Dynamic process of cold crystallization of poly(butylene terephthalate) solids revealed by fluorescence spectroscopy

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ABSTRACT

The crystallinity of poly(butylene terephthalate) (PBT) films was investigated by comparing measurements of fluorescence and density. It was found that the ratio of the fluorescence intensity at 320 nm to that at 365 nm can be an effective indicator of crystallinity. The dynamic process of cold crystallization was directly observed for PBT films prepared using a spin-casting method on quartz disks by means of fluorescence measurements at several temperatures between 360 and 400 K. The cold crystallization 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 cold crystallization was determined to be 24 kJ/mol, indicating that rotation around carbon–carbon bonds in a butylene unit of PBT participates in reorientation and crystallization. The present work should provide a quick and nondestructive method for determining the crystallinity of PBT factory products.

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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 [1–6]. 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 [7–12].

Simply speaking, fluorescence is a photon released from an excited state of a molecule. The excited state can be readily formed by the irradiation of light to a usual molecule in the ground state, but since the duration time of the excited state is usually very short, it goes back to the ground state by releasing the excitation energy as heat and/or fluorescence. What we are interested in is how a molecule behaves during its excited state: for example if it deactivates normally or associates with another molecule to form another excited species and so on. Thus, we can label a chromophore that is not a special one in a polymer only by the irradiation of light and can observe its behavior that should be as it is.

Aromatic polyesters such as poly(ethylene terephthalate) (PET) and poly(1,4-butylene terephthalate) (PBT) have quite important applications as engineering plastics. PET has a fluorescent phenylene moiety in the main chain showing its fluorescence peak at 330–340 nm in fluid solution, but thick PET films showing fluorescence with fine structures at 369 and 387 nm have been assigned to the phenylene ground-state dimer [13–16], which has an absorption peak at 336 nm. However, the intrinsic luminescence of PET films was not well characterized until we studied PET films prepared by a spin-casting method, which provides the most reproducible conditions to prepare films [9–11]. Finally we found that PET fluorescence consists of two fluorescent components in addition to the ground-state dimer: one with a peak near 330 nm coming out from the main-chain phenylene groups in the crystalline region and the other at longer wavelengths from the phenylene in the amorphous region [9,10].

Relative to the number of studies on PET solids, only a few reports were published on the fluorescence of PBT solids [17–19], however, the shapes of the fluorescence spectra reported were different from one another. The differences among these observations of PBT fluorescence are attributable to the conditions in which the films were prepared, such as film thicknesses, impurities, crystallinities and so on. Thus, we investigated the relationship between the fluorescence behavior and crystallinity of PBT films

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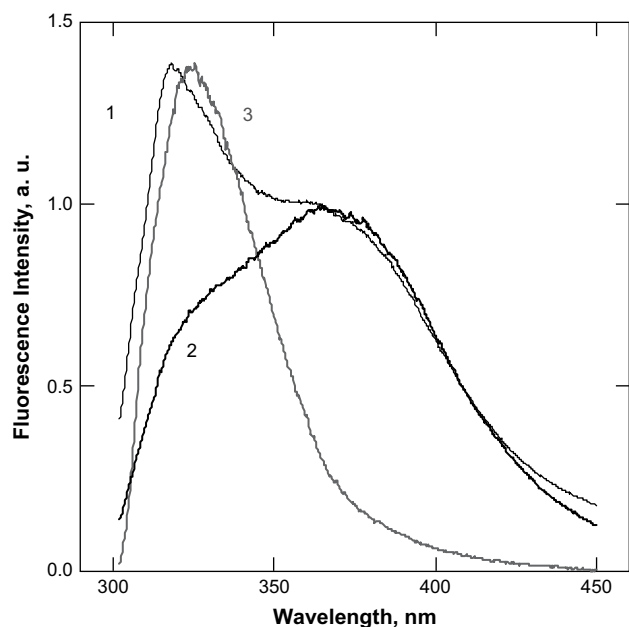E-mail address: edhitag@ipc.shizuoka.ac.jp (H. Itagaki).

Fig. 1. Fluorescence spectra of PBT thin films cast at 200 °C (1) and cast at 40 °C (2) on quartz disks together with the spectrum of 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) solution (3) of PBT. The excitation wavelength is 290 nm.

[12], prepared by a spin-casting method, which can produce films having perfectly the same properties. Throughout the fluorescence measurements of PBT thin films having different crystallinities, the main-chain phenylene fluorescence near 320 nm and that near 365 nm was assigned to monomer fluorescence mainly from crystalline regions and excimer fluorescence from amorphous regions, respectively, as shown in Fig. 1.

Fig. 2A demonstrates the arrangement of molecules in the crystal of α form of PBT determined through the analysis of x-ray diffraction by Yokouchi et al. [20]: the unit cell dimensions are $a = 0.483$ nm, $b = 0.594$ nm, $c = 1.159$ nm, $\alpha = 99.7°$, $\beta = 115.2°$, and $\gamma = 110.8°$ for the α form, and $a = 0.495$ nm, $b = 0.567$ nm, $c = 1.295$ nm, $\alpha = 101.7°$, $\beta = 121.8°$, and $\gamma = 99.9°$ for the β form. Two phenylene groups must be within 0.35 nm in order to interact with each other such as the formation of a ground-state dimer or an excimer. However, because the distances between two phenylene groups are 0.44 and 0.42 nm in α and β crystalline

forms of PBT, respectively, the π-electron of the phenylene groups in a crystalline form is isolated from the others whatever the crystalline forms of PBT are. Thus, it means that the phenylene groups in a crystalline form exhibit so-called monomeric fluorescence. This is the reason why the phenylene fluorescence in the crystal region is almost identical to that in a fluid solution (Fig. 1). On the contrary, some phenylene moieties in the amorphous region can be within a distance of 0.35 nm from a phenylene group (Fig. 2B), and thus they can form an excimer.

The goal of the present study was to monitor the dynamic process of PBT cold crystallization, since we have succeeded in getting information on PBT 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.

2. Experimental

2.1. Film preparation

The poly(1,4-butylene terephthalate) (PBT) sample used in the present study was purchased from Aldrich Co. ($M_v = 38,000$). Because no difference of fluorescence behavior was observed between both the samples as received and the ones purified by repeated dissolution and precipitation, we used the PBT sample without any purification. The PBT films for the fluorescence measurements were prepared on quartz disks by using a spin-casting method from a 1% solution of 1,1,1,3,3,3-hexafluoro-2-propanol (HFP), and dried by extensive pumping under vacuum for more than 3 days at a constant casting temperature. After the influx of dry nitrogen gas into the oven, the films were quickly transferred into a vacuum desiccator and quenched to room temperature under vacuum. More than four films under the same preparation method were prepared to ascertain the reproducibility. The films were left on the quartz disks for ease of handling during subsequent measurements. The PBT films for determining weight percentage crystallinity were prepared by using the same spin-casting method on glass disks of 10-cm diameter from a 1% HFP solution.
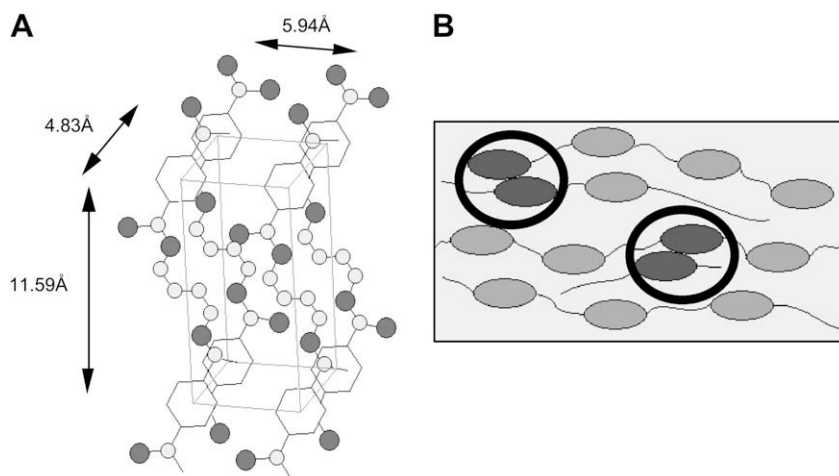

Fig. 2. (A) Arrangement of molecules in crystal of the α form of PBT after Yokouchi et al. [20], (B) sketch of interaction between main-chain phenylene groups of PBT in the amorphous region: the phenylene groups emphasized in a circle may form an excimer in the excited state or a ground-state dimer.

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

The density of PBT 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 1.396 (α form) and 1.282 g/cm^3 [21], respectively.

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

UV absorption spectra were measured on a Shimadzu UV-2200. Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-4500 spectrofluorometer. Films on quartz disks were set at 45° to the exciting beam. The temperature dependence of PBT films was measured in a cryostat under vacuum. 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 4–24 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 PBT films that were prepared in the perfectly same manner: they were prepared on quartz disks by using a spin-casting method from a 1% HFP solution and by drying under vacuum at 40 °C for 3 days. All the PBT films prepared in the same manner were found to have identical properties. Weight percentage crystallinity of the films was determined to be 26%. This relatively low value of crystallinity could be due to our preparation way using a spin-casting method from HFP solutions where PBT molecules are supposed to take random coil conformation. Moreover, it is already known that the formation of crystalline region is restricted in thin films prepared using a spin-casting method [24,25].

The d.s.c. scans were made on some PBT films prepared in the same way in order to determine the thermal features. Fig. 3 shows the heating d.s.c. curve of a PBT film. The peak temperature of the endothermic areas due to the melting was 495 K, while the
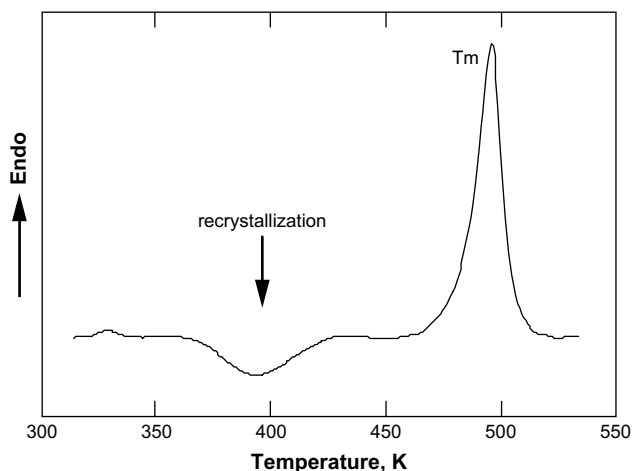

Fig. 3. D.s.c. heating curve for a PBT film used in the present work: scan rate was 20 °C min^{-1}.

exothermic area due to cold crystallization, whose peak was 393 K, began at 360 K and ended at 430 K in this case. Once a PBT sample was annealed at higher temperatures such as 470 K, its d.s.c. curve was found not to show exothermic peaks as shown in Fig. 3.

We have previously shown that the PBT fluorescence reflects whether the main-chain phenylene ring is in the crystal region or the amorphous one as explained in Introduction [12]: the fluorescence of phenylene group in the crystalline region shows its peak around 320 nm while that in the amorphous region shows its peak around 365 nm. Thus, the ratio of the fluorescence intensity at 320 nm, I_{320}, to that at 365 nm, I_{365}, can be an indication of the crystallinity of PBT films, although I_{320} consists of monomeric fluorescence from both crystalline and amorphous regions. Then, r is defined as

$$r = I_{320}/I_{365} \tag{1}$$

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

We have already obtained the relationship between the weight percentage crystallinity and its fluorescence intensity ratio, r, of the PBT films prepared in the same manner shown above [12]. The plot of r versus the crystallinity gave a straight line [26] and r can be a quite effective indicator of the crystallinity of PBT thin films as well as that of PET thin films [9–11].

In order to ascertain the stability of the crystallinity of the PBT films, the fluorescence spectra of two PBT films on quartz disks prepared in the same way and kept in a dark place were measured once a week for 4 months. However, there were no changes but all the spectra were identical with one another, suggesting that the PBT films on the substrates prepared by the present method are not gradually crystallized at room temperature.

Next we tried to monitor the dynamic change of crystallinity by observing the fluorescence of PBT solids. All the PBT films studied were kept at 340 K under vacuum in a cryostat for more than 12 h in order to attain equilibrium, which could be ascertained by showing the perfectly identical fluorescence spectra. Then, the PBT films were heated abruptly to a temperature where cold crystallization should occur. Time started to be counted just when the inside temperature of the cryostat, where a film was set, reached the objective temperature. There were no cases when the temperature overshot the set temperature by 0.5 K. Finally the fluorescence spectra became to be identical with each other at each temperature. As we have already shown for PET films, the reproducibility of the temperature change is very high [10,11]. The time change of the r value for one film is precisely identical with that for other films prepared in the same way. r_∞ is defined to be the final value of r at a temperature and was determined by averaging r values that have become a constant after a long time. For example, in order to determine a τ_{cr} in Table 1, we measured r values during the long time being 15- to 20-fold of τ_{cr}. Its r_∞ value was obtained by averaging the r values keeping constant during the time being 5- to 10-fold of τ_{cr}.

In order to examine the mechanism of PBT cold crystallization in the present system, we tried to apply the time change of r value to the Avrami equation [27,28]. In general, the Avrami equation is expressed by the Avrami exponent, n, and the Avrami constant, G:

$$x_c(t) = x_{cs}[1 - \exp(-Gt^n)] \tag{2}$$

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

$$x_c(t) = r - r_0$$

$$x_{cs} = r_\infty - r_0$$

Table 1
Avrami exponents, rate constants for cold crystallization process, and time constants for cold crystallization process of PBT thin films obtained by monitoring PBT fluorescence. All the PBT films used were prepared on quartz disks by using a spin-coating method and annealed at 40 °C. The heating process of all the films observed was annealed at 340 K for 12 h and jumped up to T_f.

T_f (K)	Avrami exponent	k_{cr} (sec^{-1})	τ_{cr} (min)
360	0.918	4.70×10^{-4}	35.5
365	1.22	5.32×10^{-4}	31.3
370	1.15	5.32×10^{-4}	31.4
375	1.17	5.31×10^{-4}	31.4
380	1.10	6.58×10^{-4}	25.3
385	1.12	7.10×10^{-4}	23.5
390	1.13	8.38×10^{-4}	19.9
395	1.05	9.58×10^{-4}	17.4
400	1.12	1.01×10^{-3}	16.6

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_∞:

$$\frac{r - r_0}{r_\infty - r_0} = 1 - \exp(-Gt^n) \tag{3}$$

In Fig. 4, $\log\{-\ln[1 - ((r - r_0)/(r_\infty - r_0))]\} = \log\{\ln[((r_\infty - r_0)/(r_\infty - r))]\}$ 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 1.05 from the slope by using the least squares method. We fitted all the data to a plot of $\log\{\ln[((r_\infty - r_0)/(r_\infty - r))]\}$ versus $\log t$ and have concluded that n is nearly 1.0 (Table 1), which is nearly the same as the n values obtained for the cold crystallization process of PET films in the same manner [11]. This is the case for one-dimensional growth under the mechanism of heterogeneous nucleation. Thus, the crystallization process has been determined for PBT films prepared by a spin-casting method on quartz disks and by drying at 40 °C (the crystallinity was about 26%).

The value of the Avrami exponent, n, being 1 is quite common for cold crystallization and recrystallization of polymers [29–34].
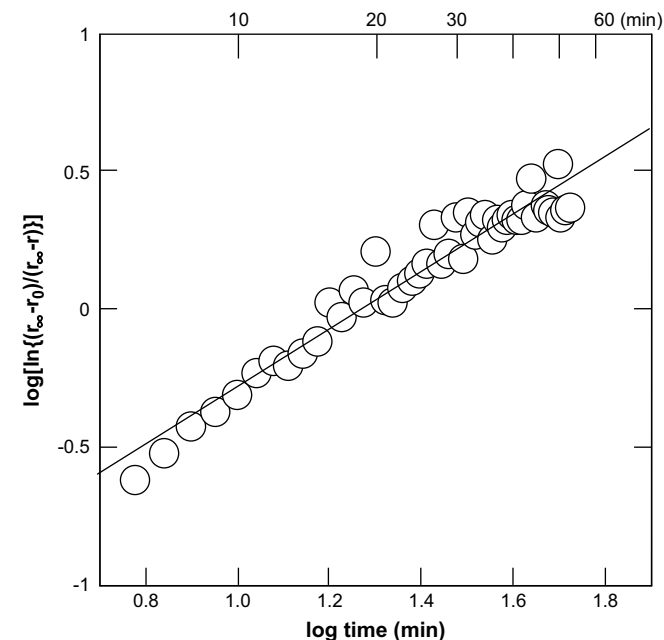
For the polymer solids whose crystallinity percentage is higher, the phenomena of cold crystallization and recrystallization are assumed to involve sub-units formed from a large number of seeds left within the outlined of the original spherulites of polyethylene [29,30] and isotactic polypropylene [31].
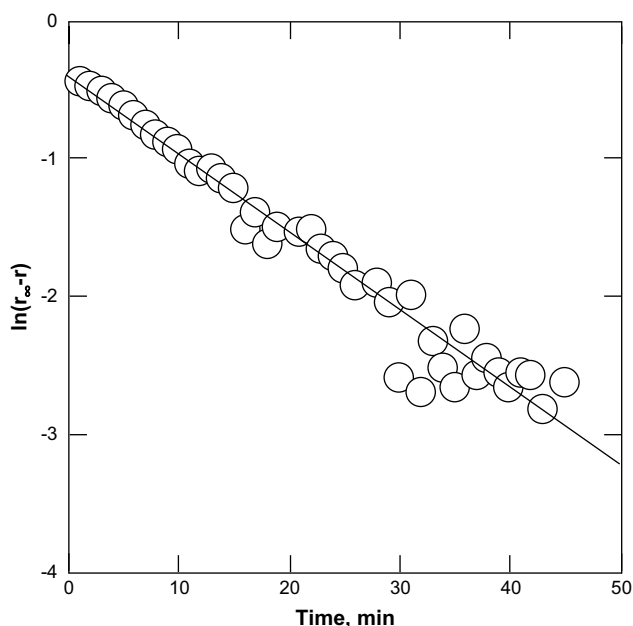
In the case of the poly(ether ether ketone) (PEEK) films being soaked in methylene dichloride and then dried in vacuum to drive off the residual solvent, the exotherm peak temperatures according to the cold crystallization were found to rise compared with those of the untreated PEEK films together with the Avrami exponent, n, being 1.0 to 1.2 [32]. These n values are quite different from the regular cold crystallization of the untreated PEEK ($n = 2.5$–2.6) or those for melt crystallization ($n = 2.5$–3.0) [35]. This is because trace solvent-induced crystallites serve probably as nucleation sites for crystal growth but the microporous nature in the solvent-treated PEEK prevented planar or spherulitic growth to occur.

The cold crystallization for uniaxially oriented fibers of PET [33] and modified PET-co-poly(ethylene glycol) (PEG) [34] also demonstrates the Avrami exponent, n, being 1. In particular, these samples showed two exothermal peaks of d.s.c. curves according to the cold crystallization: the n values for the cold crystallization process taking place at the lower temperatures were 1.0–1.2 while those at the higher temperatures were 2.0–2.2. This means that the two processes are different from each other. The former one is assumed to correspond to the crystallizing from small crystallites, where relatively short parts of some oriented chains are bundled, forming long bundle-like crystallites.

Taking into account the other cold crystallization processes whose Avrami exponent is close to 1, the cold crystallization of thin PBT films on quartz disks prepared by using a spin-casting method is considered to be difficult to grow three-dimensionally due to both the film being thin and a large number of small crystalline sites dispersed over the films. Thus, it is reasonable that its n value shows to be nearly 1.

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

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

Fig. 4. Avrami plot of the results on kinetics of cold crystallization at 395 K. The best fitting line has an inclination of 1.05.

Fig. 5. Fitting of the results at 395 K to a single exponential function. The best fitting line shows τ_{cr} to be 17 min.
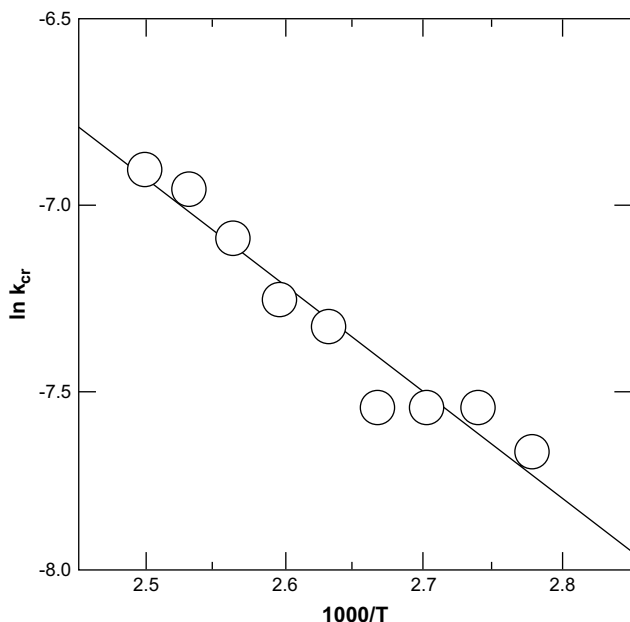
Fig. 6. Arrhenius plot of k_{cr}, rate constant for cold crystallization of PBT films.

where k_{cr} is the rate constant for cold crystallization, and A is constant. Here k_{cr} can be expressed as $k_{cr} = 1/\tau_{cr}$, where τ_{cr} is the time constant for cold crystallization. Fig. 5 shows a plot of $\ln(r_\infty - r)$ versus t for the same data shown in Fig. 4. The data gave a straight line to yield a value of 17.4 min for τ_{cr} at 395 K. In conclusion, the increase in the crystallinity of the PBT films prepared as shown above can be described by a single exponential function in the temperature region where cold crystallization takes place.

We measured the dynamic process of cold crystallization by the same method as shown in Fig. 5 at 360, 365, 370, 375, 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 24 kJ/mol. It is difficult to define the activation energy per mole in the present case. However, this value obtained is quite interesting when we compare this with the values having already obtained so far. We have studied the cold crystallization process of PET films prepared on quartz disks by using the exact same treatment, and have found that an Arrhenius plot of k_{cr} gave a straight line, yielding an activation energy as an inclination of 120 kJ/mol [11]. This large activation energy has strongly suggested that more than a few monomer units of PET must be reoriented in order for cold crystallization to occur. The cold crystallization processes of PET [33] and PET-co-PEG [34] with the Avrami exponent $n \sim 1$ explained above were found to give an activation energy of 80–110 kJ/mol, which is so similar to our value obtained by using the fluorescence measurements. Compared with the values obtained for PET solids, the present value of 24 kJ/mol is so small that this is mainly due to the rotation around carbon–carbon bond of a butylene unit. The highest energy barrier of rotation in n-butane is known to be 25 kJ/mol, which perfectly agrees with our value obtained for PBT by using an Arrhenius plot. This suggests that the cold crystallization observed for the PBT films on quartz disks would take place mainly at the sites near the small crystallites by rotational motion of butylene units. In the case of our PET films [11], the change of the crystallinity was from 11% to 24% by the cold crystallization. The initial low crystallinity might enable a bulky phenylene group to rotate because its motion is not restricted by the chains involved in

a crystalline form, but the initial crystallinity of the present PBT films is high that the growth of crystalline region should be limited. This would urge the crystallization possible to occur only by motion with low activation energy.

The method would be useful for monitoring isothermal crystallization from the melt PBT [36,37], which is one of the topics, but our cryostat has some problems for the use near 500 K, so the present study is confined to the cold crystallization processes with lower activation energy taking place at lower temperatures. The isothermal crystallization of PBT near melting temperature would be our future work.

4. Conclusion

The dynamic process of cold crystallization was directly observed for PBT films by making use of their fluorescence behaviors that the phenylene groups of PBT in a crystalline region show only monomeric fluorescence but the phenylene groups in an amorphous region can exhibit fluorescence of an excimer formed by interacting with another phenylene group. Thus, the fluorescence whose peak is at 365 nm is all from the amorphous region of PBT films, and the ratio of the fluorescence intensity at 320 nm to that at 365 nm can be an effective indicator of crystallinity. The cold crystallization process of the PBT films taking place between 360 and 400 K was monitored using the fluorescence method and found to give the Avrami exponent n being 1, which is relatively common for cold crystallization and recrystallization of polymers.

The present data show that our fluorescent method is quite effective for observing the dynamic cold crystallization process of amorphous PBT 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. Especially, the method is recommended as a simple and quick *in situ* measurement of crystallinity.

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[26] Fig. 6 in the Ref. [12]: the empirical formula is $r = 0.0463x - 0.527$ where x is the crystallinity (%), with the coefficient of determination is 0.98. All the data used were for the PBT films prepared in the same manner and the formula is valid for $26 \leq x \leq 42$.

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