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Dynamic process of recrystallization of poly(ethylene terephthalate) solids revealed by fluorescence spectroscopy

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Abstract

The crystallinity of poly(ethylene terephthalate) (PET) films was investigated by comparing measurements of fluorescence, differential scanning calorimetry and density. It was found that the ratio of the fluorescence intensity at 330 nm to that at 370 nm can be an effective indicator of crystallinity. The dynamic process of recrystallization was directly observed for PET prepared using a spin-casting method on quartz disks by means of fluorescence measurements at several temperatures between 380 and 400 K. The recrystallization of such films was found to proceed one-dimensionally under the mechanism of heterogeneous nucleation, since the Avrami exponent, *n*, was determined to be one. The apparent activation energy of recrystallization was determined to be 120 kJ/mol, indicating that more than a few monomer units of PET participate in reorientation and crystallization. The present work should provide a quick and nondestructive method for determining the crystallinity of PET factory products. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Recrystallization; Crystallinity; Fluorescence

1. Introduction

Fluorescence spectroscopy is a powerful and effective tool for studying the physical and chemical behavior of macromolecules and its use is growing rapidly [1–5]. Since fluorescence techniques are not only highly sensitive but also nondestructive, they are useful for monitoring real time changes in the formation of very small amounts of products and/or changes in the microenvironment. However, only limited information on the fluorescence properties of material polymers is now available. Therefore, we have been investigating the luminescence of material polymers with aromatic groups in the main chain [6–9].

Poly(ethylene terephthalate) (PET) is used extensively in the fiber and packaging industries. PET has a fluorescent phenylene moiety in the main chain with a fluorescence peak at 330 to 340 nm in fluid solution. However, prior to our previous study [8], the intrinsic luminescence of PET films had been less well characterized, mainly because the thickness and crystallinity of the PET films employed differed from one another. In order to clarify the fluorescence properties of PET solids, we studied PET films prepared by using a spin-casting method, which can provide the most reproducible conditions for preparing films [8,9].

Fig. 1 shows a typical fluorescence spectrum of a PET solid: broad fluorescence around 370 nm is due to the phenylene moiety whose absorption band is 290 nm, while fluorescence with fine structures at 369 and 387 nm is due to the phenylene ground state dimer [10–13] having an absorption peak at 336 nm. We measured the fluorescence behavior of PET films with different crystallinities and compared it with data obtained from differential scanning calorimetry (d.s.c.) and infrared (i.r.) absorption. Finally, we found that the fluorescence around 370 nm consists of two fluorescent components: one with a peak near 330 nm coming out from the main-chain phenylene groups in the crystalline region and another at longer wave-lengths from the phenylene in the amorphous region [8].

In the crystal region of PET, Bunn et al. [14] demonstrated from their analysis of X-ray diffraction that any phenylene group should be separated from other phenylene and carbonyl groups by more than 0.45 nm. This means that the π-electron of the phenylene groups is isolated from the others. This is the reason why the phenylene fluorescence in the crystal region is identical to that in a fluid solution. On the contrary, some phenylene moieties in the amorphous region can be within a distance of 0.35 nm from a phenylene or carbonyl group, and thus their fluorescence is shifted to

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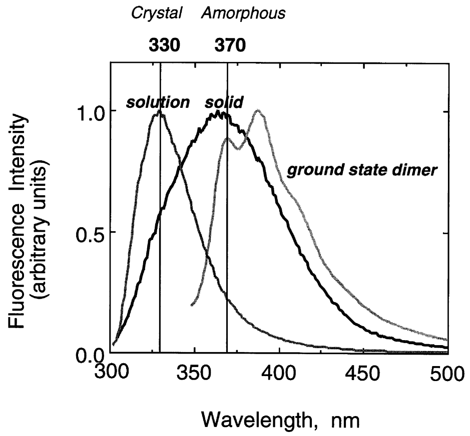

Fig. 1. Fluorescence spectra of PET; solution, PET in chloroform and trifluoroacetic acid (9:1 v/v); solid, PET film prepared by a spin-casting method; ground state dimer, PET film cut out from a commercial bottle. Excitation wavelength was 290 nm for the solution and solid, and 336 nm for the ground state dimer.

the red due to interactions involving some contributions of charge-transfer stabilization among the phenylene and carbonyl groups and/or the phenylene groups [8].

Fluorescence of the ground state dimer is not observable for thin films prepared by using the spin-casting method. However, it can be observed for a thick film such as a PET bottle, as is shown in Fig. 1. Some pairs of phenylene groups that are precisely oriented can form a ground state dimer out of many pairs interacting with one another. However, since the number of such pairs must be low, thin films seem to form only a few ground state dimers.

The goal of the present study was to monitor the dynamic process of PET recrystallization, since we have succeeded in getting information on PET fluorescence as described above. From the standpoint of material science, it is important to develop a technique to monitor in situ the change in crystallinity directly, nondestructively, and quickly in the factory environment. Here we describe a method for observing crystallization by means of fluorescence spectroscopy and for obtaining information on the crystallization process itself.

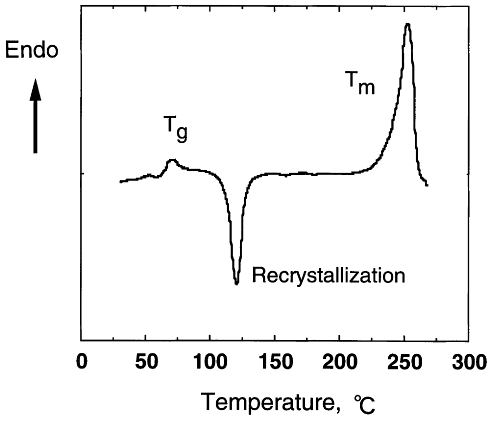

Fig. 2. D.s.c. heating curve for PET films used in the present work: scan rate was 20°C min^{-1}.

2. Experimental

2.1. Film preparation

The poly(ethylene terephthalate) (PET) sample used in the present study was purchased from Aldrich Co. (inherent viscosity = 0.59 dl/g) and purified by repeated dissolution and precipitation. The PET films for the fluorescence measurements were prepared on quartz disks by using a spin-casting method from a 1% solution of chloroform-trifluoroacetic acid (9:1 v/v), and dried by extensive pumping under vacuum for more than 3 days at 60°C. The films were left on quartz disks for ease of handling during subsequent measurements. The thickness of the PET films was measured with a Keyence VF-7500 Profile Micrometer. The PET films for density measurement were prepared by using the same spin-casting method on glass disks of 10-cm diameter from a 5% solution.

2.2. Weight percentage crystallinity, differential scanning calorimetry and fluorescence measurements

The density of PET films was measured by a pycnometer with xylene and carbon tetrachloride as media. The weight percentage crystallinity was calculated by assuming the densities of the crystal and amorphous region to be 1.455 and 1.335 g/cm^3, respectively.

D.s.c. measurements were performed on a Perkin Elmer DSC7. The instrument was calibrated to within ±0.5 K using octadecane for the low temperature region and using indium and zinc for the higher temperature region. All data were taken using a scan rate of 20°C min^{-1}.

Fluorescence spectra and fluorescence excitation spectra were measured under vacuum on a Hitachi F-4500 spectrofluorometer. Films on quartz disks were set at 45° to the exciting beam. The sample temperature was controlled by an Oxford DN1704 cryostat with an ITC-4 digital temperature controller, which could easily regulate temperature to better than ± 0.1 K; independent temperature measurement was carried out by means of a second thermocouple and a potentiometer. All samples were kept at each set temperature and spectra were run repeatedly for 6 to 24 h even after perfect duplication was obtained, since one of the main aims of the present work was to determine the time required for the equilibrium. Excitation was at 290 nm.

3. Results and discussion

First we characterized PET films prepared by using a spin-casting method and by drying at 60°C for 3 days. Films prepared in the same way were found to have identical properties. Weight percentage crystallinity of the films was determined to be 11 ± 2%. Their average thickness was measured to be 350 to 400 nm. The d.s.c. scans were made on some PET films prepared in the same way in order to determine the thermal features. Fig. 2 shows the heating

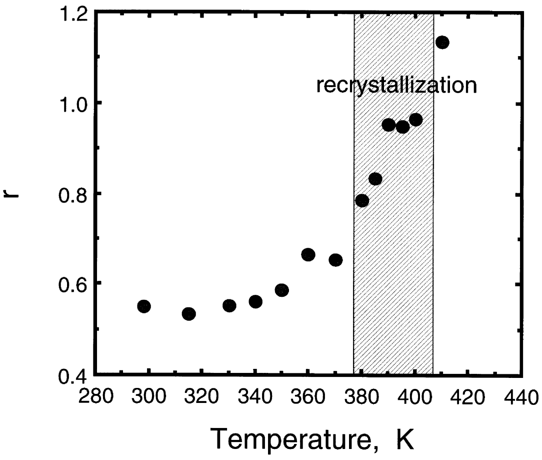

Fig. 3. Annealing temperature dependence of r. Each point is an average of some experimental values. The shaded part indicates the exothermic temperature range corresponding to the recrystallization process.

d.s.c. curve of a PET film. The peak temperature of the endothermic area due to the glass transition was 343 K, while the exothermic area due to recrystallization, whose peak was 393 K, began at 378 K and ended at 408 K.

We have previously shown by comparing both d.s.c. and i.r. measurements that the PET fluorescence reflects whether the main-chain phenylene ring is in the crystal region or the amorphous one [8]: the fluorescence around 330 nm is from the crystalline region and that around 370 nm is from the amorphous region. Thus, the ratio of the fluorescence intensity at 330 nm, I_{330}, to that at 370 nm, I_{370}, can be an indication of the crystallinity of PET films. Then, r is defined as

$$r = I_{330}/I_{370} \qquad (1)$$

The crystallinity of PET should thus be high when r is large.

Fig. 3 shows the temperature dependence of r_∞, which is an equilibrium r-value after annealing films at a constant temperature: each data point in Fig. 3 was an average of all the r_∞ values obtained by several measurements.[1] The r_∞ value at temperatures higher than 410 K was difficult to determine due to an increase in radiationless deactivation. The r_∞ value did not change very much up to 340 K, which is the glass transition temperature. However, it increased slightly between 340 and 370 K and dramatically above 380 K. The temperature dependence of r_∞ agrees well with the exothermic behavior obtained by the d.s.c. measurements showing that the recrystallization process takes place at temperatures from 378 to 408 K. The weight percentage crystallinity of the PET films was found to increase to 24 ± 1% after they were annealed at 400 K. Thus, the change shown in Fig. 3 was found to correspond completely to the change in crystallinity. Note that the equilibrium values of r_∞ at 390, 395, and 400 K precisely agreed with one another. This suggests that the final crystallinity attains the same value when the films are prepared in the same way.

Next we tried to monitor the dynamic change of crystallinity by observing the fluorescence of PET solids. All the PET films studied were kept at 370 K under vacuum for more than 12 h in order to attain equilibrium, and then were heated abruptly to a temperature where recrystallization should occur. Time started to be counted just when the temperature of the film reached the objective temperature. There were no cases when the temperature overshot the set temperature by 0.5 K. As we have already shown, the reproducibility of the temperature change is very high [9]. The time change of the r_∞ value for one film is precisely identical with that for other films prepared in the same way.

In order to examine the mechanism of PET recrystallization in the present system, we tried to apply the time change of r-value to the Avrami equation [15, 16]. In general, the Avrami equation is expressed by the Avrami exponent, n, and the Avrami constant, G:

$$x_c(t) = x_{cs}\left[1 - \exp(G{\cdot}t^n)\right] \qquad (2)$$

where $x_c(t)$ is the degree of crystallinity at time t and x_{cs} is the final degree of crystallinity. In our case, $x_c(t)$ are considered to be expressed as follows.

$$x_c(t) = r - r_0,\ x_{cs} = r_\infty - r_0$$

where r_0 is the r-value at time 0. Thus, Eq. (2) can be transformed to Eq. (3) using r, r_0, and r_∞:

$$\frac{r - r_0}{r_\infty - r_0} = 1 - \exp(G{\cdot}t^n) \qquad (3)$$

In Fig. 4,

$$\log\left\{-\ln\left[1 - \frac{r - r_0}{r_\infty - r_0}\right]\right\} = \log\left\{\ln\left[\frac{r_\infty - r_0}{r_\infty - r}\right]\right\}$$

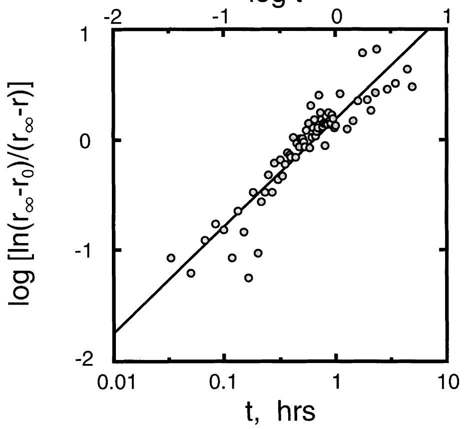

Fig. 4. Avrami plot of the results on kinetics of recrystallization at 395 K. The best fitting line has an inclination of 0.97.

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[1] We reported some average values of r_∞ in our preliminary work [9], in which we did not take into account the emission of a photoproduct which is produced when the fluorescence of a film is measured repeatedly for more than 100 times. However, since the fluorescence intensity of a PET film decreases considerably at higher temperatures, the influence of the photoproduct was found not to be negligible. In the present work, we corrected the r_∞-values and carried out many additional measurements. Thus, Fig. 3 is our final result, although it is a bit different from Fig. 1 in Ref. [9].

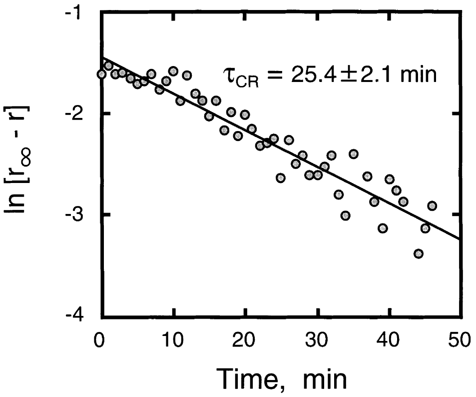

Fig. 5. Fitting of the results at 395 K to a single exponential function. The best fitting line shows τ_{CR} is 25 min.

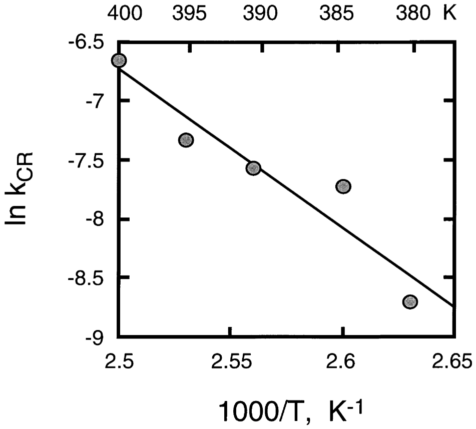

Fig. 6. Arrhenius plot of k_{CR}.

is plotted as a function of $\log t$ for the crystallization temperature at 395 K. The plot was found to give a straight line, and we have determined n to be 0.97 form the slope by using the least squares method. We fitted all the data to a plot of

$$\log\left\{\ln\left[\frac{r_\infty - r_0}{r_\infty - r}\right]\right\}$$

versus $\log t$ and have concluded that n is nearly 1.0. This is the case for one-dimensional growth under the mechanism of heterogeneous nucleation. Thus, the crystallization process has been determined for PET films prepared by a spin-casting method on quartz disks and by drying at 60°C (the crystallinity was about 11%).

Since $n = 1$, we can treat the dynamic process of crystallization as a usual single exponential function:

$$r_\infty - r = A\exp(-t/k_{\mathrm{CR}}) \tag{4}$$

where k_{CR} is the rate constant for recrystallization, and A is constant. Here k_{CR} can be expressed as $k_{\mathrm{CR}} = 1/\tau_{\mathrm{CR}}$, where τ_{CR} is the time constant for recrystallization. Fig. 5 shows a plot of $\ln(r_\infty - r)$ versus t for the same data shown in Fig. 4. The data give a straight line to yield a value of 25 min for τ_{CR} at 395 K. In conclusion, the increase in the crystallinity of the PET films prepared as described above can be described by a single exponential function in the temperature region where recrystallization takes place.

We measured the dynamic process of recrystallization by the same method as shown in Figs. 4 and 5 at 380, 385, 390, 395, and 400 K. Each value of k_{CR} was obtained by averaging either two or three sets of experimental data. Fig. 6 demonstrates an Arrhenius plot of k_{CR}, yielding an activation energy of 120 kJ/mol. It is difficult to define the activation energy per mole in the present case. However, this large activation energy strongly suggests that more than a few monomer units of PET must be reoriented in order for recrystallization to occur.

The present data show that our fluorescent method is quite effective for observing the dynamic recrystallization process of amorphous PET solids. Although our present results were confined to films prepared by using a spin-casting method on disks, we were able to obtain the quantitative transient features of the crystallization process. Fluorescence measurements using optical fibers should be useful for quick and nondestructive assessment of factory products. The method is especially recommended as a simple and quick in situ measurement of crystallinity.

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