[Transaction]

Alkaline Hydrolysis Kinetics of Poly(ethylene terephthalate) Fibers

Yutaka Kawahara^{*1,*2,#}, Taiyo Yoshioka^{*3,†}, Wataru Takarada^{*4},
Takeshi Kikutani^{*4}, and Masaki Tsuji^{*3}

^{*1}Division of Environmental Engineering Science, Gunma University, 1-5-1, Tenjin-cho, Kiryu 376-8515, Japan

^{*2}The Center for Fiber & Textile Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

^{*3}Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

^{*4}Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 S8-32 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Abstract: Kinetic analysis was applied to investigate the alkaline hydrolysis behavior of poly(ethylene terephthalate) (PET) fibers, e.g., two types of commercial fully oriented yarn (FOY), partially oriented yarn (POY), and high-speed spun (HSS) fibers. The activation energies obtained from the Arrhenius plots using the topochemical hydrolysis reaction rate constants, i.e., the apparent hydrolysis erosion speed for each PET sample, were concentrated within the range of 62.4–69.5 kJmol⁻¹ without respect to their higher-order structures. Therefore, it has been deduced that the reaction rate constant depends on the frequency factor, especially on the steric factor at constant temperature. As for the as-spun HSS fibers with higher crystallinity and lower overall molecular orientation, their rate constants could be well described using the newly defined combined parameter, i.e. the apparent lamellar size normalized in terms of birefringence and crystallinity, which implies that the larger crystallite is more effective in the topochemical hydrolysis erosion of PET fibers while crystallinity and birefringence closely related to the cohesiveness of adjacent molecular chains work negatively. However, the combined parameter proposed could not describe the hydrolysis kinetics anymore after the as-spun HSS fibers were annealed to enhance the packing of amorphous regions.

(Received 11 September, 2015 ; Accepted 1 December, 2015)

1. Introduction

In the morphological investigation of bulk crystalline polymers by using transmission electron microscopy (TEM), surface-etching techniques combined with a surface replica method, which replicates the topography of the sample surface, have often been used [1]. We have applied TEM combined with the alkaline etching technique and surface replica method to clarify the fiber structure of high-speed spun (HSS) poly(ethylene terephthalate) (PET) fibers and have succeeded in the observation of the stacked-lamella-like structure leaning at approximately 40° away from the fiber axis [2].

On the other hand, the alkaline hydrolysis treatment has been world-widely used to the surface

modification of PET fibers for garment use. Because PET itself does not have any hydrophilic groups, the enhancement in hygroscopicity, i.e. the affinity for moisture, is necessary to guarantee the comfort of the resultant PET garments. The alkaline hydrolysis treatment is also effective to give some aesthetic properties, e.g. softness, natural luster by thinning the fiber diameter accompanied with the forming of pits on the surface through the falling of TiO₂ particles mixed as a delustering material in the fibers. The reduction of weight at the treatment in the range of 10-25 % can give silk-like aesthetics to PET fibers [3].

As for the reaction mechanism between the substrate surface and the alkaline etchant, it is well known that the topochemical attack occurs when PET fibers react with alkaline solution, and thereby

corresponding author : Y. Kawahara (E-mail : kawahara@gunma-u.ac.jp)

† Present address : National Institute of Agrobiological Sciences (NIAS), Tsukuba, Ibaraki 305-8634, Japan

the reduction of fiber diameter actually proceeds rectilinearly with the treatment time [4-6]. However, the kinetic study has not been fully made to understand the mechanism of the alkaline hydrolysis reaction with PET so far.

The high-speed spinning techniques are effective for the control of the cohesiveness of molecular chains in amorphous regions where the topochemical attack occurs firstly. In the high-speed spinning process of PET, orientation-induced crystallization starts to occur when the spinning speed exceeds about 4 or 5 km/min. In this region, it is known that the solidification point of the spin line moves upward if cooling of the spin line is enhanced. For this purpose, we prepared the heating or cooling device at the exit of the spinneret. Along with the cooling effect, because of the enhanced molecular orientation in the upper stream, orientation-induced crystallization also can be promoted, and thereby the solidification temperature of molten polymer, i.e. the crystallization temperature, increases [7,8]. This leads to the higher crystallinity and larger crystallite size. Furthermore, the upward movement of the solidification point in the spin line makes the length between the spinneret and solidification point shorter. Spin-line stress at the solidification point is dominated by the integrated air friction and inertia force over a region from the spinneret to the solidification point [8]. Thus, the upward movement of the solidification point makes the solidification stress lower because of the smaller effect of the air-friction force. Birefringence of as-spun fibers is dependent on the spin-line stress at the solidification point [9]. Accordingly, the birefringence of the HSS PET fibers can be reduced markedly as compared with the conventional fully oriented yarn (FOY) produced by spinning and drawing. The high-speed spinning techniques can provide PET fibers with higher crystallinity and lower overall molecular orientation, which means that the amorphous orientation is extremely low for the HSS PET fibers compared with the regular FOY. Such structural difference between amorphous and crystalline regions is preferable not only for the preparation of the surface replica in a crystallite-level resolution for TEM, but also for the control of alkaline hydrolysis reaction rate.

In this study, influence of higher order structures of PET fibers on their alkaline hydrolysis behavior was investigated. For this purpose, we applied the kinetic analysis to this system, and discussed the

relationships between fiber structures, especially for the packing of amorphous regions, and the apparent kinetic parameters, e.g., activation energy, frequency factor, and steric factor.

2. Experimental

2.1 Materials

Four types of the PET fibers were prepared; two types of commercial fully oriented yarn (FOY), partially oriented yarn (POY), and high-speed spun (HSS) fibers. FOYs were supplied from Toyobo Co., Ltd. (Osaka, Japan); the semidull type containing approximately 7 % TiO_2 by weight for delustering, and the experimental bright type free of TiO_2 . POY and HSS fibers were produced by melt spinning using PET pellets with IV of 0.65 dLg^{-1} containing approximately 3 % TiO_2 by weight.

Before the experiments, the FOYs was washed well with diethylether by the Soxhlet extraction method.

2.2 Melt spinning

Molten polymer heated at 290°C was extruded through a spinneret of 1.0 mm diameter at a mass flow rate of 1.5–4.0 g/min per hole and was drawn at a speed of 3 km/min for POY, 5 or 6 km/min for HSS fibers using a take-up device located 330 cm below the spinneret. By attaching heating or cooling device ca.50 cm in length at the exit of the spinneret, the spinning tests by changing the ambient temperature of the zone (heating temperature: 335°C ; cooling temperature: -50°C) were also made. When the line was heated, the symbol H was added to the sample name, and when cooled, the symbol C was added. When the spinning tests were made at room temperature, i.e. without controlling the ambient temperature of the zone, the symbol N was added to the sample name. The sample names are designed in the following manner, e.g. 6C4 means that the spinning speed was 6 km/min, the cooling device was attached, and the mass flow rate 4 g/min per hole.

2.3 Alkaline etching

Alkaline etching was carried out in the aqueous solution of 1.0–2.8M NaOH with 0.1% cetyltrimethylammonium bromide (CTAB) by weight at $40-60^\circ\text{C}$ with mild mechanical agitation [5]. It was confirmed that CTAB had no effect on the morphology of etched surface. CTAB worked just as a surfactant. The amount of etchant was large enough to regard its concentration as constant during the etching

treatment. After the treatment, samples were rinsed thoroughly with distilled water and then air-dried.

2.4 Measurements

The filament diameter was measured with an optical microscope BX60 (Olympus Optical Co., Ltd., Tokyo, Japan). To obtain a reliable value of fiber diameter, the measured diameters from 10 or more filaments for each of the fiber samples were averaged.

To obtain the information on the surface morphology of fibers, SEM observation was performed on a scanning electron microscope S-3000N (Hitachi, Japan) for samples coated with vapor-deposited gold (Au).

Refractive indices parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) to the fiber axis were measured by using an interference microscope (Carl Zeiss, Jena, Germany) equipped with a polarizing filter. The birefringence was calculated as the difference between these two refractive indices.

The crystallinity (X_c) of the fibers was calculated according to the equation :

$$X_c(\%) = (\Delta H_m - \Delta H_c) \times 100 / \Delta H_f, \quad (1)$$

where ΔH_m and ΔH_c are respectively melting endothermic and cold crystallization exothermic enthalpies estimated by using a differential scanning calorimeter (DSC8230, Rigaku Co., Akishima, Japan), and ΔH_f is the heat of fusion assumed to the perfect crystal of PET, 121 J/g [10].

Wide-angle X-ray diffraction (WAXD) of the fibers was measured on an X-ray diffractometer RINT 2100FSL (Rigaku Co., Akishima, Japan) with an imaging plate RAXIS DS3 by using the $\text{CuK}\alpha$ radiation which was monochromatized with graphite and collimated with two pinholes. The sample used for X-ray diffraction were prepared by forming the fibers into a bundle. By adjusting the weight of the sample, the mass of the samples irradiated by the X-rays was kept approximately constant. The crystallite sizes L_{010} , L_{-110} , L_{100} , and L_{-105} were determined from the 010, -100, 100, and -105 diffraction peaks, respectively, by using the Scherrer equation (the shape factor was 1.0).

The degree of orientation, Π , for the crystallites parallel to the fiber axis was determined using the following equation :

$$\Pi = (\pi - \gamma) / \pi, \quad (2)$$

where γ in radians is the full width at half maximum intensity of azimuthal intensity distribution of -110 diffraction peak.

3. Results and discussion

3.1 Etching behaviors

Figs. 1, 2 show the surfaces of POY and FOY (semidull type) etched for different time-periods, respectively. It is seen that the etched surfaces for those fibers are fairly smooth as the morphologies reported previously except for the pits generated by fall of TiO_2 particles [5,11]. The shape of pits, however, is quite different between POY and FOY. The pits of FOY are of an ellipsoidal shape whose long axis is parallel to the fiber axis although the TiO_2 particles are almost spherical. Similar morphologies have been recognized previously [5]. The formation mechanism

Fig. 1 SEM photographs of hydrolyzed POY-PET fibers ; before (a), and after treatment with 2.0 M-NaOH at 50°C ; (b) diameter loss =21% ; (c) diameter loss=52%.

Fig. 2 SEM photographs of hydrolyzed FOY-PET (semidull type) fibers; before (a), and after treatment with 2.0M-NaOH at 50°C; (b) diameter loss =14%; (c) diameter loss=38%.

will be understood considering the effect of strong flow in the spinning process, which produces low-density regions, such as a void, a region consisting of weakly oriented amorphous chains, and a region consisting of un-oriented amorphous chains at the upper and lower vicinities of each TiO_2 particle. In addition, a drawing process during (or after) spinning of PET containing TiO_2 particles might also promote the formation of low-density regions at the upper and lower vicinities of each TiO_2 particle. By etching, therefore, pits of an ellipsoidal shape will be left after fall of TiO_2 particles. Moreover, in the case of FOY (bright type, free of TiO_2), such pits could not be observed and the etched surface was still fairly

smooth after thinning by the alkaline etching [5]. Therefore, it is clear that the formation of pits on the etched surface of FOY is closely related to the fall of TiO_2 particles.

Fig. 3 SEM photographs of hydrolyzed HSS(5km/min)-PET fibers; before (a), and after treatment with 2.0M-NaOH at 50°C; (b) diameter loss=14%; (c) diameter loss=53%.

On the other hand, the pits observed on the surface of the etched POY are of a spherical shape. The lower crystallinity and birefringence for the POY (see Table 1) suggest that the fiber is composed of amorphous chains which are weakly oriented in the direction of fiber axis. Thus, it is difficult to expect the strong effect of flow in the spinning process to generate low-density regions at the vicinities of each TiO_2 particle. Therefore, pits of a spherical shape were left after fall of TiO_2 particles. However, when we focus on the number of pits on the etched surface, the pits on POY predominate over the FOY although the content of TiO_2 in the FOY is about twice larger

than that of the POY. This result leads to a conclusion that some of the pits on the POY were formed due to the “density modulation” which affect the alkaline etching reaction independently of falling of TiO_2 particles.

Fig. 3 shows the surfaces of the HSS fibers etched for different time-periods. The long grooves that run parallel to the fiber axis are considered to be formed independently of the presence of TiO_2 particles. It is reasonable to assume that chemical etching of polymer bulks occurs preferentially in the region of lower density. Therefore, in the case of HSS fibers, a density modulation is considered to be formed in the direction perpendicular to the fiber axis, and it is probable that HSS fibers tend to have a fibrillar structure.

Murase [12] applied the alkaline hydrolysis treatment to the HSS fibers produced at a take-up velocity of 10 km/min and obtained a SEM photograph of the hydrolyzed fiber surface with many fine “scratch-like” striations running parallel to the fiber axis, and then concluded that the striations were formed through the removal of the regions between the microfibrils although there has been no direct evidence proving the formation of microfibrils in PET fibers so far. We once applied the alkaline hydrolysis treatment to the HSS-PET fibers coded as 6C4 in Table 2 and investigated the surface morphologies using TEM combined with the two-stage replica method, and succeeded in observing the stacked-lamella-like structure leaning at about 40° away from the fiber axis [2]. However, any microfibrillar entities could not be recognized at a level of TEM resolution.

The possible formation of the inclined arrays of adjacent lamellae by the high-speed spinning has already been proposed by Shimizu et al. [13] from a mathematical simulation on the basis of the experimentally obtained X-shaped four-point SAXS patterns. In addition, Shimizu et al. [13] have estimated the width of microfibrils from the intensity maxima on the equatorial streak of the SAXS patterns. Instead, we have reported that the equatorial streak should be ascribed mainly to the scattering from extended-chain crystal (so-called shish crystals) [2].

The formation of long grooves in Fig. 3 will be understood by applying a hierarchical fibrillar texture in LCPs (liquid crystalline polymers) [14]. When the similar alkaline etching was applied to the HSS-poly

(ethylene 2,6-naphthalene dicarboxylate) (PEN) fibers, much clearer grooves could be recognized than those observed in HSS-PET fibers [15]. PEN has the naphthalene ring which is stiffer than the benzene ring of PET, and hence PEN has a molecular structure more similar to the structure of LCPs than PET. A hierarchical structure, which is similar to the hierarchical structure in LCPs fibers, may be formed in the HSS-PEN fibers and also in the HSS-PET fibers.

Fig. 4 Etching behavior of FOY-PET fibers (semidull type) in an aqueous solution of 2.0 M NaOH at 40°C .

Compared with the HSS fibers, it seems that the FOYs tend to have higher birefringence values, but have smaller crystallite sizes although the degree of orientation for the crystallites and crystallinity are ranging within similar values of HSS fibers (see Table 1). This means that the molecular orientation in the amorphous region of FOYs is extremely higher than that in the HSS fibers. In other words, the density difference between the crystalline and amorphous regions of the FOYs is much smaller than that of the HSS fibers. Therefore, the alkaline etching reaction may occur almost evenly on the surface of FOYs due to the low density difference. Overall, it can be deduced that any grooves, which indicate the existence of fibrillar structure, did not appear on the etched surface of FOY fibers even if fibrillar structure was formed.

Fig. 4 shows a decrease in fiber diameter of the FOY (semidull type) in the course of the etching time in an aqueous solution of 2.0 M NaOH at 40°C . It is seen that the reduction of fiber diameter is well expressed by the rectilinear relationship similarly as in the previous works [4-6]. In the cases of POY and HSS fibers, the plots of diameter change vs. treatment time also became rectilinear. The rectilinear relationship can be explained by assuming the topochemical attack although the etched surface may have unevenness at a level of SEM resolution.

However, when the alkali etched surface of HSS fibers was observed using a TEM, the surface was fairly smooth [11]. Therefore the slope k in Fig. 4 can be assumed as the apparent hydrolysis reaction rate constant, i.e., the apparent topochemical hydrolysis erosion speed. Moreover, the k value extrapolated to the y axis was calculated to be 0.39 micrometer, which is small enough to regard as negligible considering an allowable experimental error. Therefore, it can be assumed that the thinning of fiber has started almost topochemically just after the immersion of fiber into the etchant. The hydrolysis reaction rate constants, k , are listed in Table 1.

Table 1 Structural Parameters for the Various PET Fibers Used for the Estimation of Activation Energy at the Alkaline Etching.

Sample code	FOY (Semidull)	FOY (Bright)	3N3 (POY)	6N1.5 (HSS)
As-spun				
Crystallinity (%)	36.1	44.4	~0	41.1
Crystallite size (nm)				
010	4.80	4.77	-	5.84
-110	4.19	3.97	-	4.81
100	3.08	3.04	-	4.85
-105	4.94	4.65	-	6.57
Degree of orientation of crystallite	0.924	0.913	-	0.944
Birefringence	0.1306	0.1387	0.0428	0.1131
Reduction rate constant k^*	1.15	1.79	10.61	6.11
Activation energy (kJ/mol)	66.7	64.8	69.5	62.4

*: The reduction rate constant k was measured in a NaOH aqueous solution of 2.0 M at 50 °C.

The k value of amorphous POY with the lowest birefringence was 6-9 times greater than those for FOYs. On the other hand, the k value of crystalline HSS with fairly disordered amorphous regions was 3-5 times greater than those for FOYs although the crystallinities for these fibers were at about 40 % (see Table 1).

3.2 Kinetic analysis

If diameter of a filament reduces topochemically as shown in Fig. 4, the fiber diameter at time t defined as $D(t)$ can be expressed by the equation as follows [16].

$$D(t)/t = -k, \quad (3)$$

The dependence of the hydrolysis reaction rate constant, k , on the absolute temperature, T , can be expressed by the Arrhenius's equation as follows [17].

$$k = A \exp\{-E/(R \cdot T)\}, \quad (4)$$

Fig. 5 Arrhenius plots of FOY-PET fibers (semidull type) etched in a NaOH aqueous solution.

where E is the heat of activation, A the frequency factor, R the universal gas constant.

Fig. 5 shows the Arrhenius plots for the FOY (semidull type) measured changing the concentration of alkaline etchant. Each plot between $\ln k$ versus T^{-1} could give a straight line within an allowable experimental error. The gradient and extrapolated values correspond to the activation energy, E , and the frequency factor, A , respectively. Similar plots could be obtained for the other PET fibers. The activation energies averaged ($n=3$) are listed in Table 1. When the activation energies are compared between the two types of FOYs, a slight difference can be recognized. The FOY (semidull type) with a little smaller crystallinity and birefringence showed a somewhat larger activation energy. However, the difference was no more than 3 %, which can be assumed within the allowable experimental error. On the other hand, when the activation energies between POY and HSS fibers are compared, it is seen that the difference in crystallinity had hardly affected their activation energies although the alkaline etching treatment can reveal the higher-order structure of PET based on the difference in the hydrolysis speed between crystalline and amorphous regions [2]. In the previous work [18] on the estimation of activation energy in the alkaline hydrolysis reaction of PET fibers, the value of 64.9 kJ/mol was reported.

It can be concluded, at least, that the higher-order structure can hardly affect the activation energy of PET for the alkaline hydrolysis reaction, and therefore at constant temperature the apparent hydrolysis reaction rate constant, k , depends on the frequency factor, A . The frequency factor can be expressed as the product of the steric factor and the collision frequency. In this study, the collision frequency is simply dependent on the concentration of alkaline etchant. Thus, the frequency factor will

depend on the steric factor. In general, the steric factor can be interpreted as the ratio of the cross section for reactive collisions to the total collision cross section. Therefore, we should focus on the cohesiveness of molecular chains especially in amorphous regions where the collision between the substrate polymer and alkaline etchant mostly occurs rather than the well packed crystalline blocks.

Table 2 Structural Parameters for the High-speed Spun PET Fibers.

Sample code	5N4	6C4	6H4	6C1.5	6N1.5
As-spun					
Crystallinity (%)	36.7	46.7	46.0	49.8	41.1
Crystallite size (nm)					
010	4.47	5.46	5.10	5.93	5.84
-110	4.28	4.55	4.90	4.78	4.81
100	3.01	4.17	3.79	4.68	4.85
-105	4.59	5.87	5.51	6.12	6.57
Degree of orientation of crystallite	0.891	0.926	0.924	0.936	0.944
Birefringence	0.0879	0.1151	0.1190	0.1024	0.1131
Reduction rate constant k^*	4.95	2.99	2.99	5.47	6.11
After the treatment in pressurized water at 130 °C					
Crystallinity (%)	52.4	48.9	48.5	45.2	45.3
Crystallite size (nm)					
010	4.95	5.62	5.28	5.83	6.09
-110	4.45	4.61	4.43	4.68	4.88
100	3.61	4.27	4.00	4.51	5.30
-105	4.60	5.65	5.29	5.97	6.17
Degree of orientation	0.911	0.922	0.924	0.914	0.931
Birefringence	0.1265	0.1314	0.1326	0.1053	0.1341
Reduction rate constant k^*	0.80	0.99	0.99	0.79	1.10

*: The reduction rate constant k was measured in a NaOH aqueous solution of 2.0 M at 50°C.

In order to investigate the influence of fiber structure on the steric factor, several types of HSS-PET fibers with different structural parameters were prepared changing the spinning conditions. Structural parameters for the as-spun HSS fibers are listed in Table 2. It is seen that the as-spun HSS fibers have higher crystallinities and lower birefringence values as compared with those of FOYs although the degrees of orientation of crystallite were in the similar range (see Table 1). Therefore, it is seen that the birefringence in amorphous regions of as-spun HSS fibers was fairly small as compared with the FOYs. This peculiar fiber structure of HSS fibers can be obtained by controlling the orientation-induced crystallization rate and the solidification point on the spin line [8].

The apparent hydrolysis reaction rate constants, k , for the as-spun HSS fibers were measured in an aqueous solution of 2.0 M NaOH at 50 °C (see Table 2). Those fibers showed much larger k values than FOYs

but became smaller than the amorphous POY.

For not only alkaline etching but also permanganic etching [16] or aminolysis reaction [19], it can be expected that the topochemical erosion will start from the amorphous surface firstly. Because the apparent hydrolysis reaction rate constant has become the largest for the amorphous POY. However, the correlation coefficient between an amorphous content, i.e., $1-X_c$, and k for the as-spun HSS fibers resulted in no more than 0.318. This means that the amorphous content is not a predominant factor. To understand this inconsistency, we assumed the hydrolysis reaction kinetics of the as-spun HSS fibers as follows.

Fig. 6 Relation between the combined structural parameters of HSS-PET fibers and reduction rate constant k measured using an aqueous solution of 2.0 M NaOH at 50°C: diamond, as-spun; square, treated in hot pressurized water at 130°C.

The cohesiveness of molecular chains fundamentally predominates the steric factor, which means that the hydrolysis decomposition starts in the disordered amorphous regions firstly. Concerning the difference in the cohesiveness of molecular chains between crystalline and amorphous regions, the difference will become more marked for as-spun HSS fibers than FOYs. Lower packing of amorphous regions of as-spun HSS fibers will bring about more preferential erosion of amorphous chains. As the result, the residual blocks of the crystallites will emerge on the fiber surface as a result of the erosion of amorphous chains surrounding crystallites. Such crystallite blocks will fall like TiO_2 particles from the surface of fiber easily as the hydrolysis treatment proceeds. Such hydrolysis erosion mechanism will accelerate the thinning of fiber markedly. On the basis of this assumption, the larger crystallite is more effective in the hydrolysis erosion of PET fibers. Fundamentally, however, both crystallinity and

birefringence closely related to the cohesiveness of adjacent molecular chains work negatively against the hydrolysis erosion. Here, we would like to propose the combined parameter, $L_{-105} \times L_{010} / \Delta n / X_c$, to understand the relationship between the higher-order structure of the as-spun HSS fibers and their hydrolysis rate constants qualitatively. This parameter is seemingly equal to the apparent lamellar size normalized in terms of birefringence and crystallinity. Thus, this parameter is a structural one defined from an empirical viewpoint. The relationship between the newly proposed parameter and the rate constant is shown in Fig. 6. The correlation coefficient of 0.913 was obtained. However, the combined parameter proposed could not describe the hydrolysis kinetics anymore after the as-spun HSS fibers were treated in pressurized water at 130 °C. The correlation coefficient decreased to 0.035. Birefringence and crystallinity of the treated fibers are listed in Table 2. It is seen that both the birefringence and crystallinity increased remarkably except for 6C1.5, which means the increase in the cohesiveness of molecular chains in the amorphous regions. Therefore, the hydrolysis rate constant were lowered to 0.8–1.1 micrometer/h. As for 6C1.5, structural modification by the treatment was accompanied by the decrease in crystallinity. It is probable that the rearrangement of molecular chains occurred not only in the amorphous regions but also in the crystallites with large internal strains. Thus, the birefringence increased after the annealing even though the destruction of crystallites occurred.

4. Conclusions

Kinetic analysis was applied to investigate the alkaline hydrolysis reaction of PET. The activation energies obtained from the Arrhenius plots for the PET fibers with different structural parameters were concentrated within the range of 62.4–69.5 kJmol⁻¹, suggesting that the apparent hydrolysis reaction rate constant depends on the frequency factor, especially on the steric factor at constant temperature. As for the as-spun HSS fibers with higher crystallinity and lower overall molecular orientation, their rate constant could be well described using the combined parameter, $L_{-105} \times L_{010} / \Delta n / X_c$, which means that the larger crystallite is more effective in the apparent hydrolysis erosion of PET fibers while fundamentally both crystallinity and birefringence closely related to

the cohesiveness of adjacent molecular chains work negatively. However, the combined parameter proposed could not describe the hydrolysis reaction anymore after the as-spun HSS fibers were heat-treated deeply by pressurized water at 130 °C.

References

1. M. Tsuji, "Comprehensive polymer science and supplement, Vol. 1: Polymer characterization," (C. Booth, C. Price. Eds.), Pergamon, Oxford, pp. 785-840 (1989).
2. T. Yoshioka, Y. Kawahara, T. Kikutani, and M. Tsuji, *J. Macromol. Sci.-Phys.*, **48**, 155-162 (2010).
3. B. M. Latta, *Text. Res. J.*, **54**, 766-775 (1984).
4. T. Hashimoto, *Sen'i Gakkaishi*, **14**, 510-514 (1958).
5. M. J. Collins, S. H. Zeronian, and M. Semmelmeier, *J. Appl. Polym. Sci.*, **42**, 2149-2162 (1991).
6. Y. Kawahara, T. Yoshioka, K. Sugiura, S. Ogawa, and T. Kikutani, *J. Macromol. Sci.-Phys.*, **40**, 189-197 (2001).
7. T. Kikutani, Y. Kawahara, T. Matsui, A. Takaku, and J. Shimizu, *Seikei-Kakou*, **1**, 333-339 (1989).
8. Y. Murase and A. Nagai, "Melt spinning. In Advanced fiber spinning technology," (T. Nakajima. Ed.), Woodhead Pub. Ltd., Cambridge, pp. 25-64 (1994).
9. I. Hammana, M. Matsui, and S. Kato, *Melliand Textilber.*, **50**, 382-388 (1969).
10. R. C. Roberts, *Polymer*, **10**, 113-116 (1969).
11. Y. Kawahara, T. Yoshioka, M. Tsuji, M. Ohara, S. Kohjiya, and T. Kikutani, *J. Macromol. Sci.-Phys.*, **39**, 701-710 (2000).
12. Y. Murase, *Sen'i Gakkaishi*, **47**, P-564-P569 (1991).
13. J. Shimizu and T. Kikutani, *J. Appl. Polym. Sci.*, **83**, 539-558 (2002).
14. L. C. Sawyer and M. Jaffe, *J. Mater. Sci.*, **21**, 1897-1913 (1986).
15. T. Yoshioka, M. Tsuji, Y. Kawahara, T. Kikutani, and S. Kohjiya, *Polymer*, **46**, 1886-1892 (2005).
16. T. Yoshioka, M. Tsuji, Y. Kawahara, S. Kohjiya, and T. Kikutani, *Sen'i Gakkaishi*, **58**, 268-272 (2002).
17. e.g., K. J. Laidler and H. Eyring, "The theory of rate processes," McGraw-Hill Book Co., Inc., New York (1941).
18. S. Kuriyama and M. Korematsu, *Sen'i Gakkaishi*, **16**, 110-114 (1960).
19. M. S. Ellison, L. D. Fisher, K. W. Alger, and S. H. Zeronian, *J. Appl. Polym. Sci.*, **27**, 247-257 (1982).