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4 -아세톡시벤조산 4'-아세톡시페닐과 이소프탈산으로부터 합성한 공중합체의 고상중합 및 섬유 성질의 변화

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Kinetic Study and Fiber Properties Changes on Solid State Polymerization of a Copolyester Derived from 4'-Acetoxyphenyl-4 -Acetoxybenzoate and Isophthalic Acid

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요 약 : 전방향족 폴리에스테르 섬유의 고상중합을 열중량분석법(TGA)으로 연구하였다. 열처리중의 감량은 말단기간의 반응으로 생기는 초산의 생성때문임을 알았으며, 고상중합은 2차반응으로 활성화 에너지가 약 100KJ / eq이었다. 최종 열처리전에 선처리를 함으로써 섬유의 융착을 방지할 수 있을 뿐 아니라 고상중합속도 및 고상중합율을 증가시킬 수 있음을 알았다. 섬유의 방사 조건이 최적 조건이 되지 못한 이유로 섬유의 물성이 아주 우수하지는 않지만, 열처리 전에 이미 PET 수준은 되었고 열처리에 의해 큰 물성의 향상을 보여주었다. 또한 열처리를 단계적으로 하였을때 더 큰 물성의 향상을 보였다.

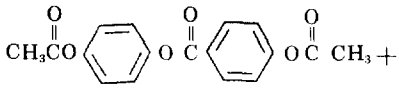
Abstract : Solid state polymerization of a wholly aromatic polyester fiber was studied by thermogravimetric analysis(TGA). The weight loss during the thermal treatment came mainly by the evolution of acetic acid produced by the reaction between two reacting chain ends. Solid state polymerization was proved to be 2nd order reaction with the activation energy of about 100KJ / eq. It was found that preheat-treatment not only prevented the sticking of the fibers but also enhanced rate of reaction and also the extent of solid state polymerization. As spun fibers already showed the physical properties comparable to those of PET even though the spinning conditions were not optimized. Fiber properties were greatly enhanced by the thermal treatment. The pre-heat treated fiber showed higher tenacity than directly heat treated one.

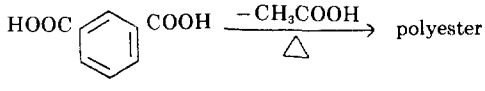
INTRODUCTION

Recently, research activities on wholly aromatic polyesters are increasing, especially on liquid crystalline polyesters.[1~6] Because of their high melting points and melt viscosities, wholly aromatic polyesters with only moderate molecular weights are processed first and solid state polymerization by thermal treatments are followed to enhance their properties. Thermal treatment of polyesters increases the molecular weight and the degree of crystallinity leading to improved physical properties.[7~10]

There are several reports about the solid state polymerization of the conventional fiexible polymers,[11~14] but there is no similar study reported for the rigid chain thermotropic aromatic polyesters. In this study, a copolyester fibers prepared from 4'-acetoxyphenyl 4 -acetoxy benzoate and isophthalic acid via melt transesterification polymerization was subjected to solid-state thermal treatment under N_2 atmosphere. The polymer was first spun into fibers and treated at three different temperatures of 250, 270, and 290℃. The weight loss followed by TGA method was kinetically analyzed. The results were compared with those obtained from the fiber that has been pre-treated for 1 hr at 200℃ and then 2 hrs at 220℃ before the final annealing at the same three different temperatures. Kinetics were analyzed by the well-known time lag method.[15~17]

Polymer was prepared by the following equation.





EXPERIMENTAL

Synthesis of 4'-acetoxyphenyl 4-acetoxybenzoate

p-acetoxybenzoyl chloride, synthesized from 180.17g (1.00mole) of *p*-acetoxybenzoic acid and excess $SOCl_2$, was dissolved in 500ml of dry toluene. In a seperate flask 130.0g (1.18mole) of hydroquinone was dissolved in a mixture of 123ml of acetic anhydride (1.30mole) and 400 ml of dry toluene. This solution was refluxed for 4 hours and cooled to room temperature. The crude product, 4-acetoxyphenol, was collected on a filter and dried. This crude 4-acetoxy phenol was dissolved in 500ml of dry pyridine, to which the p-acetoxybenzoyl chloride solution was added dropwise with vigorous stirring. The reaction mixture was allowed to stand overnight at room temperature with stirring. The whole mixture was evaporated to dryness in a rotatory evaporator. And then the solid residue was washed with enough methanol, 1M sodium bicarbonate solution and distilled water. 4'-acetoxyphenyl 4 -acetoxybenzoate formed was extracted with ethanol. The ethanol solution was poured into a large amount of water precipitating the product, which then was recrystallized twice from acetone. Its melting point was found to be 161℃ (literature value 162℃[18]) and the yield was 53%.

Polymer Preparation

In a 2 gallon autoclave equipped with a condenser, an agitator, a nitrogen purge line and torque (K_w) measuring and recording devices, 348.87g (1.11mole) of 4'-acetoxyphenyl 4 -acetoxybenzoate, 184.55g (1.11 mole) of isophthalic acid and 30ml of acetic anhydride were charged. The reactor was purged with dry nitrogen. The temperature was raised from room temperature to 250℃ in the period of 1 hour followed by a gradual raise to 280℃ while removing acetic acid that was produced by the reaction of the monomers. The temperature was further raised to 330℃ with reducing the pressure to 0.1 torr. After the torque had reached

a certain value (K_w) the polymer melt was extruded at room temperature to water bath and cut into chips.

Spinning of Fibers

The polyester thus prepared was dried for 8 hrs in a vacuum (10torr) oven at 140℃. The schematic diagram of a spinning apparatus is shown in Figure 1. The dry polymer was placed in the melting chamber and heated to 350℃. The spinnerette had 7 holes with a diameter of 0.5mm and L/D(length/diameter) ratio of 5. The spinning pressure exerted by the piston was 60Kg/cm^2 and the spin-stretch factor calculated from the ratio of the spinnerette diameter to fiber diameter was about 4. Take-up speed varied from 240 to 420 m/min.

Solid State Polymerization

The fibers were washed with acetone to remove finish oil and dried in a vacuum oven at 140℃ for 5 hours before solid state polymerization. TGA method was employed[19] to follow the weight loss caused by the evolution of the acetic acid formed by solid state polymerization.

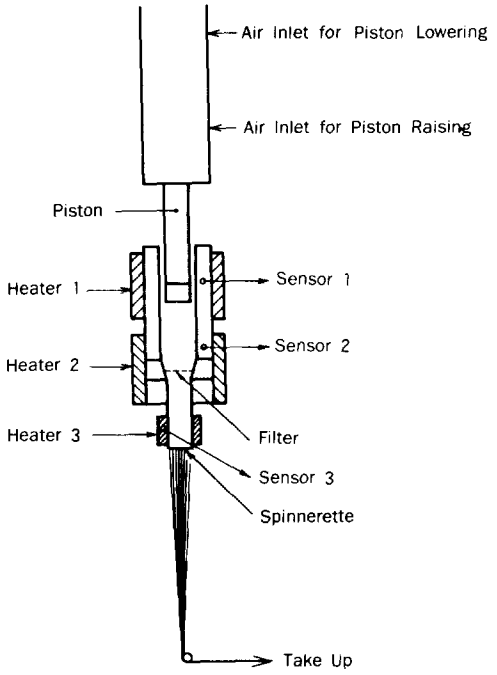


Fig. 1. Schematic diagram of spinning equipment.

Two series of experiments were performed : In the first experiment the temperature of the fiber was raised to 250℃ or 270℃ or 290℃ at a heating rate of 20℃/min with the nitrogen flow rate of 50ml/min and then maintained at that temperature for a desired period of time. In the second experiment the fibers were preheattreated for 1 hour at 200℃ followed by 2 hours heat treatment at 220℃ before the final reaction at 250℃ of 270℃ or 290℃ for a desired period of time. The whole scale of the TGA chart was adjusted to represent 5% weight loss instead of the usual 100% scale.

CHARACTERIZATION

To confirm the structure of the reaction product, all of the materials evolved from the solid state polymerization chamber were condensed and analyzed by high pressure liquid chromatography(Water's, Model-244), FT-IR (FTS-20, Digilab) and FT-NMR(WP-80-SY, Bruker) spectroscopy.

Solution viscosities were measured at 30℃ in a Cannon-Ubbelohde viscometer using a p-chlorophenol/pentafluorophenol/chloroform (3/3/4 by volume) mixture. The concentration of the solution was 0.1g/100ml. Thermal analysis was performed on a DSC-2(Perkin-Elmer) instrument with scanning auto zero at a heating rate of 10℃/min. The heat of fusion and temperature were calibrated against the indium standard. All of DSC runs were performed under a dry N_2 atmosphere.

The crystalline properties were examined by an X-ray diffractometer (D-MAX IIIB, Rigaku) with Ni-filtered CuKα radiation at a voltage of 35K, current of 15 mA and scan speed of 1°/min, respectively. Mechanical properties of the fibers were measured on an Instron (Instron Ltd. Model 1123). The length of the sample was 25cm and stretching speed was 25cm/min.

RESULTS AND DISCUSSION

Polymerization and General Properties of the Polymer

The reaction mixture was turbid in the beginning of the reaction, but soon became a transparent solution. As polymerization was continued the melt again became turbid due to the formation of liquid crystalline phase as the the molecular weight of the polymers formed became high enough.

The inherent viscosity of the original polymer was 0.76. The glass(T_g) and melting transition temperatures(T_m) were 134.9℃ and 312.4℃, respectively. Further characterization of the polymer was reported elswhere.[20]

Solid State Polymerization

The solid state polymerization reaction occurs through the chemical reaction between $-COOH$ and $-OCOCH_3$ terminal groups in the polymer chains by ester exchange reaction. There may be some other side reactions beside this main reaction. Two examples are anhydride formation between two carboxylic acid end groups and ester exchange reactions involving ester groups in the backbone. But main reaction was the acetic acid forming ester exchange reaction, which was proved by the analysis of the evolved products.

Because of the difficulties in the determination of the chain end concentrations and molecular weights, etc., the kinetics was followed by the weight loss data collected by TGA during the solid state polymerization. The assumptions we made are as follow :

1. The two kinds of terminal groups exist in an equal number.
2. The reaction is second order.
3. The reactivities of the same type terminal functional groups are equal.
4. The infinite weight loss is taken as the initial functional group concentration that can react.

First assumption can not be proved and probably incorrect. Although the polymer was prepared from the equimolar dicarboxylic acid and diacetate monomers, there might have been a preferential loss of one component during polymerization. For the sake of the simplicity, however, this precondition was assumed to be true. The second assumption can be verified easily by the experimental data. The third assumption has been well proved in step-growth polymerizations. The fourth assumption is based on the consideration that all of the chain ends can not react in solid state reaction. What can react must be in the same region where the two chain ends can collide. The kinetic equation[15] used for second order reaction was

$$\lambda - \lambda' = a \cdot k(t' \cdot \lambda' - t \cdot \lambda) - a \cdot k \cdot \lambda_\infty \cdot \Delta t$$

where λ is weight loss at time t, a the initial concentration of chain ends that can participate in the reaction, k reaction rate constant and λ_∞ weight loss at infinit time, respetively. The corresponding quantity of λ at t' is λ and Δt equals $(t'-t)$. Consequently, a plot of the quantities of $(\lambda - \lambda')$ against those of $(t' \cdot \lambda' - t \cdot \lambda)$ should be linear and has a slope of "$a \cdot k$". The value of "a" must be known to obtain "k". From the intercept "λ_∞" can be calculated. The rate constant and activation energy can be calculated assuming that the initial concentration, a, is equal to λ_∞ obtained from such a kinetic analysis. Initial concentration, a, was calculated using the following equation :

$$a = \frac{(\lambda_\infty - \lambda_0) \times \text{density of fiber}}{\text{molecular weight of acetic acid} \times 100} \times 1{,}000 \text{ mole} / l$$

The results of weight loss measurment during the solid state polymerization are summerized in Table 1. Representative TGA thermograms are shown in Fig. 2. According to this figure the pretreated fiber shows higher degree of weight loss than the directly heat-treated fiber.

Table 1. Weight Loss with Time

Time. hr	250℃	270℃	290℃	@+250℃*	@+270℃*	@+290℃*
0	0.04	0.20	0.30	0.64	0.85	0.85
1	1.20	1.83	2.40	1.41	2.75	2.75
2	1.67	2.29	2.69	1.84	2.97	2.97
3	1.92	2.48	2.83	2.10	3.13	3.13
4	2.08	2.60	2.91	2.26	3.25	3.25
5	2.20	2.69	2.98	2.37	3.34	3.34
6	2.27	2.73	3.00	2.46	3.40	3.40
7	2.35	2.79	3.06	2.50	3.46	3.46
8	2.40	2.83	3.08	2.58	3.51	3.51
9	2.44	2.84	3.13	2.61	3.57	3.57
10	2.47	2.87	3.15	2.65	3.61	3.61
11	2.50	2.90	3.18	2.68	3.66	3.66
12	2.52	2.94	3.21	2.74	3.69	3.69
13	2.55	2.95	3.23	2.75	3.70	3.70
14	2.57		3.26	2.77	3.74	3.74
15	2.59		3.28	2.81	3.75	3.75
16	2.61		3.30	2.85		

*@ means preheat-treatment at 200℃ for 1 hr and 220℃ for 2 hr.

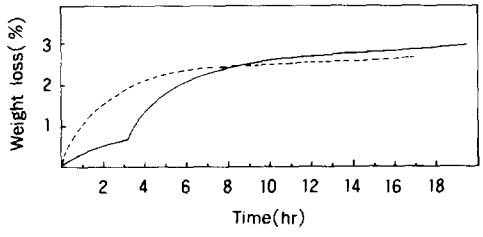


Fig. 2. Weight loss during solid state polymerization at 250℃. The solid line is for the sample treated at 250℃ after pretreatment at 200℃ and 220℃ and the broken line is for the sample that was treated at 250℃ without pretreatment.

The weight loss after 16 hours heat treatment at 250℃ was 2.61% for the fiber treated in one step, whereas it was 2.85% for the fiber pre-annealed for 1 hr at 200℃ and for 2hr at 220 ℃. The weight loss during this pre-treatment was about 0.6 weight%. It was confirmed by the FT-IR and FT-NMR spectroscopy that the weight loss came about practically quantitatively from evolution of acetic acid.

Since only the chain ends in the amorphous region should be close enough to each other and responsible for the solid state reaction being considered here, our observation implies that preheat-treatment makes the fibers contain higher concentration of reactive chain ends in the amorphous region. This assumption is supported by the fact that solid state polymerization is conducted below T_m of crystalline region and, therfore, the chain ends in the crystalline region are immobile and locked in place. This makes them unreactive. The preheat-treatment certainly causes larger number of chain ends come together forming domains where the polar functional groups with higher degree of mobility are localized.

In order to see whether this reaction follows second order reaction kinetics, a plot of $1/[\lambda_\infty - \lambda]$ against reaction time was attempted (Fig. 3). All of the three plots reveal excellent linear relationships, proving that the reactions are indeed of second order.

Change in Morphpology During Solid State Polymerization

Crystalline properties of the fibers before and after heat-treatment are tabulated in Table 2. The preheat-treated fibers have higher degree

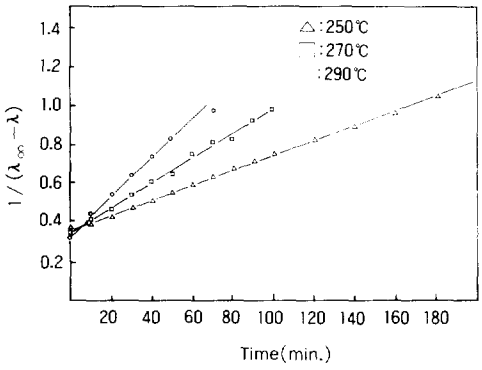


Fig. 3. Plot of $1/(\lambda_\infty - \lambda)$ vs. reaction time.

of crystallinity and larger apparent crystal size than directly heat-treated fibers.

Solid state polymerization proceeded to a minor extent increasing inherent viscosity number from 0.76 only to 0.78(0.6% wt. loss) when preheat-treatment was performed for 1 hour at 200℃ and then again 2 hours at 220 ℃. Degree of crystallinity(DC) did not increase when annealed at 200℃. Consequent heat treatment at 220℃, however, resulted in substantial enhancement in DC from 22 to 43%. This implies that during preheat-treatment at 200℃

Table 2. Change of Fiber Properties by Heat Treatment

	η	Melting Range ℃	ΔH_m joule / g	T_m*a ℃	DC %	ACS*b nm
as-spun	0.76	275.1 - 316.9	0.41		22	3.2
heat-treatment at 200℃ 1hr	0.76	275.5 - 316.8	0.38		23	4.0
Pre-treatment at 200 & 220℃	0.78	351.3 - 336.6	4.10		43	6.3
heat-treatment at 250℃ 1hr	0.76	299.4 - 321.8	2.70		40	3.2
2	1.38	301.6 - 334.4	3.82		40	4.8
3		233.3 - 332.2	3.91		41	5.7
5		304.3 - 332.2	3.92		44	6.6
6	1.64	306.5 - 334.4	4.16		44	7.7
9		304.3 - 337.7	4.23			
12		315.8 - 340.9	4.40			
15		318.0 - 348.6	4.54			
16		320.2 - 352.4	5.19			
heat-treatment at @ 250℃ 1hr		262.3 - 338.8	4.21	311.1	44	6.6
2	1.52	265.0 - 341.5	4.27	312.8	47	7.1
3	1.58	287.4 - 337.7	4.52	319.6	48	7.7
4		291.2 - 332.8	4.78	320.9		
5	2.31	295.6 - 332.2	4.97	322.0		
6		293.9 - 333.3	5.39	323.1		
10		285.2 - 343.2	5.80	332.8		
heat-treatment at 290℃ 1hr		266.5 - 329.2	5.06	300.7	45	4.1
2		283.9 - 342.2	5.44	314.9	48	5.0
4		308.7 - 349.1	4.99	331.9	52	7.0
6		309.9 - 354.9	5.62	334.8	53	7.5
20		326.2 - 368.3	5.58	353.4		
heat-treatment at @ 290℃ 1hr		302.1 - 343.1	5.52	330.7	48	4.2
2		303.2 - 351.2	5.61	334.5	54	5.0
4		317.1 - 356.4	5.82	341.6	55	6.8
6		321.7 - 357.0	6.06	342.2	58	7.8
16		332.2 - 365.0	6.00	350.6		

*a Obtained from 2nd DSC thermogram

*b Apparent crystallite size caculated from diffraction of Miller plane (110) using the Ruland equation(23).

for 1 hr segmental motion in amorphous region is not active enough, but that at 220℃ polymer chains in amorphous regions undergo ready conformational rearrangement leading to further crystallization.

Apparent crystallite size after heat treatment at 220℃ was 6.3nm which is about twice the initial size, 3.2nm. Growth in crystallite size suggests that the enhanced DC came mainly from the growth of the originally existing crystallites. Formation of new nuclei appear to be minor. As a result, the preheat-treated fibers have less amorphous portion in the initial stage of solid state polymerization compared with the direct heat-treated ones. This means that chain ends in preheat-treated fibers are more highly localized, which would allow faster reaction between the terminal functional groups.

The melting point of the polymer, in general, increased on annealing from about 305℃(before heat treatment) to 320℃. The X-ray diffraction patterns(Fig. 4) as a function of annealing time reveal that the as-spun fiber has relatively low crystallinity (22%) and consist of smaller crystallites (3.2nm), wherease the fiber preheat-treated for 1 hour at 200℃ and 2 hours at 220℃ has much higher degree of crystallinity (43%) and larger size crystallites(6.3nm). Almost full development of crystallinity requires only 1 hour heat-treatment at 250℃(Fig. 4). The extent of solid state polymerization, however, is only about 40% during this period of time.

According to Fig. 5 the rate of crystallization is very slow at 200℃, moderate at 220℃ and rapid at 250℃. In a separate experiment heat treatment for 15 hours at 200℃ resulted in 27% of degree of crystallinity with apparent crystallite size of 4.9nm. This indicates that only reorganization of the defect zones in amorphous region and growth of existing crystallites occured at 200℃ and 220℃ as shown in Figure 6. Figure 6 clearly demonstrates the existence of larger crystallites size in preheat-

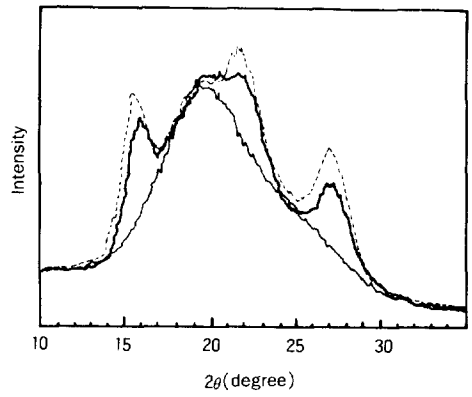


Fig. 4. X-ray diffraction pattern of the fibers as a function of heat-treatment conditions. Thin line is for the as-polymerized sample and thick line for the sample heat treated at 200℃ for 1 hr and the broken line is for the sample heat treated at 250℃ for 1 hr after preheat-treatment.

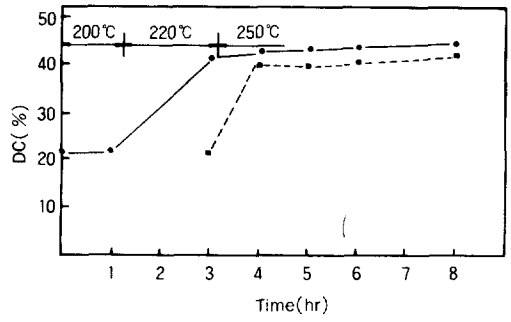


Fig. 5. Degree of crystallinity vs. heat-treatment time. The solid line is for the samples subjected to preheat-treatment befor the final heat treatment at 250℃, and the broken line for the sample heat treated only at 250℃ without preheat treatment.

treated fibers than in directly heat-treated ones. Smaller crystallite size for the directly heat-treated fibers suggests the production of new nuclei leading to rapid crystallization that would reduce the chance of chain end rearrangement. At high temperatures (250℃, 270℃ and 290℃) the crystallization proceeded faster than solid state polymerization. The larger number of nuclei would result in lower degree of crystallinity with more crystal defects and

smaller crystallite size, hence more amorphous portion in the final fibers.

Kinetics Analysis

The reaction rate constants, initial concentrations, ultimate weight losses and activation energies were calculated by the time lag method.[16]

$$(\lambda' - \lambda) = -a \cdot k\ (t' \cdot \lambda' - t \cdot \lambda) + a \cdot k \cdot \lambda_\infty \cdot \Delta t$$

From the slope of the plot $-(\lambda - \lambda')$ versus $(t' \cdot \lambda' - t \cdot \lambda)$ (Fig. 7), "$a \cdot k$" can be calculated. From the intercepts one can caculate λ_∞ values. As mentioned earlier it was assumed that λ_∞ equals the concentration of end groups that can react during the solid state polymerization. In other words, initial concentrations were assumed to be the same as λ_∞ values. Since premature weight loss was observed during heating from room temperature to the temperature of solid state polymerization, this value has to be substracted from the original values.

From Fig. 7 one can see that plots of $(\lambda' - \lambda)$ versus $(t' \cdot \lambda' - t \cdot \lambda)$ are linear. And λ_∞ values calculated from the intercepts of the graphs and experimental values are given in Table 3. Where λ_0 is the weight loss that was observed during heating to a desired reaction temperature for solid state polymerization. This table tells us that λ_∞ values are slightly greater than experimental values and that preheat- treatment results in higher values than direct heat-treatment. Such an observation indicates pre-heat treatment not only prevent sticking of fibers, but also helps solid state polymerization. Higher λ values are obtained for higher temperature experiments. Initial concentration of reactive functional groups was calculated from λ_∞ value using the following equations. As mentioned earlier weight loss was assumed to come only by acetic acid evolution. Since the data used for λ is a weight %, following relationship is used in the calculation of concentration.

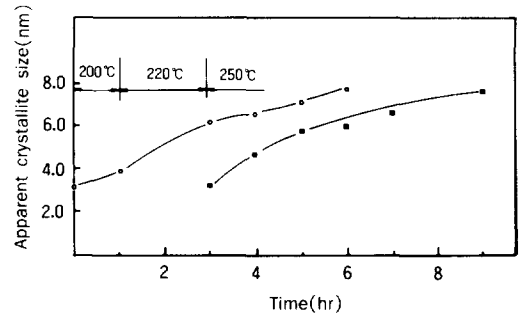


Fig. 6. Change of apparent crystal size during heat-treatment. The open circles are for the samples preheat treated befor the final heat treatment at 250℃, and the squares for the sample heat treated only at 250℃ without preheat treatment.

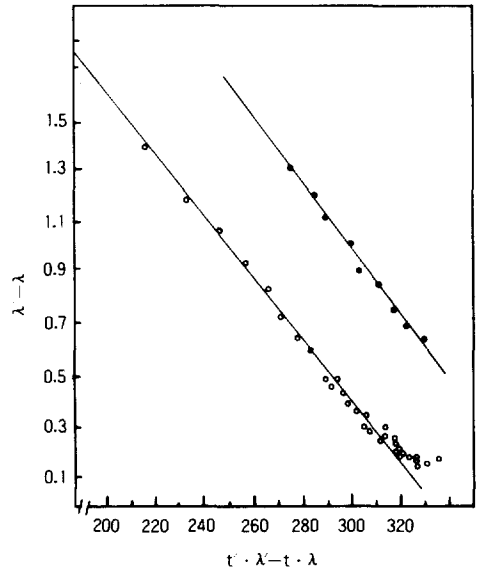


Fig. 7. Plots of $-(\lambda - \lambda')$ vs. $(t' \cdot \lambda' - t \cdot \lambda)$ at 250℃. The open circles are for the samples heat treated only at 250℃. (8 hrs) without preheat treatment and the folled circles are for the samples preheat treated at 200℃ for 1 hr and 220℃ for 2 hrs befor the final heat treatment at 250℃ (8 hrs).

$$\frac{\lambda_\infty}{\text{molecular weight of acetic acid(M)}}$$

=equivalent of acetic acid produced / 100g of sample

The following value corresponds to the equivalent of $-COOH$ (or $-OCOCH_3$) in 100g of polymer that can react :

$$\frac{\lambda_\infty / M \times \text{density of fiber}}{100g} \times 1000$$
$$= \text{eq. of} -COOH \text{ (or} -OCOCH_3) / 1\,l.$$

The density was assumed to remain constant throughout the heat treatment(1.38), although it changed from 1.38(before heat-treatment) to 1.41 after about 1 hr heat treatment. Afterwards this value remained practically constant.

Activation Energies

Fig. 8 shows an Arrhenius plot for the two series of solid state polymerizations. From the slopes of the graphs activation energies were calculated to be 100 and 109 KJ/mole of acetate group, respectively. Surprisingly these values are about the same considering simplified model. Jabarin et al.[21] reported activation energy of 75KJ/mole for solid state polymerization of PET and Korshak et al.[22] 146KJ/mole for PET melt polymerization. These results suggest that the activation energies calculated above are in an acceptable range.

Initial concentration of chain ends that can react in solid state, "a", reaction rate constant, "k", and activation energy, "E_a", for solid state condensations are summerized in Table 3. Here we can see practically similar E_a and larger "k" for pre-annealed fibers than for the fibers subjected single step heat-treatment. Therefore, the difference in rate constants must be interpreted in terms of concentration effect of functional groups.

Change of Fiber Properties After Solid State Polymerization

Comparision of the properties of the fibers before and after heat-treatment is given in Table 4. From the table it can be seen that the fibers that had been preheat-treated have higher tenacity and initial modulus. This must be, as pointed out earier, due to higher degree of crystallinity, larger apparent crystal size and higher molecular weight.

Unfortunately, inherent viscosities or molecular weights of the final fibers could not be measured because of their insobility. However,

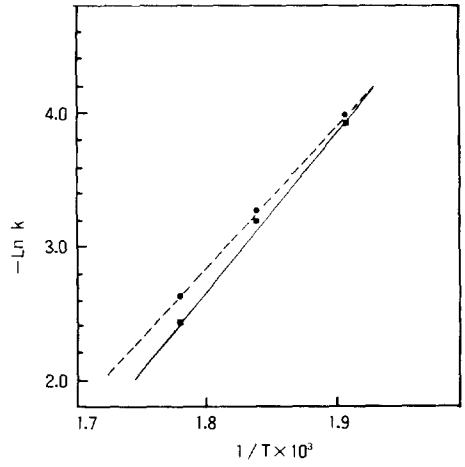


Fig. 8. Arrhenius plots for heat-treatment. The circles are for the preheat treated samples and the squares are for the samples heat treated only at 250℃ without preheat treatment.

Table 3. The Values of Kinetic Data for Solid State Polymerization

λ, %	250℃	270℃	290℃	@ +250℃*	@ +270℃*	@ +290℃*
λ (exp)	2.62	2.95	3.38	2.85	3.25	3.76
λ_∞	2.88	3.21	3.56	3.60	3.73	4.01
a · k	0.013	0.023	0.055	0.013	0.030	0.066
λ_0	0.030	0.20	0.30	0.64	0.67	0.85
a, eqv / l	0.657	0.692	0.749	0.680	0.703	0.726
k, l / eqv · m	1.9×10^2	3.3×10^2	7.3×10^2	$1.9K\times10^2$	4.2×10^2	9.2×10^2
E_a, KJ / mole		100			109	

* @ means preheat-treatment at 200℃ for 1 hr and at 220℃ for 2 hr.

Table 4. Fiber Properties Before and After Heat-Teatment

Heat Treatment Condition	Denier	Tenacity GPa	Elongation %	Modulus GPa	Orientation Angle,°
as spun	7.0	0.40	2.5	32	22
250℃ × 8 hr	7.0	1.05	3.3	39	23
@ + 250℃ × 8 hr*	7.1	1.61	3.2	40	22

* @ means preheat-treatment at 200℃ for 1 hr and at 220℃ for 2 hr.

in the early stage of solid state polymerization, inherent viscosity could be measured as shown in Table 2. It clearly demonstrates that the preheat-treatment increases inherent viscosity. The tensile properties of the one-step heat-treated fibers should be taken as approximation because of the sticking of the fibers during annealing, but it was apparent that they were poorer than those of preheat-treated fibers.

The data presented in Table 4 also illustrate that heat-treatment brings about remarkable enhancement in tenacity, but less so in modulus. This phenomenon appears to be general for thermal treatment of fibers obtained from aromatic polyesters.[7~10] Although the fiber spinning condition was not optimized, the mechanical strength of the present heat-treated fibers are significantly better than that of poly(ethylene terephthalate).

CONCLUSION

Kinetics of solid state polymerization of an LC aromatic polyester was quantitatively studied. The degree of crystallinity and rate of solid state polymerization were higher when the fibers were heat-treated stepwise than directly heat treated. This was explained by the process of remelting of small imperfect crystalites and conformational rearrangement of polymer chains in amorphous regions to give higher crystallinity when the preheat-treated fiber was again heat-treated at a higher temperature. This not only leads better fiber properties but also results in faster and higher degree of solid state polymerization. The solid state polymerization was 2nd order reaction. And fibers that have higher crystallinity showed faster reaction rate. This tells us the reaction is kinetic-controlled reaction rather than diffusion controlled reaction. This method can be used for the optimization of annealing condition of wholly aromatic polyester fibers.

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REFERENCES

1. H. F. Kuhfuss and W. J. Jackson, Jr., U. S. Pat., 3,778,410(1978).
2. W. J. Jackson and H. F. Kuhfuss, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2043(1976).
3. B. -W. Jo, R. W. Lenz, and J. -I. Jin, *Makromol. Chem. Rapid Commun.*, **3**, 23(1982).
4. B. -W. Jo, R. W. Lenz, and J. -I. Jin, *Eur. Polym. J.*, **18**, 233(1982).
5. S. G. Cottis, J. Economy, and L. C. Wohrer, U. S. Pat., 3,975,487(1976).
6. S. G. Cottis, J. Economy, and B. E. Nowak, U. S. Pat., 3,673,595(1972).
7. J. J. Kleinschuster, T. C. Pletcher, J. R. Schaefgen, and R. R. Luise, Ger. Offen, 2,520,819(1975).
8. J. J. Kleinschuster, T. C. Pletcher, J. R. Schaefgen, and R. R. Luise, Ger. Offen, 2,520,820(1975).
9. J. J. Kleinschuster, T. C. Pletcher, J. R. Schaefgen, and R. R. Luise, Belg. Pat.

828,935(1975).
10. J. J. Kleinschuster, T. C. Pletcher, J. R. Schaefgen, and R. R. Luise, Belg. Pat. 828,936(1975).
11. S. Chang, M. F. Shen, and S. -M. Chen, *J. Appl. Polym. Sci.*, **28**, 3289(1983).
12. T. M. Chang, *Polym. Eng. Sci.*, **10**, 364 (1970).
13. B. I. Lee and R. G. Grisky, *J. Appl. Polym. Sci.*, **10**, 105(1965).
14. O. A. Gunder, and I. M. Livshits, *Plastich-eskie. Massy.*, **9**, 24(1962).
15. J. W. Moore and R. G. Pearson, "Kinetics and Mechanism" 3rd ed. John Wiley & Sons Inc., New York, 1985, page 73.
16. J. H. Espenson, *J. Chem. Edu.*, **39**, 160 (1962).
17. S. W. Tobey, *J. Chem. Edu.*, **39**, 473(1962).
18. W. R. Krigbaum, R. Kotter, T. Ishkawa, and H. Hakemi, *Eur. Polym. J.*, **20**, 225(1984).
19. "Thermal Analysis", Proceedings of the Seventh International Conference on Thermal Analysis, Vol. 1, Ed. by B. Miller, John Wiley & Sons., London, P. 38(1984).
20. H. J. Park, Ph. D. Thesis, Chemistry Department, College of Sciences, Korea University, Seoul 136-701, Korea(1987).
21. S. A. Jabarin and E. A. Lofgren, *J. Appl. Polym. Sci.*, **32**, 5315(1986).
22. V. V. Korshak, *Bull. Acad. Sci. U. S. S. R., Div. Chem. Sci. S. S. R.*, 463(1958).
23. W. Ruland, *Acta Cryst.* **14**, 1,180(1961).