The crystalline behavior of macromolecule depends strongly on the flexibility of chain segment. For polyethylene (PE), the chain could fold easily into ordered lamella. For poly(*p*-phenylene terephthalamide) (PPTA) or poly(*p*-phenylene benzobisthiazole) (PBT), the rigid chain could only aggregate to liquid crystal or poor packed crystal. For moderately flexible polymers, e.g. poly(aryl ether ether ketone) (PEEK) [1], poly(phenylene sulfide) (PPS) [2,3], PEN [4], a rigid amorphous fraction (RAF) is proposed as interphase between isotropic amorphous and crystal phase.

The thermal behavior of the RAF has been characterized well using DSC technique by Cheng and Wunderlich [2, 4, 5]. According to generally accepted suggestion, the RAF was assigned to an anisotropic interphase without lateral order, which showed trans rich conformation in micro-scale [5]. However, until now, the suggestion has not been verified by experimental and the kinetic mechanism of formation of the interphase has not been investigated.

In the present work, the assignment of molecular conformation of RAF was studied, and the RAF growth of PEN was firstly traced by time resolved FTIR measurements. The Raman and DSC measurements were also

performed for comparison.

2. Experimental

2.1 Specimens

The amorphous PEN films with a thickness of 8mm were kindly supplied by Tenjin Co. For FTIR measurement, the PEN was compression molded at 300 °C for 10 min to prepare specimens with a thickness of about 10 μm. Both thick and thin films were annealed in a series of time for time dependent testing of isothermal crystallization in DSC, Raman and FTIR spectroscopy. All specimens were quenched into ice water after heat treatment. For phase assignment, the specimen was stretched at room temperature at a drawing ratio of 3. 2.

2.2 DSC Measurement

The DSC measurements were carried out using a Shimadzu TA-50WS Differential Scanning Calorimeter at a heating rate of 20 °C/min.

For the isothermal crystallization from glass state, the specimens were heated to the isothermal temperature at a heating rate of 100 °C/min.

2.3 Raman Spectroscopy

Raman spectra were examined by a NR-1800 Laser Raman Spectrophotometer, Japan Spectroscopic Co. Ltd. Before measurement, the so-called "photobleaching" method was carried out to remove the fluorescence suffi-

Fig. 1 The time dependence of trans-gauche conformational interchange during isothermal crystallization for PEN in the region of 1060-1260 cm^{-1} of Raman spectra.

ciently.

2.4 FTIR Spectroscopy

FTIR spectra were examined by a JIR-6000 Fourier Transform Infrared Spectrometer, JEOL Ltd., in microscopy mode. A hot stage, Mettler FP82HT (Mettler Instrument AG.), was loaded into microscopy system for in-situ measurement. The specimens were heated to the isothermal temperature at a heating rate of 100 $^{\circ}\text{C}/\text{min}$. The sampling period was 10 seconds in the case of 10 scans per time for time resolved measurements.

3. Results and Discussion

3.1 Raman Spectra

Fig.1 shows the time dependence of Raman spectra during isothermal crystallization for PEN in the region of 1060-1260 cm^{-1} . The 1097 cm^{-1} band of Raman spectra for polyethylene terephthalate (PET) [6] is assigned to Ag C-O stretching mode of the planar molecule in crystalline phase or trans conformer in amorphous phase, and used to characterize the conformational and packing changes during annealing and drawing. In the case of PEN specimen, due to the structural similarity, the Ag C-O stretching mode is also found, but shifts to 1101 cm^{-1} . The scattering intensity of the trans confor-

mational band at 1101 cm^{-1} increases during annealing, which indicates that the gauche conformer changes to trans conformer. In addition, the 1100 cm^{-1} and 1220 cm^{-1} bands also changes after heat treatment. Such trans gauche conformational interchange might be ascribed to the transformation of the random coil of PEN molecule into ordered extended chain, which are incorporated into a crystalline lattice during annealing treatment.

3.2 DSC Measurement

3.2.1 The Method to Estimate the Weight Fraction of RAF

The ratio of heat of fusion between semi-crystalline specimen and 100% crystal is used to characterize crystallinity W_c [5].

$$W_c = (\Delta H_f^{sc} - \Delta H_f^c) / \Delta H_f^c \quad (1)$$

where ΔH_f^{sc} is the heat of fusion of semi-crystalline PEN; ΔH_f^c is the exothermal heat of crystallization; ΔH_f^p is the heat of fusion of perfect crystalline PEN, which is extrapolated from the plot of ΔH_f^{sc} vs. crystallinity determined from wide angle X-ray diffraction (WAXD) measurement and equals to 147.7 J/g [7].

The ratio of heat capacity increase ΔC_p in T_g between amorphous and semi-crystalline specimens is applied to characterize the liquid-like amorphous weight fraction W_a .

$$W_a = \Delta C_p^{sc} / \Delta C_p^a \quad (2)$$

where ΔC_p^{sc} and ΔC_p^a are the heat capacity increase ΔC_p in T_g of semi-crystalline and amorphous specimens respectively.

Thus, the weight fraction of rigid amorphous, can be defined as

$$W_{RAF} = 1 - W_c - W_a \quad (3)$$

3.2.2 The Growth of RAF Analyzed by DSC Measurement

Fig. 2 shows the DSC thermogram for the isothermal crystallization of PEN at 180 $^{\circ}\text{C}$ with different annealing time. With the increase of annealing time, the exothermal crystalline peak shifts to low temperature, and decreases to zero, which indicates the completion of crystallization.

By using the equation (3), the weight fraction of the three components, crystalline, liquid-like amorphous and RAF of PEN are worked out as shown in Fig. 3. The weight fractions of the three components are 0.29, 0.34 and 0.37 respectively after the isothermal crystallization at 180 $^{\circ}\text{C}$. The RAF grows simultaneously with crystal during the isothermal crystallization, which supports the

Fig. 2 The DSC thermogram for PEN isothermally annealed specimens at 180 °C with different annealing time.

folding model proposed by Flory and Yoon [8].

The determination of RAF from DSC measurement shows some difficulty in the early stage of isothermal crystallization because the baseline standard is difficult to be identified, which might induce some systematic error in equation (1). In the following study, it will be proved that FTIR is an available method to detect RAF precisely and quickly in the whole stage of thermal process.

3.3 FTIR Spectroscopy

Strobl [9] has developed a Raman spectroscopic method successfully for detecting the interphase of HDPE. The method was applied by Mandelkern [10] et.al. From their work, the interphase thickness of HDPE is about 10-15Å which is in agreement with the result estimated in the lattice lamella simulation.

Comparing to the Raman spectra of PEN as shown in Fig. 1, the FTIR spectra gives far richer information due to its strong dipolar moment and asymmetrical molecular structure. Similar to PET, the FTIR spectra in three wavenumber regions, 2800-3200 cm^{-1} , 1300-1650 cm^{-1} , and 750-1100 cm^{-1} can be used to characterize crystallization kinetics of PEN. Ouchi [11] found that there ex-

Fig. 3 The weight fraction of three components, crystal, liquid-like amorphous and RAF in the case of 180 °C isothermal crystallization by DSC measurement.

isted crystal field splitting in the region of 750-1100 cm^{-1} after annealing as shown in Fig. 4 by studying the six types of polyester. Therefore, in the present work, the region of 750-1100 cm^{-1} is focused to characterize the RAF growth.

3.3.1 Internal Absorbance Standard

In order to choose a internal absorbance standard, the time dependence of FTIR spectra during isothermal crystallization was examined. The hot stage was loaded into FTIR system for a in-situ measurement to ensure the constant testing spot and thickness during or after heat treatment.

By calculating the integrated absorbance of the bands in the whole FTIR spectra region, the most stable band in 890-950 cm^{-1} is selected an internal standard, in which the integrated absorbance showed few change (error < 2-3%) during annealing. The band is assigned to highly localized δ_{CH} bending vibration of naphthalene ring [11]. Fig. 5 shows the error function during isothermal crystallization. After cooling to room temperature, the error is much smaller, only about 0.2%.

3.3.2 The Method to Estimate the Fraction of RAF in FTIR

Generally, the chains in polymer crystal are too far apart and the intermolecular forces are so small that very few polymers exhibit the crystal field splitting, ex-

Fig. 4 The contour map of FTIR spectra split during isothermal crystallization for PEN in the region of 780-1080 cm^{-1} , the right part is the DSC thermogram of isothermal crystallization, the bottom part is the spectra before and after heat treatment.

Fig. 5 The error function during isothermal crystallization at 180 $^{\circ}\text{C}$ for finding an internal standard.

cept PE. In the case of PEN, the α crystalline unit has tight structure [11]. The distance between the neighboring molecular planes perpendicular to the naphthalene ring is 3.54 $\text{\AA}$ that is smaller than 3.7 $\text{\AA}$, the sum of van der Waals radius of CH_2 and a half thickness of an aromatic ring. Due to the intermolecular interaction [12] resulted from so abnormally short distance in crystalline PEN, the 920 cm^{-1} amorphous band splits into sharp crystalline bands at 931.5 cm^{-1} and 904.5 cm^{-1} during isothermal crystallization [11]. The sharp crystalline bands at 931.5 cm^{-1} and 904.5 cm^{-1} , not being found or showing weak shoulder in amorphous phase, increase significantly with the decrease of 920 cm^{-1} amorphous band after heat treatment. The half width of the splitting bands are about 5 cm^{-1} , a third of that of amorphous band, which is very helpful for band decomposition in data processing.

On the other hand, the intermolecular interaction forces fall off at a rate of r^6 in according to the Lennard-Jones potential function, where r is the distance between

Fig. 6 The subtraction method to resolve the pure crystalline spectrum from amorphous and semi-crystalline spectra. The bottom spectrum is from amorphous specimen. The middle spectrum is from semi-crystalline specimen, heat-treated at 220 °C for 60 min; the broken line spectrum of amorphous specimen is fitted as an baseline. The upper spectrum is a resolved crystalline spectrum.

chains. The splitting band should not be originated from interphase, in which there do not exist regular short intermolecular distance owing to disordered conformation. Therefore, the splitting bands could be applied to characterized the crystalline core, excluding the interphase. The subtraction method is applied to resolve the pure crystalline spectra [12] as shown in Fig. 6. The band between 890cm⁻¹ and 950cm⁻¹ has been proved no integrated absorbance change during heat treatment. Thus, the crystallinity Φ_c can be defined as

$$\Phi_c = (I_{931.5\text{cm}^{-1}}^{c/sc} + I_{904.5\text{cm}^{-1}}^{c/sc}) / I_{920\text{cm}^{-1}}^{sc} \quad (4)$$

$$= 1 - I_{920\text{cm}^{-1}}^{a/sc} / I_{920\text{cm}^{-1}}^a$$

where $I_{931.5\text{cm}^{-1}}^{c/sc}$ and $I_{904.5\text{cm}^{-1}}^{c/sc}$ are the integrated absorbance of crystalline bands resolved from semi-crystalline specimen at 931.5cm⁻¹ and 904.5cm⁻¹ respectively; $I_{920\text{cm}^{-1}}^{sc}$ is the integrated absorbance of semi-crystalline specimen in the region of 890cm⁻¹-950cm⁻¹; $I_{920\text{cm}^{-1}}^{a/sc}$ is the integrated absorbance of amorphous band resolved from semi-crystalline specimen at 920cm⁻¹; $I_{920\text{cm}^{-1}}^a$ is the integrated absorbance of amorphous specimen in the region of 890cm⁻¹-950cm⁻¹. $I_{920\text{cm}^{-1}}^a$ is equal to $I_{920\text{cm}^{-1}}^{sc}$ according to chapter 3. 3. 1.

Fig. 7 The effect of drawing on 920cm⁻¹ and 1042cm⁻¹ bands. The upper spectra was from drawn specimen. The bottom spectra was from isotropic specimen.

On the other hand, the neat amorphous band at 1018-1062cm⁻¹, which is assigned to C-O stretching vibration of gauche conformation [11], may be used to characterize the weight fraction of isotropic amorphous Φ_a .

$$\Phi_a = I_{1042\text{cm}^{-1}}^{sc} / I_{1042\text{cm}^{-1}}^a \quad (5)$$

where $I_{1042\text{cm}^{-1}}^{sc}$ and $I_{1042\text{cm}^{-1}}^a$ are the integrated absorbance of semi-crystalline and amorphous specimen at 1042cm⁻¹ respectively.

Thus, the weight fraction of rigid amorphous RAF can be defined as

$$\Phi_{RAF} = 1 - \Phi_c - \Phi_a \quad (6)$$

3.3.3 The Phase Assignment Analysis in FTIR

From the equation (4), the crystallinity also can be estimated by the integrated absorbance change of amorphous 920cm⁻¹ band. Comparing to the equation (5), the 920cm⁻¹ and 1042cm⁻¹ might represent two types of non-crystalline parts. The suggestion was verified by checking the FTIR spectrum of the necking area of the stretched specimen. As shown in Fig. 7, the 920cm⁻¹ band exhibits no obvious change in the shape and absorbance on drawing, while the 1042cm⁻¹ band decreases significantly with about 46.1% loss of absorbance, which indicates that the 920cm⁻¹ band corresponds to the amorphous phase with both isotropic and anisotropic chain conformation, while the 1042cm⁻¹ band to the isotropic amorphous phase only. Therefore, in the case of semicrystalline specimen, the 920cm⁻¹ band originates from the isotropic amorphous and anisotropic interphase, and the 1042cm⁻¹ band originates from the isotropic amorphous only.

Fig. 8 The weight fraction of three components during isothermal crystallization at 180 °C, (a) obtained from FTIR spectra, (b) obtained from time resolved FTIR spectra.

3.3.4 The Weight Fraction of RAF Measured from Quenched Specimen and in situ Annealed Specimen

The FTIR spectra of polymers measured at high temperatures may be influenced by the emission of radiation from the specimen itself. The two types of experiment were applied to investigate the time-dependence of RAF growth during isothermal crystallization. In the first one, the specimens were annealed in a hot stage, then quenched into ice water in a series of annealing time. The FTIR measurements of the annealed specimens were performed at room temperature. The second one was that the specimens were set into hot stage that was loaded under infrared beam directly and the time-resolved measurements were carried out.

Fig. 8a and 8b show the weight fraction of the three components during isothermal crystallization at 180 °C from both methods respectively. The results are consistent well with each other, except that time resolved data has some delay comparing to the quenched specimen, which indicates that the emission of radiation has no significant influence on in-situ measurement. It is also found that the both results from FTIR measurements are consistent with that from DSC measurements as shown in Fig. 3. The crystallinity from FTIR measurement is not larger than that from DSC measurement, which proved that the band used for characterizing the crystallinity

originated from crystalline core, not from trans conformer of all three phases in general case.

According to the Flory lamella model [8], the adjacent reentry is unfavored for polyethylene. Most of the reentry occurs at sites separated by two or three lattice steps, which constructs a rough surface of 10-15Å thickness. In the case of PEN, its chain is composed of a relatively large, rigid naphthalene ring segment and flexible segment. The rigid segment hinders the chain reentry. The chain folding consumes more space and extends far out of the lamella lattice surface, which induces the thick interphase for PEN. On the basis of the model, the weight fraction of interphase for PEN from FTIR, in the order of 0.3 to 0.4, sounded reasonable.

Fig. 9a and 9b show the weight fraction of the three components of PEN during isothermal crystallization at 160 °C from both methods respectively. The half-life time of isothermal crystallization is 60 min, which allows to investigate the early stage behavior of interphase growth. It is interesting to find that the interphase growth has some delay to the crystal growth in the first stage of nucleation during isothermal crystallization. The interphase growth accelerates after the first stage.

4. The Isothermal Crystallization Study in FTIR and DSC Measurement

The three phase model has been proposed to explain the crystalline kinetic mechanism. The reliability that

Fig. 9 The weight fraction of three components during isothermal crystallization at 160 °C, (a) obtained from FTIR spectra, (b) obtained from time resolved FTIR spectra.

Fig. 10 The isothermal crystallization thermogram from DSC measurement at different temperature.

whether the Avrami's equation can be applied to the three phase model was checked. The DSC measurement was carried out in the general method [13]. Fig. 10 shows the isothermal crystallization thermogram from DSC measurement.

In the case of FTIR measurement, the 1042cm^{-1} amorphous band is used to characterize the fraction of amorphous phase by equation (5), then the Avrami's equation [14] is given as below :

$$\Phi_a(t) - \Phi_a(\infty) = \exp(-kt^n) \quad (7)$$

where t is isothermal crystallization time, $\Phi_a(t)$ and $\Phi_a(\infty)$ are the weight fraction of amorphous phase at time t and final stable state respectively. n is Avrami index. k is a rate constant.

Fig. 11 shows the Avrami plot calculated from both FTIR and DSC measurements. The Avrami index is about 1.81 from FTIR and 1.79 from DSC, which are in good agreement with each other. The Avrami index $n \approx 2$ suggests that the crystallization of PEN is the heterogeneous nucleation and two dimensional crystal growth. The lower Avrami index also indicates low order spacial construction of lamella, which may be induced from poorly

Fig. 11 Avrami plot calculated from both FTIR and DSC measurements in the case of isothermal crystallization at 180 °C.

ordered crystalline phase and thick interphase.

5. Conclusion

From band assignments, it is suggested that the RAF is not isotropic state, but oriented and trans-rich phase without lateral order.

The FTIR measurement of the interphase growth is in agreement with DSC measurement, which confirms that the FTIR technique is an available method to characterize the interphase growing quantitatively.

In the case of isothermal crystallization at 180 °C, the interphase grows simultaneously with crystal, which supports Flory and Yoon's lamellar model. In the case of 160 °C, the interphase growth is suggested acceleration after the first stage of nucleation.

The Avrami index $n \approx 2$ from DSC and FTIR measurements suggests the heterogeneous nucleation and two dimensional crystal growth for the crystallization of PEN.

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